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Hui Zhang¹, Jie Bao¹, Baojie Li², Jiulong Wu², Qizheng An², Aidong Wu¹(✉), Hui Su³(✉), Qinghua Liu²(✉)

¹ Department of Radiation Oncology, The First Affiliated Hospital of USTC, Division of Life Sciences and Medicine, University of Science and Technology of China, Hefei 230001, China

² National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei 230029, China

³ National & Local Joint Engineering Laboratory for New Petro-chemical Materials and Fine Utilization of Resources, College of Chemistry and Chemical Engineering, Hunan Normal University, Changsha 410081, China

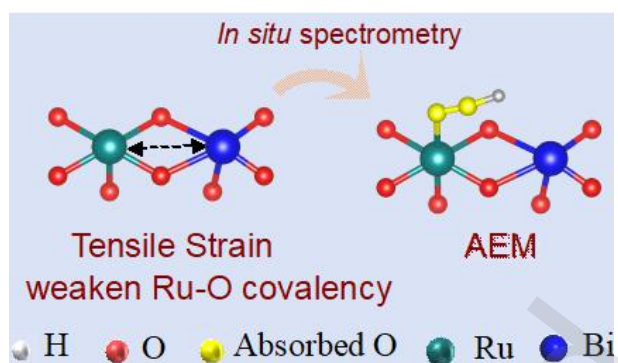
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The incorporation of Bi into the RuO₂ lattice induces low- valence Ru and compressive lattice strain, which collectively weaken Ru–O covalency. This facilitates a stable adsorbate evolution pathway, thereby enhancing the acidic oxygen evolution reaction performance in a PEM electrolyzer.

Lone-pair Bi stabilized low-valent Ru sites with modulated Ru-O covalency for efficient acidic oxygen evolution

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³ National & Local Joint Engineering Laboratory for New Petro-chemical Materials and Fine Utilization of Resources, College of Chemistry and Chemical Engineering, Hunan Normal University, Changsha 410081, China

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✉ Address correspondence to Qinghua Liu, qhliu@ustc.edu.cn; Hui Su, suhui@hunnu.edu.cn; Aidong Wu, flkaidongwu@163.com



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ABSTRACT: Ruthenium dioxide (RuO_2) is a promising and cost-effective substitute for iridium oxide in the acidic oxygen evolution reaction (OER), but its application is hindered by the intrinsic trade-off between catalytic activity and stability due to the dissolution of high-valent metal sites. Herein, we design a heavy p-block element Bi-modified RuO_2 electrocatalyst in which the lone-pair electrons of Bi stabilize low-valence Ru and introduce tensile strain, yielding weakened metal-oxygen covalency and overcoming the activity-stability limitation. In situ spectroscopies confirm that the Bi lone-pair inhibits Ru overoxidation, ensuring outstanding structural stability of $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$, and simultaneously promote the formation of the pivotal $^*\text{OOH}$ intermediate, confirming a stable adsorbate evolution pathway instead of the traditional lattice oxygen mechanism. This highlights the critical role of bond covalency in stabilizing surface Ru and oxygen sites for enhanced acidic-OER durability. As a result, the $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$ electrocatalyst delivers an ultralow overpotential of 269 mV at 100 mA cm^{-2} and a small Tafel slope of 65.8 mV dec^{-1} . When implemented as the anode catalyst in a practical proton-exchange membrane water electrolyzer, $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$ enables a current density of 3.0 A cm^{-2} at a cell voltage of only 1.837 V and sustains stable operation for 40 h at 200 mA cm^{-2} .

KEYWORDS: strain engineering; bond covalency; oxygen evolution mechanism; *in situ* technique

1 Introduction

Utilizing renewable electricity to produce and store hydrogen offers a viable pathway to alleviate the fossil fuel crisis[1-5]. Currently, proton exchange membrane water electrolysis (PEMWE) stands out as a promising and sustainable technology for producing green hydrogen because of its numerous advantages, including high purity, instantaneous current response, low ohmic loss, high-current density operation and strong compatibility with renewable power sources[6-8]. However, the sluggish oxygen evolution reaction (OER) and highly corrosive anodic environment in the PEMWE cause severe catalyst degradation, limiting the commercial prospects of the PEMWE[9,10]. Iridium oxide (IrO_2) is widely employed as a commercial OER catalyst in PEMWE due to its robust acid resistance, but its high cost impedes its large-scale deployment in industrial electrolyzers[11-13]. Thus, developing active, long-lasting and cost-effective substitutes for IrO_2 -based electrocatalysts is highly desirable for improving PEMWE performance and facilitating its large-scale application but remains a major challenge.

Rutile-phase RuO_2 is widely regarded as a promising replacement owing to its higher acidic OER activity and lower price relative to IrO_2 [14-16]. Nevertheless, RuO_2

suffers from unsatisfactory stability in harsh acidic and oxidative environments, primarily owing to the activation of lattice oxygen through lattice oxygen mechanism (LOM), and the consequent over-oxidation of Ru into high-valence soluble species such as RuO_4 [17-19]. Various strategies, including heteroatom doping, defect engineering, and heterojunction construction have been developed to improve the activity and durability of RuO_2 -based catalysts under acidic conditions[20]. For instance, Sun et al. introduced oxygen vacancies to modulate the local coordination structures of RuO_2 and promote metallic Ru-Ru interactions, thereby suppressing Ru over-oxidation and enhancing its stability during the acidic OER[21]. Despite these advancements, achieving a favorable balance between catalytic activity and stability for RuO_2 -based catalysts remains challenging. Recent studies have demonstrated that tuning the covalency of active metal-oxygen (M-O) bonds through electronic structure modulation can influence OER performance and lattice-oxygen participation[22]. Accordingly, introducing suitable metal dopants into RuO_2 to tailor the electronic structure and Ru-O covalency may provide a promising approach for improving the catalytic performance of RuO_2 . The corrosion-resistant heavy p-block metals possess high stability in acidic environments and

distinctive lone-pair electron features, which provide a high possibility of regulating the electronic structure and Ru–O bond. However, the catalytic mechanism of heavy *p*-block-element-modified RuO₂ remains scarcely systematically explored in acidic OER systems, hindering the rational design of high-performance Ru-based catalysts.

In this study, Bi species with 6s² lone-pair electrons were deliberately introduced into the RuO₂ lattice to construct a *p*-block Bi-modified RuO₂ electrocatalyst through a one-pot glucose-blowing and annealing strategy. At the atomic level, the lone-pair electrons of Bi stabilize low-valence Ru and induce tensile strain, yielding weakened Ru–O bond covalency and breaking the activity–stability trade-off. Accordingly, the Bi_{0.2}Ru_{0.8}O₂ electrocatalyst displays an ultralow overpotential of 269 mV at 100 mA cm⁻² and a remarkably small Tafel slope of 65.8 mV dec⁻¹ for the OER in 0.5 M H₂SO₄. More interestingly, when employed as the anode in a PEM electrolyzer, the catalyst achieved high activity, with a cell voltage of 1.837 V at 3 A cm⁻² at 80 °C, surpassing the performance of most reported RuO₂-based catalysts. Combined *in situ* Ru *K*-edge X-ray absorption spectroscopy, synchrotron radiation Fourier transform infrared spectrometry and differential electrochemical mass spectrometry analyses demonstrate that Bi doping suppresses lattice-oxygen participation, stabilizes the Ru oxidation state and maintains structural stability, thereby inducing the reaction pathway transition of Bi_{0.2}Ru_{0.8}O₂ from the conventional LOM to the AEM. This work highlights the role of bond covalency in simultaneously enhancing the activity and durability of Ru-based OER catalysts, offering a promising route toward cost-effective PEM water electrolysis.

