# Journal of Materials Chemistry A



View Article Online

# PAPER



Cite this: DOI: 10.1039/d5ta01484k

Received 22nd February 2025 Accepted 18th April 2025

DOI: 10.1039/d5ta01484k

rsc.li/materials-a

### Introduction

Proton-exchange membrane water electrolysis (PEMWE), driven by intermittent renewable energy sources, presents an efficient and environmentally friendly route for producing green hydrogen.<sup>1</sup> Although  $IrO_2$  is currently the leading anode

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- <sup>†</sup> Electronic supplementary information (ESI) available: Experimental details, additional experimental data and figures, and supplementary discussion. See DOI: https://doi.org/10.1039/d5ta01484k

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# Reversible lattice oxygen participation in $Ru_{1-x}O_{2-x}$ for superior acidic oxygen evolution reaction<sup>†</sup>

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A stable and efficient RuO<sub>2</sub>-based electrocatalyst for the acidic oxygen evolution reaction (OER) is essential to replace the current IrO<sub>2</sub> anode in proton-exchange membrane water electrolysis (PEMWE). Herein, we introduce RuO<sub>2</sub> catalysts designed with coexisting oxygen and ruthenium vacancies using a metal–organic pyrolysis method. In 0.5 M H<sub>2</sub>SO<sub>4</sub> using a three-electrode configuration, the catalyst delivers a low overpotential of 193 mV at 10 mA cm<sup>-2</sup>. Experimental and theoretical analyses reveal facet-dependent mechanisms: oxygen vacancies stabilize (110) and (101) facets by suppressing excessive Ru vacancy formation during reconstruction, while Ru vacancies on (101) uniquely activate lattice oxygen to enable a reversible lattice oxygen-mediated (LOM) cycle. DFT calculations rationalize this behavior: Ru vacancies lower the deprotonation of adsorbed hydroxyl (RDS) to 1.51 eV on (101) facets, while lattice oxygen replenishment and durable cycling. In contrast, the (110) facet suffers from prohibitive barriers (>2.0 eV) in both adsorbate-driven and lattice oxygen pathways. Consequently, the (101)-dominant catalyst operates stably at 100 mA cm<sup>-2</sup> in PEMWE for 200 h, outperforming the conventional IrO<sub>2</sub> benchmark.

electrocatalyst, its limited availability and high cost hinder the widespread adoption of PEMWE.<sup>2,3</sup>

Recently, RuO<sub>2</sub>-based materials have emerged as promising, cost-effective alternatives for the oxygen evolution reaction (OER).<sup>4</sup> Unlike the traditional adsorbate evolution mechanism (AEM), which is constrained by a scaling relation between OH and OOH intermediates, the lattice oxygen mechanism (LOM) circumvents this issue through direct O–O coupling.<sup>5-8</sup> However, the slow replenishment of lattice oxygen by water molecules in the electrolyte can lead to structural instability due to the formation of numerous lattice oxygen vacancies.<sup>9,10</sup> Achieving stability through a reversible lattice oxygen participation cycling process remains a significant challenge.

Vacancy engineering has shown to be an effective strategy for altering the adsorption/desorption behavior of oxygenated intermediates.<sup>11-16</sup> By introducing oxygen vacancies into the RuO<sub>2</sub> lattice, the availability of lattice oxygen can be reduced, potentially suppressing the LOM pathway and shifting the reaction towards the AEM pathway.<sup>17-19</sup> Mu's research suggests that multiscale defects (O vacancies and grain boundaries) in MD-RuO<sub>2</sub>-BN weaken Ru–O bonds and reduce Ru oxidation states, suppressing the LOM while promoting the AEM path.<sup>18</sup> Zagalskaya's systematic study reveals that Ru vacancies in RuO<sub>2</sub> promote the lattice oxygen mechanism (LOM) by drastically reducing the LOM overpotential *via* O 2p-band shifts and lattice destabilization.<sup>20</sup> Notably, Pan's group reported that both

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anionic and cationic vacancies on (110) promoted the AEM pathway over the LOM.<sup>17</sup> Ru vacancies in Ru<sub>1-x</sub>O<sub>2</sub> enhance acidic OER activity by lowering the d-band center and optimizing the adsorption energies of intermediates (reducing the \*O  $\rightarrow$  \*OOH energy barrier to 1.61 eV), promoting the AEM pathway. O vacancies in RuO2-x suppress lattice oxygen participation (LOM) by weakening Ru-O bonds, thereby improving stability (400 h at 10 mA  $cm^{-2}$ ) while maintaining AEM dominance. However, prior efforts predominantly focused on single-vacancy modifications (O<sub>v</sub> or M<sub>v</sub>), while the synergistic effects of dual vacancies remained poorly understood. Moreover, these strategies often neglect the facet-dependent vacancy dynamics. Most DFT studies on RuO<sub>2</sub> primarily model the (110) facet, while vacancy impacts on the (101) facet remain underexplored despite experimental evidence demonstrating its higher activity compared to (110).

