

Research Highlight

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Oxygen coverage effect promotes oxygen evolution reaction

Haoyang Lin, Pengfei Liu*, Huagui Yang*

Key Laboratory for Ultrafine Materials of Ministry of Education, School of Materials Science and Engineering, East China University of Science and Technology, Shanghai 200237, China.

*Correspondence to: Prof. Pengfei Liu, Prof. Huagui Yang, Key Laboratory for Ultrafine Materials of Ministry of Education, School of Materials Science and Engineering, East China University of Science and Technology, No. 130 Meilong Road, Xuhui District, Shanghai 200237, China. E-mail: pfliu@ecust.edu.cn; hgyang@ecust.edu.cn

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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^[1]. Previously, for rational design of OER catalysts, oxygen adsorption energy (ΔG_{O}) was first introduced by Rossmeisl and Nørskov *et al.* to describe the OER activity^[2,3], and the standard free energy change $\Delta G_{\text{O}}^0 - \Delta G_{\text{OH}}^0$ was universally applied as the activity descriptor with a volcano-type relationship^[4–6]. In this work, besides the conventional binding energetics of $\Delta G_{\text{O}}^0 - \Delta G_{\text{OH}}^0$, 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 $\Delta G_{\text{O}}^0 -$



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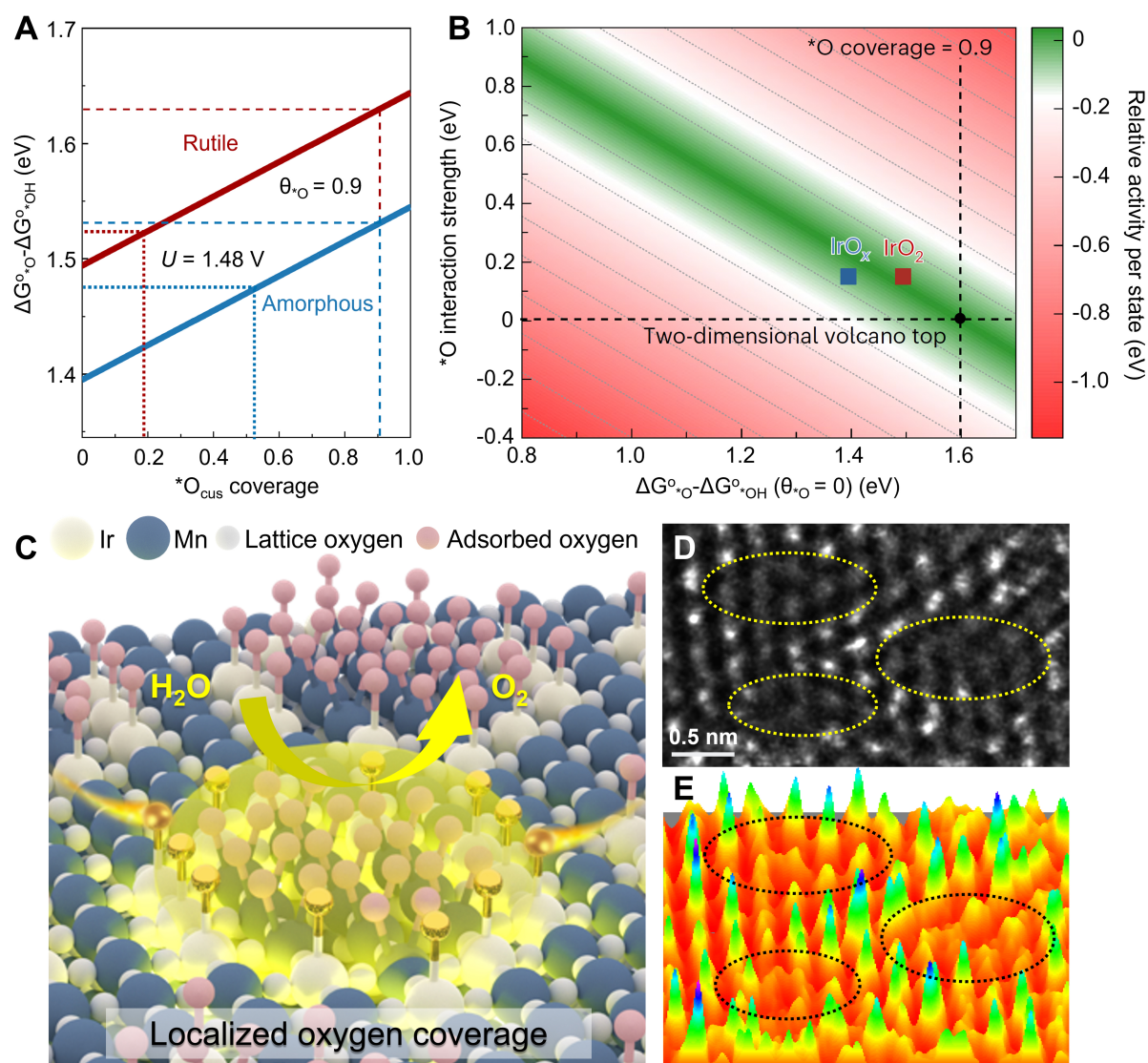


Figure 1. (A) Experimentally determined $\Delta G^\circ_{\text{O}} - \Delta G^\circ_{\text{OH}}$ values at different oxygen coverages; (B) Effects of the $^*\text{O}$ interaction strength and $^*\text{O}$ binding strength on the OER activity. Reproduced with permission^[7]; (C) Schematic illustration 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-O_v catalyst and the corresponding three-dimensional surface plot with atom-overlapping. Reproduced with permission^[7].

$\Delta G^\circ_{\text{OH}}$ 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]^[7]. A new metal-support configuration of dense atomic grids was constructed through high-density Ir sites (~ 10 atoms per nm^2) supported on MnO_{2-x} [Figure 1D and E]. Initial Mn-O_v coordination defects in 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^{(II-δ)-} 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⁻² and a striking mass activity which was 380 times higher than commercial IrO₂ 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⁻².

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^[7]. 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^[8]. Furthermore, for impure water electrolysis such as seawater electrolysis, the oxygen coverage effect can also act as a powerful handle to prevent Cl⁻ 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.

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Conflicts of interest

All authors declared that there are no conflicts of interest.

Ethical approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

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Hao Yang Lin

Hao Yang Lin received his B.S. degree from East China University of Science and Technology (ECUST) in 2022. He is currently a Ph.D. candidate under the supervision of Prof. Hua Gui Yang in the School of Materials Science and Engineering at ECUST. His current research interests focus on the design of advanced nanomaterials for proton exchange membrane-based water electrolysis.



Peng Fei Liu

Peng Fei Liu received his B.S. and Ph.D. degrees from East China University of Science and Technology (ECUST) in 2013 and 2018, respectively, and then worked in Prof. Hua Gui Yang's group as a Postdoctoral Research Fellow. Since 2020, he has served as an Associate Research Fellow/Professor at ECUST. His current research interests involve the design and synthesis of inorganic functional materials with well-defined structures for electrocatalysis.



Hua Gui Yang

Prof. Hua Gui Yang received his Ph.D. degree from the National University of Singapore in 2005. He joined the University of Queensland in 2007 as a Postdoctoral Research Fellow. After completing his postdoctoral training, he returned to China and assumed a professorship at East China University of Science and Technology in late 2008. His main research interests lie in the rational design and fabrication of functional materials for solar fuels.