2 Experimental Section

2.1 Synthesis of Bi-doped RuO₂.

A mixture of 10.0 g glucose and 2.0 g urea was dissolved in 10.0 mL deionized water and stirred to obtain a homogeneous solution. Subsequently, 0.4 mmol RuCl₃ and 0.1 mmol Bi(NO₃)₃·5H₂O were added at room temperature. Then, the resulting solution was heated at 150 °C for 10 h in an oven to yield a porous foam, which was then annealed in a muffle furnace at 400 °C for 10 h with a heating rate of 5 °C min⁻¹. After cooling to room temperature, the obtained product was subsequently immersed in 1 M HCl for 12 h, followed by thorough washing with ethanol and deionized water. The resulting product was then vacuum-dried to yield Bi_{0.2}Ru_{0.8}O₂ catalyst. The same preparation procedure was applied to synthesize Bi_{0.1}Ru_{0.8}O₂ and Bi_{0.3}Ru_{0.8}O₂ by varying the amount of Bi(NO₃)₃·5H₂O added.

2.2 Synthesis of sRuO₂.

The preparation process of sRuO₂ catalyst was similar to that of Bi-doped RuO₂, except that Bi(NO₃)₃·5H₂O was not added.

2.3 Characterization

The SEM and TEM analyses were conducted at the Experimental Center for Engineering and Materials Science, University of Science and Technology of China. The SEM images were performed on a Gemini SEM 500 instrument, whereas TEM, HRTEM, and EDS mapping were carried out using a JEM-2100F microscope. XRD patterns were recorded

on a Philips X'Pert Pro Super diffractometer with Cu Kα radiation ($\lambda = 1.54178 \text{ \AA}$), scanning over a 2θ range of 20–80°. The concentration of Ru and Bi were quantified by ICP-OES (Plasma Quad). Electron paramagnetic resonance (EPR) measurements were conducted on a JES-FA 200 spectrometer (JEOL). Atomic-resolution HAADF-STEM images, EELS spectra, and elemental mapping were acquired using a Thermo Fisher Scientific Themis Z microscope. XPS data were collected on a Thermo NEXSA G2 spectrometer utilizing an Al-Kα X-ray source ($h\nu = 1486.6 \text{ eV}$) at the Instrument Center for Physical Science, University of Science and Technology of China. Ru *K*-edge XAFS spectra were measured on beamline BL11B of Shanghai Synchrotron Radiation Facility (SSRF), and the resulting spectra were processed using the Athena software.

3 Results and discussion

3.1 Synthesis and characterization of Bi_{0.2}Ru_{0.8}O₂

The Bi-doped RuO₂ (Bi_{*x*}Ru_{0.8}O₂, where *x* denotes the molar ratio of Bi, with values of 0.1, 0.2, and 0.3 for the samples) electrocatalysts were synthesized by incorporating *p*-block Bi atoms into the RuO₂ lattice through a one-pot glucose-blowing strategy followed by annealing and acid washing (Fig. S1). Briefly, RuCl₃ and Bi(NO₃)₃ were dissolved in a uniform solution of glucose and urea. When the mixture was heated in the oven, the thermal decomposition of urea released gases, thereby creating a porous foam. The resulting solid was then subjected to pyrolysis at 400 °C for 10 h in air to remove the glucose framework, followed by acid washing to eliminate Bi-related impurity species, yielding the final catalyst (Bi_{*x*}Ru_{0.8}O₂). In addition, synthetic RuO₂ nanocrystals (sRuO₂) without Bi incorporation were prepared as a control sample.

The transmission electron microscopy (TEM) images clearly reveal uniform nanoparticulate crystals with an average length of ~6 nm for Bi_{0.2}Ru_{0.8}O₂ samples (Fig. 1a and 1b). The high-resolution TEM (HRTEM) displays lattice fringes of 0.323 nm corresponding to the (110) plane of the rutile framework (Fig. 1c)[23]. In comparison, the lattice spacing decreases slightly to 0.318 nm in sRuO₂ (Fig. S2). The spherical aberration corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) is further applied to investigate the crystal structure of Bi_{0.2}Ru_{0.8}O₂ (Fig. 1d). Clear lattice fringes with interplanar spacings of 0.323 nm are observed, which are assigned to the (110) plane of RuO₂. The ordered metal atom arrangement without evidence of separate bismuth oxide phases indicates successful substitution of Bi into the RuO₂ lattice. The intensity of the HAADF-STEM signal is proportional to the atomic number of different elements[24]. Therefore, the brighter dots can be identified as heavier Bi atoms. The intensity profile in Fig. 1e further confirms the presence of single Bi atoms in Bi_{0.2}Ru_{0.8}O₂. The X-ray diffraction (XRD) pattern of Bi_{0.2}Ru_{0.8}O₂ shows diffraction peaks consistent with those of rutile RuO₂ (PDF#40-1290), with no detectable bismuth oxide phases, confirming the formation of Bi-doped rutile RuO₂ structure (Fig. 1f)[25]. Additionally, the diffraction peak of Bi_{0.2}Ru_{0.8}O₂ shifts to lower angles relative to those of sRuO₂ as the shift becomes more pronounced as the Bi content increases (Fig. S5),

indicating slight lattice expansion, consistent with an increased interplanar spacing[26]. The inductively coupled plasma-optical emission spectrometry (ICP-OES) analysis confirm the atomic ratio of Bi: Ru is around 1:4.46. The

energy dispersive spectroscopy (EDS) mapping images of $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$ indicate a homogeneous distribution of Bi, Ru, and O (Fig. 1g-1j).