In our study, we propose a dual-vacancy engineering strategy that synergistically integrates oxygen  $(O_v)$  and ruthenium vacancies (Ru<sub>v</sub>) on (101)-dominant RuO<sub>2</sub>, where ethanol-mediated precursor modulation directs facet-dependent annealing and defect formation. Intriguingly, Ov suppresses excessive Ruv generation by elevating its formation energy, while Ruv on the (101) facet uniquely activates lattice oxygen via a low-barrier LOM pathway, driving the O-O coupling barrier down to 1.02 eV. This triggers rapid oxygen replenishment and sustains a self-healing LOM cycle, as directly observed through in situ structural tracking. In contrast, the (110) facet resists both AEM and LOM activation regardless of the vacancy type, exhibiting prohibitive barriers (>2.0 eV) that preclude efficient oxygen cycling. The paradigm shift from irreversible AEM-dominated degradation to facet-guided LOM reversibility enables the (101)-dominant catalyst to operate stably in PEMWEs at 100 mA cm<sup>-2</sup> for 200 hours. By resolving the facet-dependent roles of dual vacancies, this work redefines vacancy engineering in acidic OER, emphasizing crystallographic control as a cornerstone for designing stable, high-performance catalysts.

### **Results and discussion**

#### Preparation and structural characterization

Typically, RuO2 was obtained via the solvothermal method with  $RuCl_3 \cdot xH_2O$  and urea as the precursor in ethanol followed by annealing treatment (EtOH-RuO<sub>2</sub>). For comparison, DI-RuO<sub>2</sub> was synthesized through a similar procedure, except that the solvent was deionized water (a detailed preparation process is shown in the ESI Experimental section<sup>†</sup>). First, scanning electron microscopy (SEM) was employed to investigate the morphology of the fabricated samples. Before the heat treatment, the EtOH-RuO<sub>2</sub> precursor nanoparticles exhibited a smooth surface with an average diameter of  $1.1 \ \mu m$  (Fig. 1a, ESI Fig. S1<sup>†</sup>). After calcination treatment at 300 °C in air, EtOH-RuO<sub>2</sub> retained its size, as shown in Fig. 1b. Further observation found the random distribution of triangular cone-like protrusions on the surface (Fig. 1c and d). Different annealing temperatures were also used to investigate the morphology evolution; the SEM images showed that the surfaces were smooth when the temperature was 150, 200, and 250 °C. As the



Fig. 1 Morphological and microscopic analysis of  $EtOH-RuO_2$ . SEM images of (a)  $EtOH-RuO_2$ -pre and (b–d)  $EtOH-RuO_2$ ; (e) TEM and (f) HRTEM of  $EtOH-RuO_2$ ; (g–i) magnified views of the region shown in (f) (scale bars: 100 nm in (b, c and e), 5 nm in (f), 1 nm in (g–i)); (j–l) HAADF-STEM image and the corresponding elemental maps of  $EtOH-RuO_2$ .

temperature continued to increase to 300 °C, conical protrusions began to appear (Fig. S2<sup>†</sup>). The morphological transition in EtOH-RuO<sub>2</sub> is governed by temperature-dependent organic passivation dynamics. At 300 °C, complete decomposition of residual urea-derived species eliminates surface passivation, enabling anisotropic RuO2 crystallization and the emergence of conical protrusions (Fig. S3<sup>†</sup>).<sup>21,22</sup> DI-RuO<sub>2</sub>-pre displays significant size heterogeneity, characterized by a considerable density of submicron particles (as low as 0.2 µm) interspersed with sporadic large aggregates exceeding 2 µm, resulting in a nonuniform particle size distribution of DI-RuO<sub>2</sub> (Fig. S4<sup>†</sup>). Brunauer-Emmett-Teller (BET) surface area analysis (Fig. S5 and Table S1<sup>†</sup>) reveals that EtOH-RuO<sub>2</sub> exhibits a lower specific surface area (20.64 m<sup>2</sup> g<sup>-1</sup>) than DI-RuO<sub>2</sub> (35.64 m<sup>2</sup> g<sup>-1</sup>), confirming that the enhanced catalytic performance is independent of particle size reduction. Intriguingly, the ethanol-derived catalyst shows a superior mesoporous architecture, originating from its unique conical surface protrusions that generate nanoscale porosity and facilitate mass transport.23

Then, transmission electron microscopy (TEM) images provided a more precise morphology observation. As shown in Fig. 1e and f, EtOH–RuO<sub>2</sub> comprises irregular tetrahedral conical particles. As depicted in Fig. 1g–i, the lattice fringes with spacings of 1.61 Å and 2.42 Å were ascribed to the (220) and (101) planes of rutile RuO<sub>2</sub>, respectively. The HAADF-STEM and corresponding elemental mapping images (EDS) in Fig. 1j–l show the uniform distribution of Ru and O over the particles, indicating the successful preparation of RuO<sub>2</sub>. For DI-RuO<sub>2</sub>, cubic particles with a lattice spacing of 3.08 Å were observed, corresponding to (110) planes of standard rutile RuO<sub>2</sub> (Fig. S6†).<sup>24</sup> The EDS mapping results also confirmed the uniform distribution of Ru and O elements (Fig. S7†). The variations in the morphology and homogeneity might be

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attributed to the solvent effect. A lower polarity (6.6) and higher molecular weight of ethanol are conducive to avoiding excessive nucleation, allowing for slow and uniform growth of the nuclei.25,26 In contrast, the high polarity (10.2) and lower molecular weight of water lead to stronger interactions, which may result in mutual attraction and agglomeration between nuclei.27 Thus, the precursor is prepared in different solvents with varying surface energies, resulting in distinct phase transformation pathways during annealing and different surface morphologies.<sup>28</sup> Moreover, it should be noted that the catalyst is synthesized through a highly reproducible ambientair process: (1) precursor coordination under mild reflux (65 °C at 1 atm), (2) filtration/drying, and (3) air-annealing at 300 °C, avoiding energy-intensive hydrothermal/pressurized steps. Systematic quantification reveals >90% Ru utilization after accounting for post-synthesis losses (filtration retention, particle attrition during grinding, and airborne dispersion).

