

Research Highlight

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# Oxygen coverage effect promotes oxygen evolution reaction

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**How to cite this article:** Lin H, Liu P, Yang H. Oxygen coverage effect promotes oxygen evolution reaction. *Chem Synth* 2024;4:71. <https://dx.doi.org/10.20517/cs.2024.123>

**Received:** 3 Sep 2024 **First Decision:** 9 Oct 2024 **Revised:** 12 Oct 2024 **Accepted:** 22 Oct 2024 **Published:** 12 Nov 2024

**Academic Editor:** Xiang-Dong Yao **Copy Editor:** Pei-Yun Wang **Production Editor:** Pei-Yun Wang

**Keywords:** Iridium-based electrocatalysts, oxygen coverage, oxygen evolution reaction

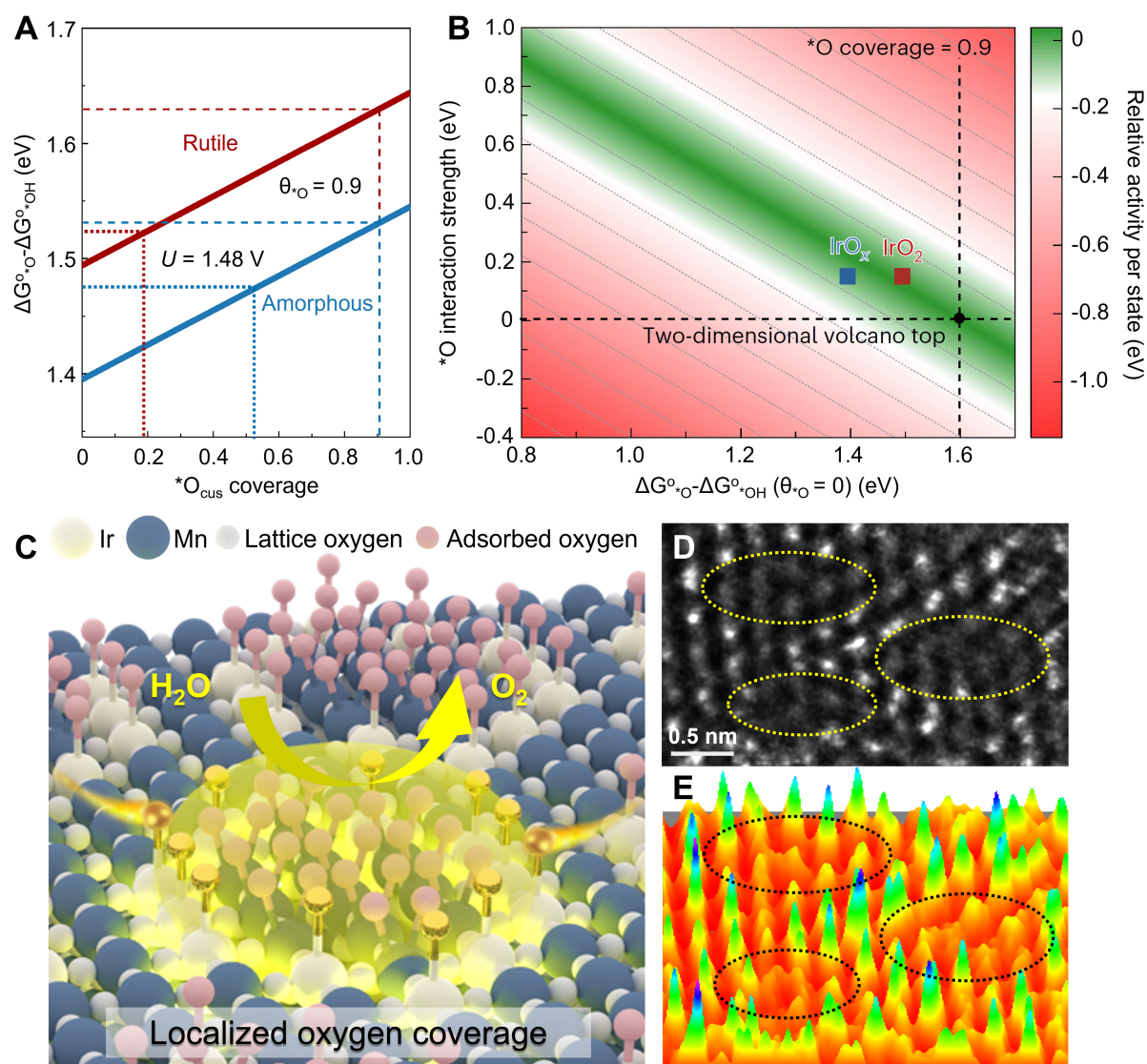
Green hydrogen production powered by water electrolysis stands as a promising technology for renewable energy transition and storage. However, oxygen evolution reaction (OER) with sluggish multi-electron-transferred process has limited the overall efficiency of water splitting. For iridium-based benchmark materials, understanding the intrinsic water oxidation kinetics and realizing accurate activity descriptors are key factors to help design better electrocatalysts for practical application of water electrolysis.