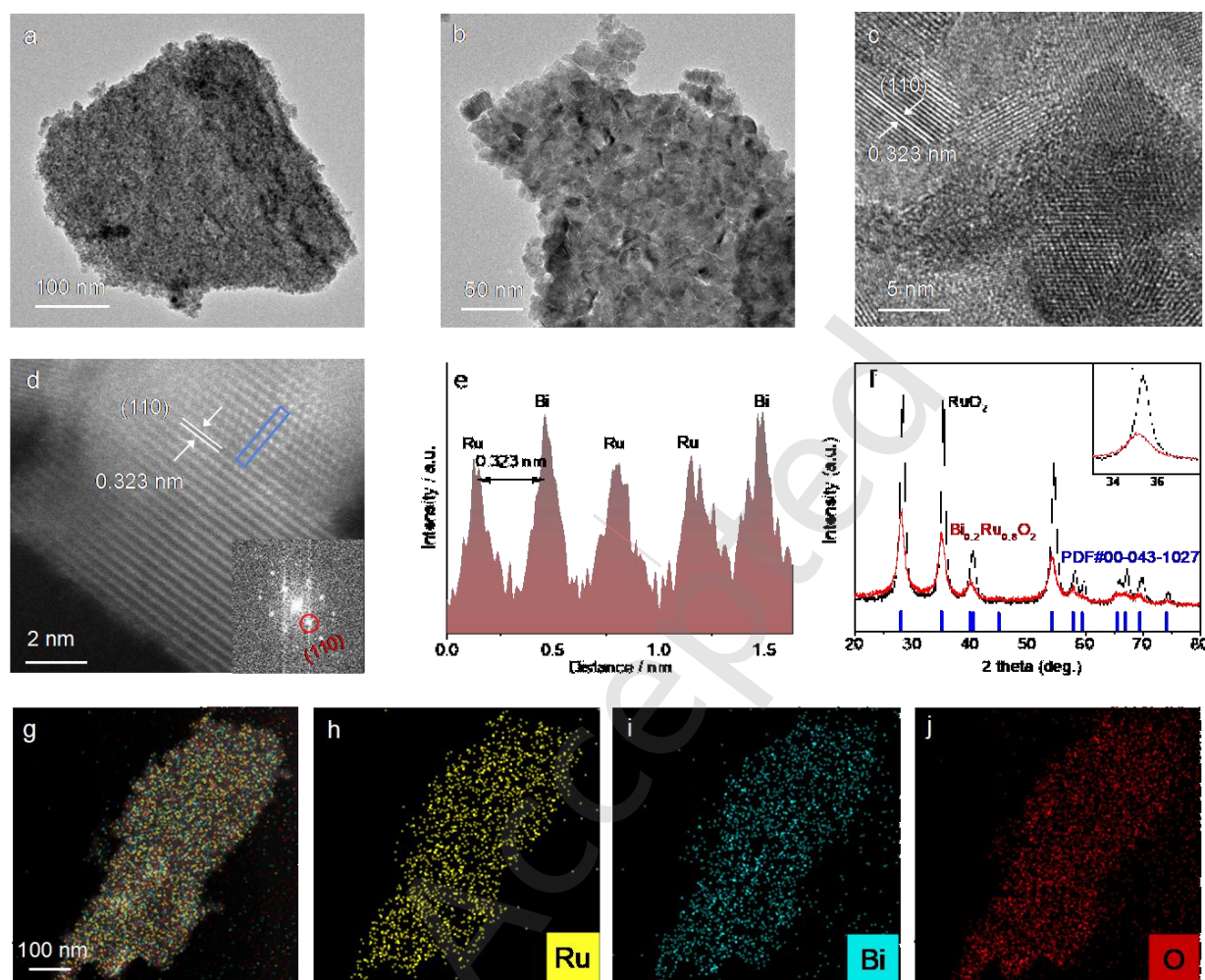


Fig. 1. Structural characterizations of electrocatalysts. (a, b) TEM images, and (c) HRTEM image, and (d) HAADF-STEM image and corresponding fast Fourier transform pattern, and (e) the corresponding intensity profile of the blue boxes shown in (d) for $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$ catalyst. (f) XRD patterns and extended XRD patterns of $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$ and sRuO_2 . (g) Elemental mappings of Bi, Ru and O in $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$ catalyst.

3.2 Electronic structure characterizations

To elucidate the surface chemical states of Bi and Ru in $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$, X-ray photoelectron spectroscopy (XPS) measurements were performed. In the Ru 3p XPS spectra of $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$, the characteristic peaks located at 462.85, 464.85, 485.13, and 487.15 eV can be attributed to the Ru 3p_{3/2} and Ru 3p_{1/2} with their satellites, respectively. Additionally, the binding energy of $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$ shift toward lower compared with those of sRuO_2 , implying the presence of lower-valence Ru species in $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$ (Fig. 2a). The reduced valence state of Ru can effectively mitigate Ru over-oxidation[27]. For the Bi 4f XPS spectrum of $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$, two principal peaks centered at 158.7 eV and 164.0 eV are observed, corresponding to Bi 4f_{7/2} and Bi 4f_{5/2} of Bi³⁺, respectively (Fig. S7). For the O 1s spectra (Fig. 2b), the peaks at approximately 529.87 eV, 530.48 eV, and 531.57 eV are attributed to lattice oxygen, hydroxyl species, and

adsorbed H₂O in sRuO_2 . The peaks of O 1s in $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$ shift negatively relative to those of sRuO_2 , indicating increased electron density on Ru and O in $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$. Moreover, electron paramagnetic resonance (EPR) measurements verify the absence of oxygen vacancies in $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$ (Fig. S8). X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) analyses were employed to probe the electronic states and local coordination environments of the as-prepared samples. The Ru *M*-edge spectra of $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$ exhibit a pronounced red shift relative to that of sRuO_2 , consistent with the Ru XPS results (Fig. 2c). The O *K*-edge XANES spectra of sRuO_2 catalyst in the Fig. 2d display two pronounced features at 529.2 and 532.4 eV, assigned to the transitions of O 1s electrons into hybridized O 2p – Ru 4d *t*_{2g} and *e*_g states resulting from octahedral field splitting. A broader peak at higher energy arises from hybridization between the O 2p orbital and Ru 5sp states. Compared to those of sRuO_2 , the

lower t_{2g}/e_g intensity ratio and the lower fission energy value of 10Dq between t_{2g} and e_g in $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$ indicate weakened Ru–O covalency and more Ru^{n+} species ($3 < n < 4$) [28,29]. As shown in Fig. 2e, the Ru K-edge XANES spectra of sRuO_2 and $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$ are positively shifted relative to that of Ru foil, confirming the oxidation state of Ru in the two samples. Compared with that of sRuO_2 , the absorption edge position of $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$ shows a lower energy shift, suggesting a reduced Ru oxidation state, which is consistent with the results of the XPS characterization [30]. The Fourier

transforms (FTs) of the Ru K-edge EXAFS spectrum in sRuO_2 show two dominant peaks at $\sim 1.5 \text{ \AA}$ and $\sim 3.09 \text{ \AA}$, which can be assigned to the first Ru–O shell and the next nearest Ru–Ru shell, respectively (Fig. 2f). The nearly identical Ru K-edge EXAFS spectra of $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$ and sRuO_2 suggest analogous local coordination motifs after Bi incorporation. The Ru–O bond in $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$ is marginally longer compared with that of sRuO_2 , which consequently affects the adsorption of reaction intermediates at the metal sites.