More characterization studies were conducted to reveal the phase and crystal structure information. As shown in the X-ray diffraction (XRD) spectra (Fig. 2a), several prominent characteristic peaks located at  $28.0^{\circ}$ ,  $35.1^{\circ}$ , and  $54.3^{\circ}$  were observed for both EtOH–RuO<sub>2</sub> and DI-RuO<sub>2</sub>, corresponding to (110), (101) and (211) planes of rutile-type RuO<sub>2</sub> (PDF # 43-1027). Rietveld refinement of the XRD data confirms the structural integrity and yields precise lattice parameters (Fig. S8 and Table S2†). The EtOH–RuO<sub>2</sub> sample exhibits larger lattice parameters than

DI-RuO<sub>2</sub>, indicating significant lattice expansion. This tensile strain aligns with the increased interplanar spacing observed in TEM and further deviates from the standard rutile-phase RuO<sub>2</sub> parameters, suggesting structural distortion induced by the synthesis route. Moreover, a significant increase in the peak area ratio of (101)/(110) of EtOH-RuO<sub>2</sub> than that of DI-RuO<sub>2</sub> is observed, indicating that the main exposed crystal plane of EtOH-RuO<sub>2</sub> is (101). At the same time, the surface of DI-RuO<sub>2</sub> is predominantly dominated by (110).

X-ray photoelectron spectroscopy (XPS) was subsequently conducted to investigate the surface electronic and chemical states of the final fabricated electrocatalysts. For the O 1s XPS spectrum in Fig. 2b, the peak could be deconvoluted into three peaks with binding energies at 529.1, 530.4, and 532.1 eV, corresponding to lattice oxygen (O<sub>L</sub>), oxygen adsorbed at oxygen vacancies (O<sub>V</sub>), and surface-adsorbed oxygen species (O<sub>A</sub>), respectively.29 The overall shift of the O 1s peak toward lower binding energies in EtOH-RuO<sub>2</sub> suggests an increase in electron density around lattice oxygen. EtOH-RuO<sub>2</sub> exhibits a significantly higher oxygen vacancy concentration than DI-RuO<sub>2</sub>, as validated by XPS  $(O_V/(O_V + O_L) = 41.5\% \text{ vs. } 32.4\%)$ (Fig. 2b, S9 and Table S3<sup>†</sup>). Oxygen vacancies have been demonstrated to modulate electronic structures to lower reaction energy barriers, enhance electrical conductivity to facilitate charge transfer and create abundant active sites.<sup>30-32</sup> As for the Ru 3p XPS spectra, compared with DI-RuO<sub>2</sub>, the peak position of



**Fig. 2** Advanced structural and electronic characterization of EtOH-RuO<sub>2</sub> and DI-RuO<sub>2</sub>. (a) XRD spectra, (b) O 1s and (c) Ru 3p XPS spectra of EtOH-RuO<sub>2</sub> and DI-RuO<sub>2</sub> for EtOH-RuO<sub>2</sub> and DI-RuO<sub>2</sub>; (d) Ru K-edge XANES spectra of EtOH-RuO<sub>2</sub>, DI-RuO<sub>2</sub>, Ru foil, and standard RuO<sub>2</sub>; (e) corresponding Fourier-transformed  $k^3$ -weighted EXAFS spectra; (f and g) corresponding wavelet transform images of EtOH-RuO<sub>2</sub> and DI-RuO<sub>2</sub>.