Recently reported in *Nature Catalysis*, through clever analysis of the absorption spectra in *operando* time-resolved ultraviolet-visible (UV-vis) spectroscopy, Liang *et al.* have quantified the active site density and oxygen binding strengths on different iridium oxides, unveiling the effect of adsorbate-adsorbate interactions on O–O bond formation<sup>[1]</sup>. Previously, for rational design of OER catalysts, oxygen adsorption energy ( $\Delta G_{\text{O}}$ ) was first introduced by Rossmeisl and Nørskov *et al.* to describe the OER activity<sup>[2,3]</sup>, and the standard free energy change  $\Delta G_{\text{O}}^{\circ} - \Delta G_{\text{OH}}^{\circ}$  was universally applied as the activity descriptor with a volcano-type relationship<sup>[4-6]</sup>. In this work, besides the conventional binding energetics of  $\Delta G_{\text{O}}^{\circ} - \Delta G_{\text{OH}}^{\circ}$ , an additional oxygen coverage effect showed how the interactions between adsorbates can control the OER kinetics [Figure 1A]. A clever modification of the conventional activity descriptor was made, as shown in the improved three-dimensional volcano plot [Figure 1B]. Accordingly, the previous descriptor  $\Delta G_{\text{O}}^{\circ} -$



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**Figure 1.** (A) Experimentally determined  $\Delta G^{\circ}_{\text{O}} - \Delta G^{\circ}_{\text{OH}}$  values at different oxygen coverages; (B) Effects of the  $*\text{O}$  interaction strength and  $*\text{O}$  binding strength on the OER activity. Reproduced with permission<sup>[7]</sup>; (C) Schematic illustration of oxygen coverage effect on atomic grid structure toward accelerated O–O bond formation; (D and E) Atomic-resolution high-angle annular dark field scanning transmission electron microscopy image of atomic grid structure on Ir-Mn- $\text{O}_v$  catalyst and the corresponding three-dimensional surface plot with atom-overlapping. Reproduced with permission<sup>[7]</sup>.

$\Delta G^{\circ}_{\text{OH}}$  was deconvoluted into: (1) the intermediate binding strength without oxygen coverage [ $\Delta G^{\circ}_{\text{O}} - \Delta G^{\circ}_{\text{OH}} (\theta_{\text{O}} = 0)$ ], and (2) the interaction strength between adsorbates [ $\Delta G^{\circ}_{\text{O}} - \Delta G^{\circ}_{\text{OH}} (\theta_{\text{O}} = 0) + r\theta_{\text{O}}$ ]. Thereby, an optimized catalyst design could be directed by balancing the two opposing effects. Thus, the conventional optimal binding energetics can be broken by increasing the oxygen coverage in the case of over-strong  $*\text{O}$  binding at active sites.