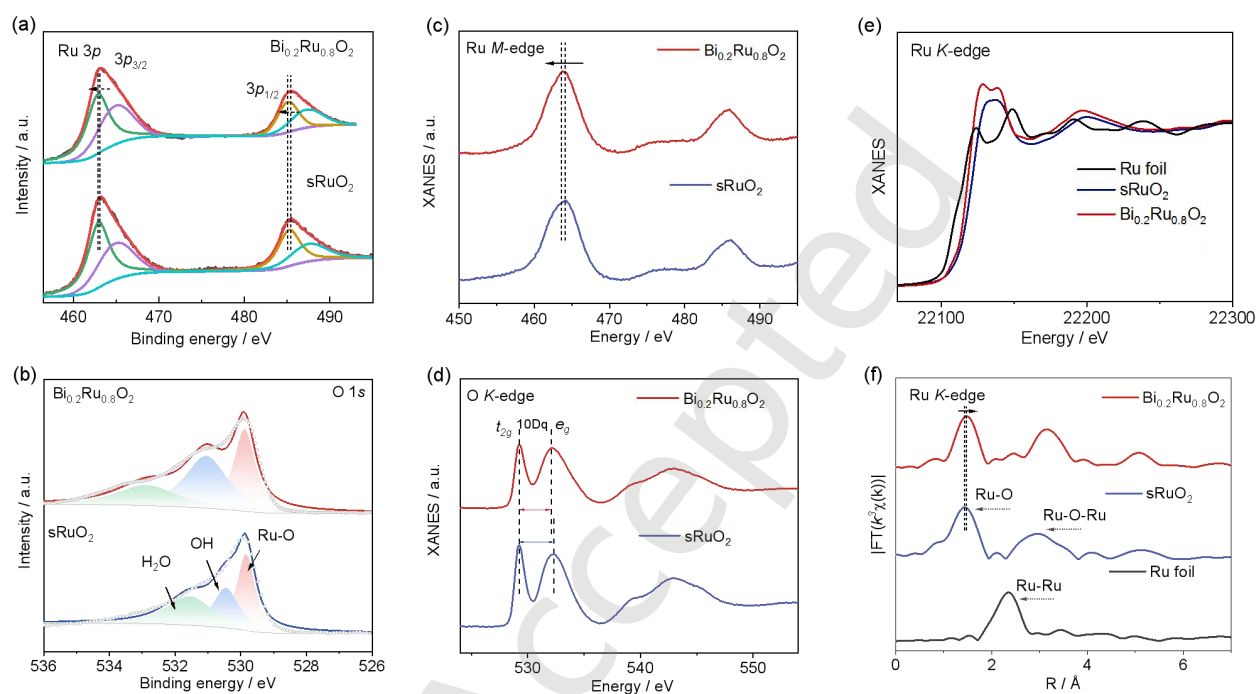


Fig. 2. Electronic structure characterizations of electrocatalysts. (a) Ru 3p XPS spectra, and (b) O 1s XPS spectra, and (c) Ru M-edge, and (d) O K-edge XANES spectra analysis of $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$ and sRuO_2 samples. (e) XANES spectra at the Ru K-edge, and (f) Fourier transforms (FTs) of the Ru K-edge EXAFS oscillations of $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$, sRuO_2 and Ru foil.

3.3 Electrocatalytic OER performance

The OER activity of $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$ was investigated in 0.5 M H_2SO_4 aqueous electrolyte using a three-electrode setup. The most favorable Bi doping concentration was identified through controlled optimization, leading to the selection of $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$ as the representative catalyst (Fig. S9). Fig. 3a shows the iR-corrected linear sweep voltammetry (LSV) curves of $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$ and reference catalysts. The $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$ sample delivers 10 mA cm^{-2} at an overpotential of 201 mV, markedly lower than that of sRuO_2 (270 mV @ 10 mA cm^{-2}) and commercial RuO_2 (referred to as cRuO_2) (349 mV @ 10 mA cm^{-2}), confirming that Bi incorporation effectively enhances the OER activity. Moreover, to achieve a current density of 100 mA cm^{-2} , the $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$ catalyst requires an overpotential of only 269 mV, which is 160 mV lower than that of sRuO_2 (Fig. S10). The LSV curves without iR compensation are shown in Fig. S11. As shown in Fig. 3b, $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$ exhibits a Tafel slope of 65.8 mV dec^{-1} , substantially smaller than that of sRuO_2 ($101.4 \text{ mV dec}^{-1}$) and cRuO_2 (208 mV dec^{-1}), indicating faster reaction kinetics. To elucidate the intrinsic catalytic activity, the

electrochemically active surface area (ECSA) was estimated from the electrochemical double-layer capacitance (C_{dl}) obtained via cyclic voltammetry at different scan rates [30]. The $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$ exhibits the highest C_{dl} (17.13 mF cm^{-2}), which is 2-3 times greater than that of sRuO_2 (8.23 mF cm^{-2}) and cRuO_2 (6.29 mF cm^{-2}), indicating a substantially larger number of accessible active sites (Fig. 3c and S12). After normalizing the OER activity by ECSA, $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$ maintains superior intrinsic activity compared with sRuO_2 , confirming that the enhanced OER performance arises not only from the enlarged surface area but also from the intrinsic activity promoted by Bi doping (Fig. S13). The mass activity (M.A.) and turnover frequency (TOF) reach $\sim 1078.76 \text{ A gRu}^{-1}$ and 1017.01 h^{-1} at 1.53 V, 10 times higher than those of sRuO_2 (Fig. S14). The $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$ electrocatalyst exhibits competitive performance, featuring low overpotential, favorable Tafel slope, elevated M.A. and TOF (Fig. 3d). We employed in situ electrochemical impedance spectroscopy (EIS) measurements under various applied potentials to reveal the charge-transfer characteristics. In the Bode phase diagrams, $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$ and sRuO_2 display nearly identical phase angles in the high-frequency domain ($\approx 10^2$ – 10^4 Hz),

suggesting comparable oxidation responses associated with their inner-layer resistance (Fig. 3e and S15). The phase-angle peaks in the low-frequency region ($\approx 10^{-2} - 10$ Hz), which reflect the interfacial charge-transfer processes occurring at the electrolyte-catalyst interface, progressively diminish with the increasing applied potential, following the trend $\text{cRuO}_2 > \text{sRuO}_2 > \text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$ (Fig. 3f)[31-33]. This behavior indicates that $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$ facilitates more rapid electron transfer and thus promotes faster OER kinetics[34]. The Nyquist plots further corroborate the accelerated

interfacial charge-transfer process of $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$ evidenced by its markedly smaller semicircle across all external biases (Fig. S16). The EIS data conducted at 1.497 V vs. RHE were quantitatively fitted using the equivalent circuit model shown in Fig. S17. The $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$ exhibits the lowest charge-transfer resistance (R_{ct}) value than sRuO_2 and cRuO_2 , which is consistent with its superior OER activity (Table S1) [35]. These characteristics establish $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$ as a cost-effective and efficient acidic OER catalyst.