EtOH-RuO<sub>2</sub> shifted 0.1 eV towards a lower binding energy, indicating a decrease in the Ru valence state (Fig. 2c and S10<sup>+</sup>). UV-vis DRS analysis yielded direct bandgap values of 1.94 eV (EtOH-RuO<sub>2</sub>) and 2.15 eV (DI-RuO<sub>2</sub>) (Fig. S11<sup>†</sup>). The narrowed bandgap in EtOH-RuO2 originates from oxygen vacancyinduced mid-gap defect states, as corroborated by its enhanced absorption below the bandgap and broadened absorption edge-characteristic features of vacancy-mediated light harvesting. These results align with established oxygen and metal vacancy mechanisms, where defect states reduce bandgap energies and extend optical absorption through defect-level transitions.33,34 Then, the analysis of the XPS and Fourier transform infrared spectroscopy (FTIR) spectra of the precursors (Fig. S12 and S13<sup>†</sup>) suggested solvent-induced differences in the crystal structure of both EtOH-RuO<sub>2</sub> and DI-RuO2. Ru K-edge spectra through X-ray absorption near-edge spectroscopy (XANES) were further collected to analyze the electronic structure of Ru quantitatively. For comparison, Ru foil and standard RuO2 were employed as references. As shown in Fig. 2d, the negative shift of the edge for EtOH-RuO<sub>2</sub> reveals its lowered Ru average oxidation valence relative to that of DI-RuO<sub>2</sub>, which is in good agreement with XPS results. The reduced Ru oxidation state in EtOH-RuO2 stems from dual Ru/ O vacancy compensation and the reductive annealing environment during urea decomposition, which simultaneously suppresses Ru oxidation and promotes oxygen vacancy formation.<sup>22</sup> The extended X-ray absorption fine structure (EXAFS) and wavelet transform of the Ru K-edge are also used to investigate the coordination features (Fig. 2e-g). Two characteristic peaks at 1.50 Å and 3.13 Å are attributed to the Ru-O bond and Ru-Ru scattering path, respectively, as further validated by the wavelet transform (WT) analysis.<sup>35</sup> Oxygen vacancies contribute to the observed decrease in Ru-O coordination. Still, the simultaneous and pronounced weakening of Ru-Ru scattering signals (2.2-3.7 Å) cannot be explained solely by oxygen vacancies (Table S4, Fig. S14<sup>†</sup> and 2e-g). Ru vacancies disrupt the periodic arrangement of Ru atoms, introducing lattice disorder that further attenuates the Ru-Ru scattering paths.<sup>36-38</sup> Hence, the coexistence of cation and anion vacancies in oxide materials is well-documented. Charge compensation and structural optimization are critical for stabilizing such defects, thus confirming dual-vacancy engineering as a viable strategy for stabilizing defective oxide systems.<sup>39-41</sup> The changes in the electronic structure make it promising to optimize the intermediate adsorption behavior and lead to subsequent performance enhancements.

# Mechanistic insights into solvent effects on RuO<sub>2</sub> structural evolution during calcination

The structural divergence between  $DI-RuO_2$  and  $EtOH-RuO_2$  after calcination arises from solvent-mediated precursor coordination and calcination-triggered kinetic-thermodynamic reconfiguration.

The DI-RuO<sub>2</sub>-pre completes major decomposition below 256 °C, enabling surface-diffusion-dominated growth during 300 °C annealing, favoring the formation of low-surface-energy

cubic morphologies with facet ratios near thermodynamic equilibrium (Fig. S3<sup>†</sup>). In contrast, the EtOH–RuO<sub>2</sub> precursor remains in its intermediate decomposition stage at 300 °C, promoting kinetically driven growth along high-energy facets (Fig. S15<sup>†</sup>). This results in sharp conical protrusions and an elevated proportion of metastable (101) facets within a short 3 h annealing period.<sup>42</sup>

The unstable oxygen environment (evidenced by elevated O 1s binding energy) and absence of Ru-N bonding in EtOH-RuO2-pre render Ru in a coordinatively unsaturated, metastable state, distinct from the stable metal-nitrogen coordination in DI-RuO2.43 This metastable configuration markedly lowers Ru migration energy barriers, facilitating ligand dissociation and lattice detachment during annealing, thereby favoring ruthenium vacancy formation kinetically.44 Concurrently, rapid urea decomposition releases NH<sub>3</sub> and CO<sub>2</sub>-the reducing nature of NH<sub>3</sub> suppresses complete Ru oxidation (yielding a lower Ru oxidation state) while necessitating oxygen vacancy generation via charge compensation.<sup>21,45,46</sup> Gas-induced structural discontinuities further enable low-energy Ru migration pathways. Ultimately, non-equilibrium cooling and synergistic electron compensation stabilize both oxygen and ruthenium vacancies, culminating in elevated defect retention after 300 °C air annealing.