Our recent work has also demonstrated the oxygen coverage effect to promote O–O bond formation during the OER process [Figure 1C]<sup>[7]</sup>. A new metal-support configuration of dense atomic grids was constructed through high-density Ir sites ( $\sim 10$  atoms per  $\text{nm}^2$ ) supported on  $\text{MnO}_{2-x}$  [Figure 1D and E]. Initial Mn- $\text{O}_v$  coordination defects in  $\text{MnO}_{2-x}$  give rise to electrochemical generation of enriched oxygen coverage as

probed by the increased Mn-O coordination intensity under OER potentials from *operando* X-ray absorption fine structure (XAFS) spectra. Moreover, the Ir grid lines proceed with highly electrophilic nature of Ir-O<sup>(II-δ)-</sup> bonds during OER, facilitating oxygen radicals on Ir sites directly coupling with the rich oxygen adsorbates on support Mn sites. Thereby, an ultra-low OER overpotential of 166 mV at 10 mA·cm<sup>-2</sup> and a striking mass activity which was 380 times higher than commercial IrO<sub>2</sub> were achieved on this catalyst. The oxygen coverage effect also conforms to the practical operation at an oxygen-enriched environment on the anode side of the proton exchange membrane water electrolyzer, which leads to a low cell voltage of 1.58 V to reach the current density of 1 A·cm<sup>-2</sup>.

In summary, the oxygen coverage effect can be complementary to the conventional binding energetics. Based on this insight, future active OER catalysts can be predicted and designed far beyond the current models. Those non-precious metal-based materials, which have not been considered as promising catalysts owing to inappropriate oxygen binding strength, could be activated by optimizing oxygen coverage through crystallinity design, defect engineering, porosification treatment, and so on. Moreover, OER pathways, including enriched oxygen coverage-induced oxygen pathway mechanism (OPM), can be considered to overcome the scaling relationship between the intermediates<sup>[7]</sup>. Conventional lattice oxygen mechanism (LOM) can also be modified with high oxygen coverage, which aids in replenishing the surface oxygen vacancies that resulted from lattice oxygen oxidation and avoids structural collapse<sup>[8]</sup>. Furthermore, for impure water electrolysis such as seawater electrolysis, the oxygen coverage effect can also act as a powerful handle to prevent Cl<sup>-</sup> binding and aids the exclusive selectivity toward OER.

## DECLARATIONS

### Authors' contributions

Wrote the draft manuscript: Lin H

Revised and rewrote some parts of the manuscript: Liu P, Yang H

### Availability of data and materials

Not applicable.

### Financial support and sponsorship

This work was financially supported by the National Natural Science Foundation of China (22239001) and the Shanghai Pilot Program for Basic Research (22TQ1400100-12).

### Conflicts of interest

Liu P is a Junior Editorial Board Member of the journal *Chemical Synthesis*, while the other authors have declared that they have no conflicts of interest.

### Ethical approval and consent to participate

Not applicable.

### Consent for publication

Not applicable.

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## REFERENCES

1. Liang C, Rao RR, Svane KL, et al. Unravelling the effects of active site density and energetics on the water oxidation activity of iridium oxides. *Nat Catal* 2024;7:763-75. DOI
2. Rossmeisl J, Qu ZW, Zhu H, Kroes GJ, Nørskov JK. Electrolysis of water on oxide surfaces. *J Electroanal Chem* 2007;607:83-9. DOI
3. Rossmeisl J, Logadottir A, Nørskov JK. Electrolysis of water on (oxidized) metal surfaces. *Chem Phys* 2005;319:178-84. DOI
4. Gloag L, Somerville SV, Gooding JJ, Tilley RD. Co-catalytic metal-support interactions in single-atom electrocatalysts. *Nat Rev Mater* 2024;9:173-89. DOI
5. Deng L, Hung SF, Lin ZY, et al. Valence oscillation of Ru active sites for efficient and robust acidic water oxidation. *Adv Mater* 2023;35:e2305939. DOI PubMed
6. Oener SZ, Bergmann A, Cuenya BR. Designing active oxides for a durable oxygen evolution reaction. *Nat Synth* 2023;2:817-27. DOI
7. Lin HY, Yang QQ, Lin MY, et al. Enriched oxygen coverage localized within Ir atomic grids for enhanced oxygen evolution electrocatalysis. *Adv Mater* 2024;36:e2408045. DOI PubMed
8. Gou W, Zhang S, Wang Y, et al. Oxygen spillover from RuO<sub>2</sub> to MoO<sub>3</sub> enhances the activity and durability of RuO<sub>2</sub> for acidic oxygen evolution. *Energy Environ Sci* 2024;17:6755-65. DOI



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