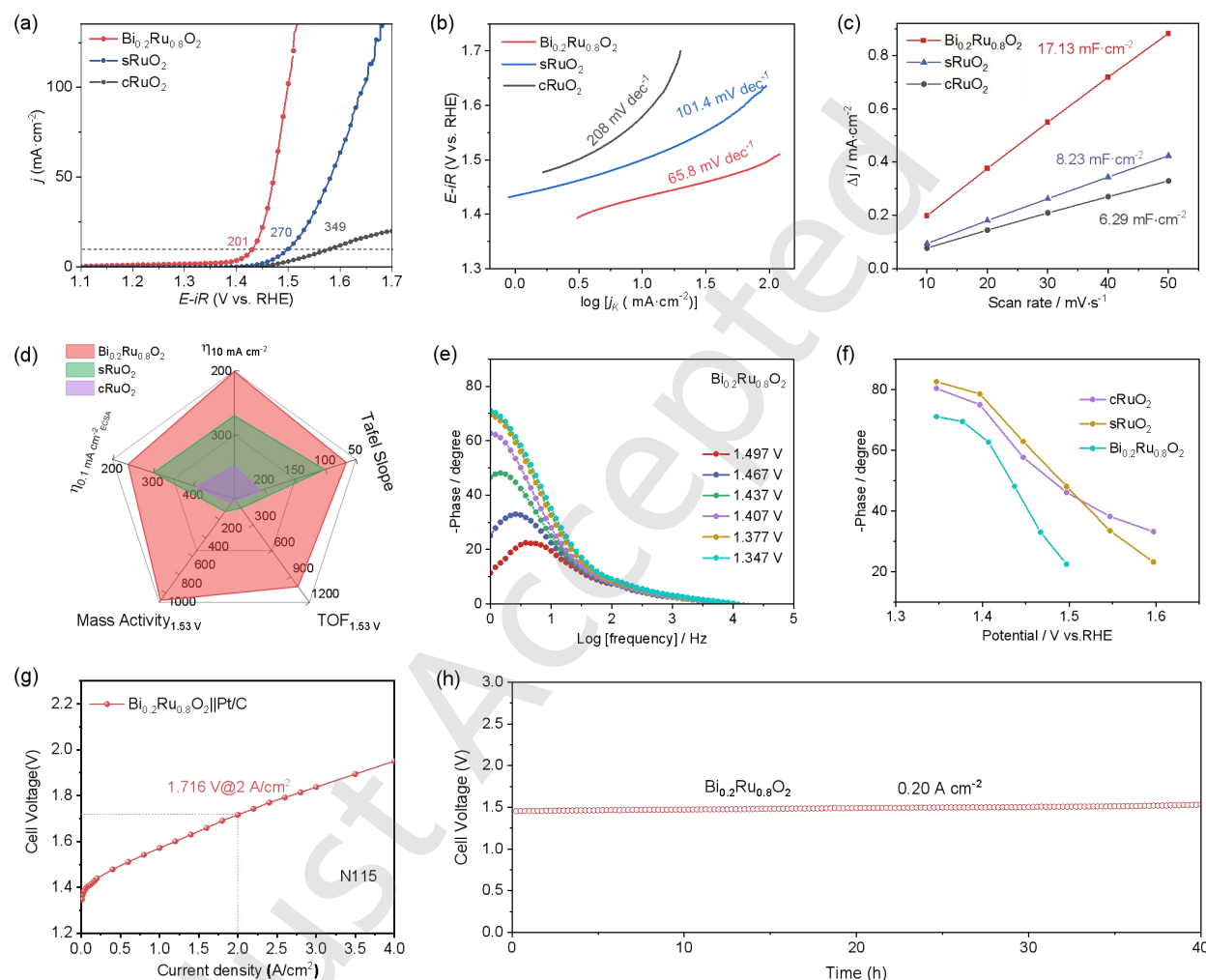


Fig. 3. Performance of the electrocatalysts. (a) LSV curves, and (b) Tafel plots, and (c) Double layer capacitance (C_{dl}) diagrams of $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$, sRuO_2 and cRuO_2 electrocatalysts in 0.5 M H_2SO_4 electrolyte. (d) Comprehensive comparison of $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$, sRuO_2 and cRuO_2 for OER in a radar chart. (e) Bode phase plots of $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$ recorded in 0.5 M H_2SO_4 electrolyte at various OER potentials. (f) Response of the phase angle to varying applied potentials for the $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$, sRuO_2 and cRuO_2 . (g) Polarization curves of PEM electrolyzers using $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$ catalyst as the anodic catalyst and commercial Pt/Ti as the cathodic catalyst at 80 °C. (h) The chronopotentiometry curve of the PEM device using $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$ catalyst at 0.20 A cm^{-2} .

The durability of electrocatalysts under acidic conditions is an indispensable factor determining their practical applicability for water-splitting. The durability of $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$ was evaluated via CV cycles in 0.5 M H_2SO_4 . Notably, $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$ maintained robust stability even after 10000 CV cycles (Fig. S18), confirming its long-term robustness under acidic OER conditions. Chronopotentiometry stability tests reveal that $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$

exhibits remarkable long-term stability compared to cRuO_2 . Specifically, $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$ maintains nearly constant potential over 120 h at 10 mA cm^{-2} , while cRuO_2 rapidly deactivates within 20 h (Fig. S19). Inductively coupled plasma mass spectrometry (ICP-MS) was employed to quantitatively assess the elemental dissolution behavior of the catalysts during the OER stability tests. Notably, the Ru leaching from $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$ is only 1.3%, which is markedly lower than that of cRuO_2 (Table S2). Consistently, the S-number of

$\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$ is markedly higher than that of cRuO_2 (Table S3). Collectively, the results demonstrate that the incorporation of Bi into the RuO_2 lattice markedly enhances corrosion resistance and durability. Furthermore, TEM and HRTEM images confirmed that the morphology and lattice spacing of $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$ remained largely unchanged after OER test (Fig. S20). Clearly, the XRD results demonstrate that the crystalline phase of $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$ remains well preserved after the durability test (Fig. S21). Post-stability XPS analysis reveals a slight increase in the Ru valence state of $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$, implying self-oxidation of Ru within the oxidation potential window (Fig. S22). The Bi 4f core level of $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$ after operation exhibited a shift to lower binding energies compared to the fresh sample, suggesting enhanced electron density at the Bi sites (Fig. S22c). The alteration in valence state indicates the participation of Bi during the OER process.

To assess the practical applicability of $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$ under

actual industrial operating conditions, the electrocatalytic performance was further evaluated in a proton exchange membrane (PEM) electrolyzer with a large electrode area of 5 cm^2 under constant temperature of $80\text{ }^\circ\text{C}$, using Nafion 115 as the proton exchange membrane and commercial Pt/C as the cathode electrocatalyst. The polarization I-V curve indicates that $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$ -based 5 cm^2 PEM electrolyzer can achieve current densities of 1, 2, and 3 A cm^{-2} at cell voltages of 1.571, 1.716, and 1.837 V, respectively (Fig. 3g). Notably, this performance surpasses the U.S. Department of Energy's 2025 benchmark of 3 A cm^{-2} at 1.9 V[36]. Meanwhile, under continuous operation at 0.2 A cm^{-2} , the cell voltage increases by only $\sim 70\text{ mV}$ after 40 h (Fig. 3h). The cell also maintains good stability at higher current densities (Fig. S23), further demonstrating durability under PEMWEI operating conditions.