#### Evaluation of acidic OER performance

To reveal the effect of Ru and O vacancies on the OER performance, the catalyst inks were dip-coated on a glassy carbon electrode and assessed in a three-electrode setup in 0.5 M H<sub>2</sub>SO<sub>4</sub> electrolyte (mass loading: 0.51 mg cm<sup>-2</sup>). Commercial ruthenium oxide (Com-RuO2) and commercial iridium oxide (Com-IrO<sub>2</sub>) were also tested for comparison. As evidenced by the linear sweep voltammetry (LSV) curves shown in Fig. 3a, EtOH-RuO<sub>2</sub> exhibited superior acidic OER activity, requiring ultralow overpotentials of 193 mV and 256 mV to achieve current densities of 10 and 100 mA cm<sup>-2</sup>, which is smaller than those of DI-RuO<sub>2</sub>  $(207 \text{ mV} @ 10 \text{ mA cm}^{-2}, 289 \text{ mV} @ 100 \text{ mA cm}^{-2}), \text{ Com-RuO}_2$  $(244 \text{ mV} \otimes 10 \text{ mA cm}^{-2}, 424 \text{ mV} \otimes 100 \text{ mA cm}^{-2})$  and Com-IrO<sub>2</sub>  $(357 \text{ mV} \circledast 10 \text{ mA cm}^{-2}, \text{ over } 400 \text{ mV} \circledast 100 \text{ mA cm}^{-2})$ . In addition, the obtained Tafel curves in Fig. 3b show that EtOH- $RuO_2$  displayed a Tafel slope value of 52.9 mV dec<sup>-1</sup>, indicating fast OER kinetics compared to DI-RuO<sub>2</sub> (73.4 mV dec<sup>-1</sup>), Com- $RuO_2$  (102.8 mV dec<sup>-1</sup>) and Com-IrO<sub>2</sub> (147.3 mV dec<sup>-1</sup>). The fast kinetics could further be evidenced by the electrochemical impedance spectrum (EIS) at 1.43 V (Fig. 3c). The smallest EIS semicircle radius of EtOH-RuO2 suggests the lowest charge transfer resistance  $(R_{ct})$ , determined by faster electron transfer occurring on the active site.<sup>47</sup> The fitting  $R_{\rm ct}$  is 12.5  $\Omega$ , 16.6  $\Omega$ , and 184.1  $\Omega$  for EtOH-RuO<sub>2</sub>, DI-RuO<sub>2</sub>, and Com-RuO<sub>2</sub>, respectively (the simulated circuits are shown in Fig. S16<sup>†</sup>). The unexpectedly high R<sub>ct</sub> of Com-RuO<sub>2</sub> might be due to the inactivation caused by dissolution during this constant-potential test. In addition, the determined electrochemical double-layer capacitance  $(C_{dl})$  of EtOH-RuO<sub>2</sub> is 35.55 mF cm<sup>-2</sup>, based on non-Faraday capacitance current measured at different scanning rates (Fig. S17<sup>†</sup>), which in turn was used to estimate the electrochemically active surface area (ECSA).48 To further



**Fig. 3** Electrochemical OER performance evaluation. (a) LSV curves, (b) Tafel plots corresponding to the polarization data, (c) electrochemical impedance spectroscopy, (d) LSV curves normalized to the electrochemical surface area, and (e) chronopotentiometry curve recorded at 10 mA  $cm^{-2}$  for EtOH–RuO<sub>2</sub>, DI–RuO<sub>2</sub>, Com–RuO<sub>2</sub> and Com–IrO<sub>2</sub>. (f) Polarization curve of PEMWEs obtained at 60 °C with EtOH–RuO<sub>2</sub> and Com–IrO<sub>2</sub> as the anodic catalyst; (g) the cell voltage of PEMWEs measured at a current density of 100 mA cm<sup>-2</sup> at 60 °C.

determine the intrinsic activity of the active sites, the current density is normalized to ECSA, as shown in Fig. 3d. As observed, the specific activity still decreased in the order of EtOH–RuO<sub>2</sub>, DI-RuO<sub>2</sub>, Com-RuO<sub>2</sub>, and Com-IrO<sub>2</sub>, which confirms that EtOH–RuO<sub>2</sub> possesses the highest intrinsic activity. In practical hydrolysis applications, stability plays an even more important role than the activity. First, the chronopotentiometry (CP) test was performed at a current density of 10 mA cm<sup>-2</sup> in a three-electrode system to evaluate the stability. As shown in Fig. 3e, Com-RuO<sub>2</sub> showed rapid inactivation, and Com-IrO<sub>2</sub> was stable for only about 30 h. Significantly, EtOH–RuO<sub>2</sub> could be operated continuously for 500 h with only a slight increase in potential (0.109 mV h<sup>-1</sup>), while DI-RuO<sub>2</sub> completely lost activity after 350 h. The excellent stability results demonstrated that EtOH–RuO<sub>2</sub> might be a superb electrocatalyst in the PEMWE device.

Then, the PEMWE device was assembled with the prepared EtOH-RuO<sub>2</sub> and Com-IrO<sub>2</sub> as the anode and commercial Pt/C as the cathode. At 60 °C, the EtOH-RuO<sub>2</sub>-based electrolyzer achieved a current density of 2 A cm<sup>-2</sup> with a cell voltage of 1.9 V (with a mass loading of 1.5 mg<sub>Ru</sub> cm<sup>-2</sup>), outperforming most recently

reported PEMWE devices. Notably, at 1 A cm<sup>-2</sup>, the required voltage was reduced to 1.70 V, significantly lower than that of Com-IrO<sub>2</sub> (1.98 V) (Fig. 3f). Furthermore, during chronopotentiometry (CP) testing at 100 mA cm<sup>-2</sup>, the EtOH–RuO<sub>2</sub>-based device retained stable operation at ~1.48 V for over 200 h. At the same time, the commercial IrO<sub>2</sub> exhibited rapid deactivation and a substantial voltage increase within 100 h under identical conditions (Fig. 3g). These comparative data robustly confirm that our catalyst surpasses state-of-the-art IrO<sub>2</sub> in both activity and stability under industrially relevant PEMWE conditions.