3.4 Insights into the catalytic mechanism

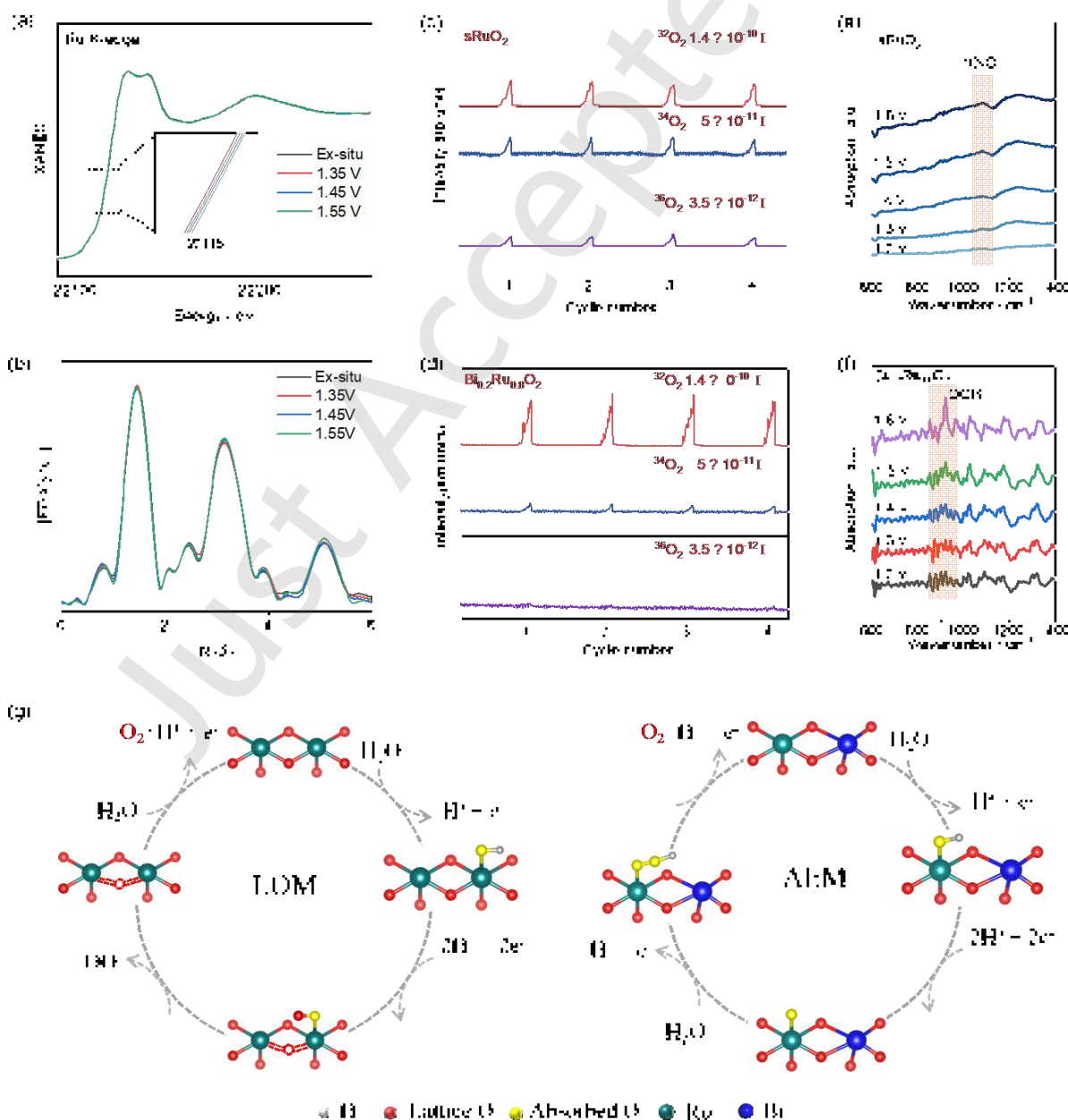


Fig. 4. Reaction mechanism of the OER. (a) In situ Ru *K*-edge XANES analyses of $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$ during acidic OER. (b) The corresponding Ru *K*-edge FT-EXAFS spectra. In situ DEMS signals of the O_2 products in a H_2^{18}O -based acidic solvent for ^{18}O -labeled (c) sRuO_2 and (d) $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$. In situ SR-FTIR spectra of (e) sRuO_2 and (f) $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$ recorded at various OER potentials. (g) Schematic illustration LOM pathway of sRuO_2 and AEM pathway of $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$.

In situ X-ray absorption spectroscopy (XAS) experiments were performed to probe the evolution of electronic structure and coordination environment of Ru during the acidic OER conditions[37, 38]. With increasing applied potential, the Ru *K*-edge XANES absorption edge of $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$ shifts slightly toward higher energy, revealing an increased in the Ru oxidation state during the OER process (Fig. 4a). The relatively stable Ru valence state indicates that Bi doping can effectively inhibit excessive Ru oxidation, thus mitigating Ru dissolution under operating conditions. The FT-EXAFS spectra of $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$ show a slight variation in peak intensity and negligible shift in peak position as the applied potential increases, suggesting high structural stability and negligible lattice-oxygen involvement under acidic OER conditions (Fig. 4b and S24). To further gain an in-depth understanding of the OER kinetics across the different catalysts, in situ differential electrochemical mass spectrometry (DEMS) and synchrotron radiation Fourier transform infrared (SR-FTIR) measurements were carried out. In-situ ^{18}O isotope-labeled DEMS was further employed to elucidate the OER pathway. The catalysts were first enriched with ^{18}O through multiple LSV cycles (1.1–1.5 V vs. RHE) in H_2^{18}O aqueous H_2SO_4 electrolyte. Subsequently, the ^{18}O -labeled catalysts were thoroughly rinsed with H_2^{16}O deionized water and subjected to in situ DEMS measurements conducted in H_2^{16}O -based electrolyte. The mass signals corresponding to $^{32}\text{O}_2$, $^{34}\text{O}_2$, and $^{36}\text{O}_2$ were detected by online mass spectrometry for both $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$ and sRuO_2 (Fig. 4c and 4d). The formation of $^{34}\text{O}_2$ stems from the coupling between surface-labeled ^{18}O and electrolyte-derived ^{16}O through the LOM pathway, indicating the involvement of lattice oxygen. Notably, the observed $^{34}\text{O}_2$ and $^{36}\text{O}_2$ signals in the sRuO_2 indicate the occurrence of LOM. For $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$, the gaseous products reveal that $^{32}\text{O}_2$ dominated the product distribution, accompanied by trace amounts of $^{34}\text{O}_2$, while no $^{36}\text{O}_2$ products were detected. Compared with sRuO_2 , the $^{34}\text{O}_2/^{32}\text{O}_2$ ratio on $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$ is significantly lower (Fig. S25). This isotopic signature indicates that the Bi doping effectively suppresses lattice oxygen over-oxidation, thereby inhibiting the LOM pathway and enhancing structural stability of $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$ [39]. To further monitor reaction intermediates generated during the OER process, in situ SR-FTIR spectroscopy was employed. For sRuO_2 , the pronounced band centered at approximately 1080 cm^{-1} is observed, which can be assigned to $^*\text{OO}$ species (Fig. 4e). This feature suggests that the oxygen evolution process of sRuO_2 is predominantly governed by continuous LOM, leading to faster dissolution and impairing stability. By contrast, the $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$ displays a feature at around 923 cm^{-1} , attributable to the O–O stretching vibration of $^*\text{OOH}$ species, a characteristic intermediate of adsorbate evolution mechanism (AEM) (Fig. 4f)[40]. The progressive enhancement of this signal with increasing applied potential indicates that the OER on $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$ predominantly proceeds via the AEM pathway. The mechanistic models were established in Fig. 4g based on in situ experimental

results. Introduction of heavy *p*-block Bi into RuO_2 lattice induces electron-rich Ru sites and weaker Ru–O covalency, thereby effectively switching the OER pathway of $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$ electrocatalyst from LOM to AEM.

4 Conclusions

The incorporation of lone-pair Bi into RuO_2 stabilizes Ru in a lower valence state and induces tensile strain, leading to weakened Ru–O bond covalency and markedly improved acidic OER electrocatalytic activity. In situ XAS, SR-FTIR and DEMS measurements indicate that the introduction of Bi effectively suppresses lattice-oxygen participation, inhibits Ru overoxidation and maintains structural stability during the OER, thereby favoring the AEM across the OER potential window. The $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$ catalyst achieves 100 mA cm^{-2} at an ultralow overpotential of 269 mV, while maintaining a stable performance for over 120 h at 100 mA cm^{-2} . When applied in a practical PEMWE, it requires only 1.837 V to achieve 3.0 A cm^{-2} with an active area of 5 cm^2 at 80°C .

Electronic Supplementary Material: Supplementary material (Experimental section, TEM, XRD, EPR, XPS, CV curves, EIS Nyquist plots) is available in the online version of this article at <https://doi.org/10.26599/NR.2026.94909189>.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and the Electronic Supplementary Material. Additional data related to this paper may be requested from the corresponding author upon request.

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Declaration of competing interest

All the contributing authors report no conflict of interests in this work.

Author contribution statement

Hui Zhang: Experimental design, writing manuscript, data curation, funding acquisition. Jie Bao: Validation. Baojie Li and Jiulong Wu: Data curation. Qizheng An: Investigation. Aidong Wu: Writing manuscript. Hui Su: Project administration, writing manuscript. Qinghua Liu: Conceptualization, writing manuscript, funding acquisition, Supervision. All the authors have approved the final manuscript.

Use of AI statement

None.