#### In situ investigation of OER mechanisms

To shed light on the excellent performance of EtOH–RuO<sub>2</sub>, *operando* differential electrochemical mass spectrometry (DEMS) with isotope labeling measurements was conducted to investigate the reaction path. The prepared samples were typically coated on the Au working electrodes and subjected to 5 LSV cycles (1–1.5 V *vs.* RHE) in the H<sub>2</sub><sup>18</sup>O electrolyte. As shown in Fig. 4a, the recorded mass signal of the gaseous products



**Fig. 4** Insights into the reaction mechanisms *via in situ* FTIR and DEMS on RuO<sub>2</sub> catalysts. (a) Differential Electrochemical Mass Spectrometry (DEMS) signals of <sup>32</sup>O<sub>2</sub>(<sup>16</sup>O<sup>16</sup>O), <sup>34</sup>O<sub>2</sub>(<sup>16</sup>O<sup>18</sup>O), and <sup>36</sup>O<sub>2</sub>(<sup>18</sup>O<sup>18</sup>O) obtained from the reaction products in the H<sub>2</sub><sup>18</sup>O aqueous H<sub>2</sub>SO<sub>4</sub> electrolyte; the ratio of <sup>16</sup>O/<sup>18</sup>O in the products of 5 LSV run for (b) EtOH-RuO<sub>2</sub> and (c) DI-RuO<sub>2</sub>. *In situ* FTIR spectrum for (d) EtOH-RuO<sub>2</sub> and (e) DI-RuO<sub>2</sub>.

suggested both EtOH-RuO2 and DI-RuO2 proceed via the LOM path, and the <sup>34</sup>O<sub>2</sub> signal in the EtOH-RuO<sub>2</sub> was significantly larger than that of DI-RuO<sub>2</sub>. Then, the integration of the mass signal <sup>16</sup>O/<sup>18</sup>O was obtained based on the DEMS profile (Fig. 3b and c); the results showed that the <sup>16</sup>O/<sup>18</sup>O ratio obviously increased from 14.4% in DI-RuO<sub>2</sub> to 76.4% in EtOH-RuO<sub>2</sub>, indicating that the OER process occurring on the EtOH-RuO<sub>2</sub> surface was dominated via the LOM path. Interestingly, as the reaction proceeded, the ratio of <sup>16</sup>O/<sup>18</sup>O gradually decreased for the EtOH-RuO<sub>2</sub> sample. The ongoing rise in the <sup>18</sup>O ratio in the oxygen product could be attributed to (1) the dynamic transformation process from the LOM to AEM path or (2) the timely replenishment of <sup>18</sup>O in the H<sub>2</sub><sup>18</sup>O to the oxygen vacancies formed after <sup>16</sup>O detachment during the LOM process, which then participated in the LOM reaction cycle. For the DI-RuO<sub>2</sub>, the ratio of <sup>16</sup>O/<sup>18</sup>O showed an upward trend, indicating that the catalyst's lattice oxygen is involved during the reaction, potentially contributing to a continuous loss of lattice oxygen.

To further determine the role played by lattice oxygen in catalysis, the electrocatalysts after the reaction were characterized. The SEM images showed that no noticeable changes were found in the morphology of the EtOH–RuO<sub>2</sub> (Fig. S18†). The XRD patterns indicate changes in the dissolution of crystal planes following the reaction (Fig. S19†). The results for DI-RuO<sub>2</sub> suggest that the (101) plane is likely more resistant to dissolution than the (110) plane.<sup>49</sup> The XPS analysis and the normalization of XPS signal intensities provide more precise insight into the changes in the surface electronic structure. For both RuO<sub>2</sub> samples, simultaneous shifts of the O 1s and Ru 3p binding energies to higher values indicate an overall increase in the oxidation state of Ru after the OER (Fig. S20 and S21†). However, distinct differences emerge between EtOH–RuO<sub>2</sub> and DI-RuO<sub>2</sub>. In the O 1s spectra, a significant intensity increase above 530 eV is observed for both catalysts post-OER. The calculated O<sub>V</sub>/(O<sub>V</sub> + O<sub>L</sub>) ratio for EtOH-RuO<sub>2</sub> shows minimal change (41.5% vs. 40.6%), whereas DI-RuO2 exhibits a substantial rise in oxygen vacancies  $(O_V/(O_V + O_L))$  increasing from 32.4% to 44.4% (Fig. S22 and Table S5<sup>+</sup>). This suggests that the intensity increase above 530 eV in EtOH-RuO2 primarily arises from adsorbed oxygen species, while DI-RuO<sub>2</sub> undergoes concurrent oxygen vacancy generation, potentially destabilizing its structure. The Ru 3p1/2 spectra, which are sensitive to surface chemical states due to their lower kinetic energy (and thus shallower probing depth), exhibit a shift to higher binding energy, confirming the partial oxidation of surface Ru species under OER conditions (Fig. S19c<sup>+</sup>). In contrast, the Ru  $3p_{3/2}$ peak, reflecting bulk-dominated states, displays negligible shifts.<sup>50</sup> Notably, the Ru 3p<sub>3/2</sub> signals of EtOH-RuO<sub>2</sub> exhibit better overlap before and after the OER compared to DI-RuO<sub>2</sub>, reflecting the stability of Ru's oxidation state. This suggests that the electronic structure and lattice stability of EtOH-RuO<sub>2</sub> remain largely unaffected during the OER while exhibiting a more active surface state, likely attributed to the efficient replenishment of oxygen vacancies.

In addition, *in situ* FTIR in attenuated total reflection (ATR) mode was employed to track reaction intermediates and detect the in situ surface structure evolution in the range from 1.2 to 1.7 V. Each spectrum was collected after the samples were stabilized at the corresponding potential for 5 min. With the potential increasing to the polarization range, compared with DI-RuO<sub>2</sub>, a slight increase in peak intensity was observed at 885 cm<sup>-1</sup>, which could be assigned to the Ru=O stretching vibration, indicating a relatively stable surface and a gentle surface reconstruction process.29 Moreover, the \*OOH band observed in both samples with peaks around  $1050 \text{ cm}^{-1}$ confirms the occurrence of the AEM reaction pathway, consistent with the DEMS analysis.<sup>51,52</sup> Importantly, the prominent \*OO characteristic stretching vibration absorption band was observed at 1195  $\text{cm}^{-1}$  for the EtOH–RuO<sub>2</sub> sample, suggesting the existence of a LOM reaction path.<sup>51</sup> Notably, a strong \*OO peak remains even after prolonged operation, indicating that the catalyst continues to perform the OER via the LOM path, thus excluding the possibility of a transition from the LOM to the AEM, as suggested in the previous DEMS analysis.

#### DFT study of catalytic mechanisms

The LOM path had been demonstrated to result in continuous surface reconstruction, destabilizing the crystal structure.<sup>11,51,53</sup> In this work, the CP test, *ex situ* XRD, SEM, XPS, and *in situ* FTIR spectroscopy proved the crystal structure's stability after the reaction. Thus, the DFT calculations were performed to gain a deeper insight into the origin of regulation of the OER performance of RuO<sub>2</sub> *via* vacancy engineering. From experimental HAADF-STEM images, it can be observed that the main exposed crystal planes are (101) and (220) for EtOH–RuO<sub>2</sub> and DI-RuO<sub>2</sub>, respectively. Thus, rutile structure RuO<sub>2</sub> with (101) and (110) (equivalent to the (220) plane) was built, and both the AEM and LOM paths were considered (Fig. 5a and b). As shown

in Fig. 5c, it is noted that the OER process on  $RuO_2(101)$  via the AEM is primarily hindered by the formation of \*OOH from O\* with a free energy change of 1.98 eV, which is the potential determining step (PDS). The O vacancy in  $RuO_{2-x}(101)$  would strengthen the adsorption of all intermediates and enlarge the PDS to 2.55 eV. In contrast, introducing Ru vacancies in  $Ru_{1-x}O_2(101)$  would lower the affinity to all intermediates, reducing the PDS to 1.51 eV. Then, the LOM is further considered to provide a comprehensive evaluation of the roles of surface O and Ru vacancies in the OER activity of RuO<sub>2</sub>(101) (Fig. 5d). During the LOM, the O\* would couple with lattice O to generate OO<sup>\*</sup>, resulting in a new O vacancy  $(O_v)$ . Then, the OO<sup>\*</sup> would desorb from the surface, and the resulting Ov would be refilled by the H<sub>2</sub>O molecule. Due to strong bond strength to lattice O,  $RuO_2(101)$  and  $RuO_{2-x}(101)$  both exhibit a large RDS of 2.31 eV and 2.86 eV, suggesting that the LOM does not apply to the surface of  $RuO_2(101)$  and  $RuO_{2-x}(101)$ . At the same time, introducing Ru vacancies in  $Ru_{1-x}O_2(101)$  would activate the

lattice oxygen and facilitate the coupling step between O<sup>\*</sup> and lattice O to form OO<sup>\*</sup> with a barrier of 1.02 eV. In comparison, converting O<sup>\*</sup> to OOH<sup>\*</sup> requires an energy uphill of 1.34 eV. Thus, the OER process *via* the LOM on  $Ru_{1-x}O_2(101)$  is thermodynamically favorable. Importantly, it's worth noting that the replenishing process of the resulting O<sub>V</sub> by H<sub>2</sub>O molecules on  $Ru_{1-x}O_2(101)$  is exothermic, indicating that the LOM pathway is reversible and the catalyst's surface remains stable during the OER process *via* the LOM, as confirmed from the DEMS analysis results. On the other hand, neither the O vacancy nor Ru vacancy in RuO<sub>2</sub>(110) would activate the lattice O and promote the LOM, which is consistent with the previous report.<sup>17,20</sup>

To reveal the nature of the effects of a vacancy on the OER performance of RuO<sub>2</sub>, the electronic properties, including projected densities of states (PDOS), band structure, and charge density difference of RuO<sub>2</sub>, RuO<sub>2-x</sub>, and Ru<sub>1-x</sub>O<sub>2</sub> were obtained (Fig. 5e and S23–S25†). It is found that the O 2p orbital center



**Fig. 5** Density functional theory insights into AEM and LOM pathways on  $RuO_2$ -based oxides. Schematic of (a) AEM and (b) LOM reaction pathways; the corresponding p orbital centers are indicated. Free energy profiles for (c) AEM and (d) LOM reaction pathways on crystal planes (101) and (110) of  $RuO_2$ ,  $RuO_{2-x}$ , and  $Ru_{1-x}O_2$ ; (e) PDOS for Ru 3d and O 2p on (101) crystal planes of  $RuO_2$ ,  $RuO_{2-x}$  and  $Ru_{1-x}O_2$ ; (f) schematic of the linear relationship between activation of lattice oxygen and the p band center. The inset shows energy level diagrams for AEM and LOM mechanisms in the OER; the Pourbaix diagram of (g)  $RuO_2$ , (h)  $RuO_{2-x}$  and (i)  $Ru_{1-x}O_2$ ; (j) vacancy formation energy for  $RuO_2$ ,  $RuO_{2-x}$  and  $Ru_{1-x}O_2$ .