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Electronic Supplementary Material

Lone-pair Bi stabilized low-valent Ru sites with modulated Ru-O covalency for efficient acidic oxygen evolution

Hui Zhang¹, Jie Bao¹, Baojie Li², Jiulong Wu², Qizheng An², Aidong Wu¹✉, Hui Su³✉, Qinghua Liu²✉

¹ Department of Radiation Oncology, The First Affiliated Hospital of USTC, Division of Life Sciences and Medicine, University of Science and Technology of China, Hefei 230001, China

² National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei 230029, China

³ National & Local Joint Engineering Laboratory for New Petro-chemical Materials and Fine Utilization of Resources, College of Chemistry and Chemical Engineering, Hunan Normal University, Changsha 410081, China

✉ Address correspondence to Qinghua Liu, qhliu@ustc.edu.cn; Hui Su, suhui@hunnu.edu.cn; Aidong Wu, flkaidongwu@163.com

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1. Electrochemical measurements

A homogeneous catalyst ink was prepared by sonicating a mixture of 750 μL deionized water, 250 μL ethanol, 30 μL Nafion solution, and 5 mg of the catalyst sample. Then, 5 μL of the homogeneous catalyst ink was loaded onto a freshly polished glassy carbon electrode (GCE) with a diameter of 0.3 cm, yielding a catalyst loading of 0.34 mg cm^{-2} . The Ag/AgCl reference electrode was calibrated in H_2 -saturated 0.5 M H_2SO_4 using two Pt wires as the working and counter electrodes. The corrected potential was determined from CV cycles scanned near the open-circuit voltage. OER performance was evaluated in O_2 -saturated 0.5 M H_2SO_4 (pH = 0) at room temperature using a CHI760E electrochemical workstation in a standard three-electrode configuration. The catalyst-loaded GCE as the working electrode, the Pt wire as the counter electrode, and the Ag/AgCl as the reference electrode. All measured potentials were converted to the reversible hydrogen electrode (RHE) scale using the equation: $E(\text{vs. RHE}) = E(\text{vs. Ag/AgCl}) + 0.059 \text{ pH} + 0.197 \text{ V}$. The polarization curves were measured at a scan rate of 10 mV s^{-1} with 95% iR correction. Electrochemical impedance spectroscopy (EIS) was conducted at a fixed potential over a frequency range of 0.1 Hz to 100000 Hz. The electrochemical active surface area (ECSA) was proportional to the double-layer capacitance (C_{dl}), which was calculated by CV curves in a non-Faradaic region at scan rates of 10–50 mV s^{-1} . Stability tests were performed at the constant current density of 10 mA cm^{-2} . The ECSA was calculated using the formula: $\text{ECSA} = C_{\text{dl}} / C_s$, where C_s commonly assumed to be 0.04 mF cm^{-2} .

The mass activity of $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$ and sRuO_2 catalysts was evaluated by generally regarding the Ru sites as the active sites. The Ru contents in $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$ and sRuO_2 were determined by ICP-OES to be 38.6 wt.% and 51.3 wt.%, respectively. Accordingly, the mass activity ($\text{A g}_{\text{Ru}}^{-1}$) of the catalyst was calculated using the following equation:

$$\text{Mass activity} = \frac{A \times J \times 10^{-3}}{\text{metal loading on the electrode} (M_{\text{metal}})}$$

Where A represents the geometric electrode area (0.07065 cm^2) and M_{Ru} is the Ru metal loading mass on the electrode.

Similarly, the turnover frequency (TOF) was estimated by assuming all Ru atom in the catalyst as active sites. The number of Ru active sites was estimated from the Ru loading mass on the electrode, and the TOF was calculated using the following equation:

$$\text{TOF} = \frac{J \times A \times N_e \times 10^{-3}}{4 \times M_{\text{metal}} \times N_A / M}$$

where J is the current density (mA cm^{-2}), N_e is electron number per Coulomb (6.24×10^{18}), M_{metal} is the mass of Ru loading on the electrode, N_A is Avogadro constant ($6.02 \times 10^{23} \text{ mol}^{-1}$), and M is the Ru molar mass ($101.07 \text{ g mol}^{-1}$).

2. PEMWE tests

To bridge the gap between lab-scale research and practical implementation, device-level assessments of the catalysts were performed under industrially relevant conditions, characterized by high current densities ($>0.1 \text{ A cm}^{-2}$) and elevated temperatures ($>60^\circ\text{C}$). The proton exchange membrane water electrolyzer (PEMWE) was assembled using synthesized $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$ as the anode catalyst with a loading of approximately 3 mg cm^{-2} . A commercial Pt/C catalyst served as the cathode. Pt-coated Ti fiber was employed as the gas diffusion layer. Nafion 115 was used as the proton exchange membrane and was pretreated sequentially in H_2O_2 , deionized water and 0.5 M H_2SO_4 at 80°C for 1 h. The catalyst inks were prepared by dispersing the corresponding catalysts (5 mg mL^{-1}) in a solvent mixture of 5% Nafion solution, isopropanol, and deionized water. The cathode ink was uniformly sprayed onto the PEM surface. The catalyst-coated PEM was subsequently hot-pressed at

120 °C for 2 min under a pressure of 2 MPa to form the membrane electrode assembly (MEA). The MEA was sandwiched between two Ti bipolar plates with serpentine flow channels defining an active area of 2 cm × 2.5 cm to complete the PEMWE cell. The electrolyzer was operated at 80 °C using distilled water supplied to the anode by a peristaltic pump. All electrochemical measurements were recorded without iR compensation.

3. In situ XAFS measurements

The Ru *K*-edge XAFS measurements were collected at the 1W1B beamline station of the Beijing Synchrotron Radiation Facility (BSRF). In situ XAFS measurements were performed with a homemade electrochemical cell. The catalyst ink was dropped on a 1 × 1 cm² carbon cloth, which served as the working electrode, with Pt wire and Ag/AgCl electrode used as counter and reference electrode, respectively. In situ spectra were recorded under a series of constant potentials ranging from 1.35–1.55 V vs. RHE.

4. In situ SR-FTIR measurements

In situ SR-FTIR measurements were performed at the BL01B beamline of the National Synchrotron Radiation Laboratory (NSRL, China) using a custom-designed top-plate electrochemical cell. The working electrode was a target catalyst-coated carbon cloth. A platinum wire and an Ag/AgCl electrode served as the counter and reference electrodes, respectively. Infrared spectra were collected after each potential had been maintained for 5 min to ensure spectral stability. The background spectrum was recorded under open-circuit conditions, followed by measurements in the OER potential range of 1.20–1.60 V vs. RHE. Each spectrum was obtained by averaging 514 scans at a resolution of 2 cm⁻¹ to achieve high signal fidelity.

5. In situ DEMS measurements

The in-situ DEMS measurements were conducted in a custom-designed electrochemical cell with a three-electrode system and a LingLu QAS100 mass spectrometer. For isotopic labeling, the 0.5 M H₂SO₄ electrolyte was prepared using H₂¹⁸O as the solvent. The incorporation of ¹⁸O into the catalyst lattice was achieved by applying LSV to the working electrode for cycles at 1.10–1.50 V vs. RHE in the H₂¹⁸O-based acidic electrolyte. After labeling, both the electrodes and the electrochemical cell were thoroughly rinsed with H₂¹⁶O to eliminate residual H₂¹⁸O. The electrodes were then transferred to an H₂¹⁶O-containing H₂SO₄ electrolyte, where LSV was subsequently performed in the range of 1.10–1.50 V vs. RHE. During this process, the evolution of O₂ (³²O₂ = ¹⁶O¹⁶O, ³⁴O₂ = ¹⁶O¹⁸O and ³⁶O₂ = ¹⁸O¹⁸O) under OER conditions was continuously monitored by mass spectrometry.