 $(\varepsilon_{p})$  exhibits a linear relationship between the energy barriers of coupling of the O\* with the lattice O, as shown in Fig. 5f. With the increase in the O 2p orbital center relative to the Fermi level, the barriers become lower. This is because the upshifts of O 2p orbital contribute to the O atom in the antibonding state below the Fermi level becoming dominant, leading to a reduction in the oxygen vacancy formation energy. Correspondingly, the activation of lattice O caused by the uplifted O 2p orbital would lower the energy barriers of coupling the O\* with the lattice O and promote the LOM pathway. According to the above calculation results, the vacancies on the surface would effectively modulate the electronic structures and thus tune the catalytic activity of RuO<sub>2</sub>. The Ru vacancy was the key to activating the OER via the LOM for  $RuO_2(101)$ . The above results, especially the descriptor,  $\varepsilon_{\rm p}$ , can guide the design of high-performance catalysts for the OER and tune their reaction mechanism.

As thermal stability also plays a key role in the performance of electrocatalysts, the nature of the long-term performance and durability of EtOH-RuO2 was also investigated by DFT simulations. Surface Pourbaix diagrams of  $RuO_2$ ,  $RuO_{2-x}$ , and  $Ru_{1-x}O_2$ and the vacancy formation energy were calculated. From Fig. 5g-i, as the electrode potential increases, the surfaces of  $RuO_2$ ,  $RuO_{2-x}$ , and  $Ru_{1-x}O_2$  are initially occupied by OH\*. With increasing electrode potential, the adsorbed OH\* can be easily oxidized to O\*. As a result, the surface is enriched with OH\* instead of remaining in its pristine state under working conditions. The adsorbed OH\* may promote the OER process and provide supplementary lattice oxygen consumption, especially for the OER process via the LOM on  $Ru_{1-x}O_2(101)$ . After introducing O vacancies on RuO<sub>2</sub>(101), creating Ru vacancies requires a higher electrode potential. As shown in Fig. 5j, the presence of O vacancies on RuO<sub>2</sub>(101) would increase the energy of the formation of oxygen vacancies, thereby hindering the generation of additional oxygen vacancies. In contrast, introducing Ru vacancies on RuO<sub>2</sub>(101) would activate the lattice O to facilitate the LOM process. As mentioned above, the resulting new oxygen vacancy could be replenished rapidly, maintaining the thermal stability of the surface during the OER process. Therefore, O vacancies on  $RuO_2(101)$  may prevent the surface from forming additional O and Ru vacancies, effectively improving surface stability. On the other hand, although the presence of Ru vacancies on RuO<sub>2</sub>(101) could boost the LOM process, easy replenishment resulted in new oxygen vacancies ensuring a reversible LOM cycling process.

## Conclusions

In this work, we synthesized  $\text{RuO}_2$  catalysts with (101) as the dominant facet in which O and Ru vacancies coexist. A comprehensive analysis of the solvent-mediated mechanisms governing the structural evolution of  $\text{RuO}_2$  during calcination has been elucidated. The facet-specific activity hierarchy is quantified as (101) > (110) through DFT studies. While the (110) facet confines the OER to high-barrier adsorbate-driven mechanisms (AEM, 2.01 eV), the (101) facet exhibits dual-pathway tunability. Oxygen vacancies elevate the formation energy of Ru vacancies, effectively preventing structural degradation during operation. Ru vacancies

activate the lattice oxygen-mediated (LOM) pathway by reducing the O–O coupling barrier to 1.02 eV: a threshold that triggers rapid oxygen replenishment and sustains a reversible LOM cycle, as validated by *in situ/ex situ* characterization. Consequently, the (101)dominant catalyst achieves an extra low overpotential of 193 mV (a) 10 mA cm<sup>-2</sup> in 0.5 M H<sub>2</sub>SO<sub>4</sub> and operates stably for 200 h at 100 mA cm<sup>-2</sup> in PEMWE, outperforming the IrO<sub>2</sub> benchmark. This work not only establishes a viable strategy to replace IrO<sub>2</sub> in acidic water electrolysis but also elucidates the facet-vacancy synergy as a dualfunctional mechanism that concurrently modulates reaction pathways and enhances stability, offering atomic-scale design principles for advanced acidic OER catalysts.

# Data availability

The data supporting this study's findings are available from the corresponding author upon reasonable request.

# Conflicts of interest

The authors declare no conflict of interest.

## Acknowledgements

This work was financially supported by the Shanghai Sailing Program (23YF1455000), Shanghai Carbon Neutral Project (23DZ1200603), Guangdong Basic and Applied Basic Research Foundation (2023A1515110920 and 2024A1515012307) and the Sichuan Science and Technology Program (2024NSFSC1141).

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