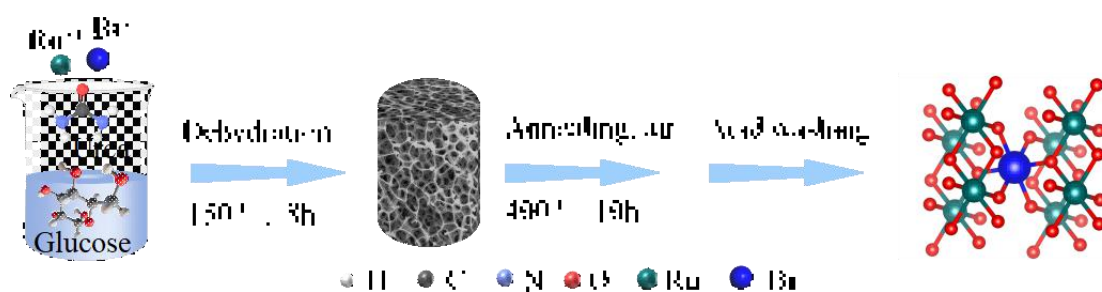


Fig. S1. Schematic illustration of the synthesizing Bi-doped RuO_2 catalysts.

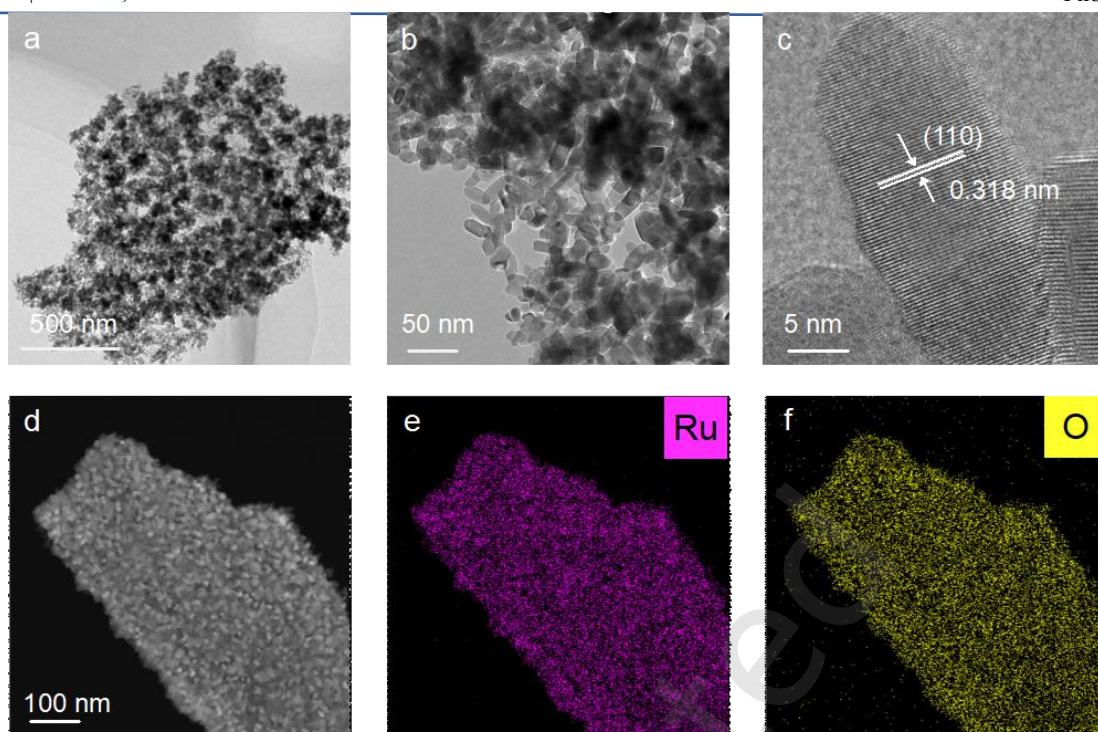


Fig. S2. (a, b) TEM images and (c) HRTEM image of the sRuO₂ catalyst. (d-f) Elemental mappings of Ru and O in the sRuO₂ catalyst.

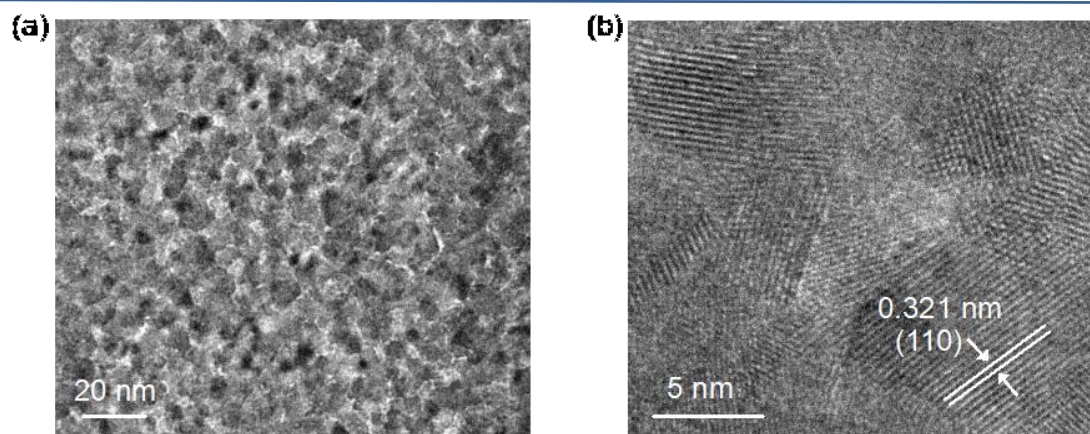


Fig. S3. (a) TEM image and (b) HRTEM image of the $\text{Bi}_{0.1}\text{Ru}_{0.8}\text{O}_2$ catalyst.

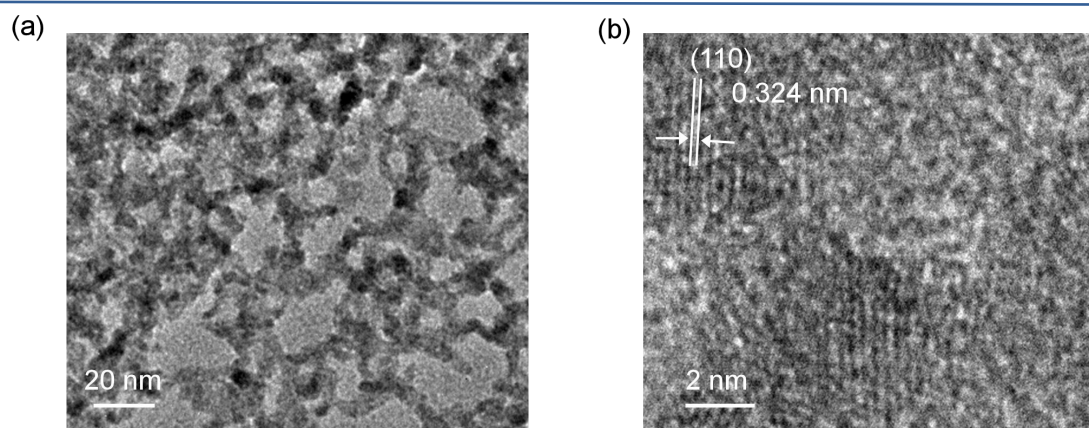


Fig. S4. (a) TEM image and (b) HRTEM image of the $\text{Bi}_{0.3}\text{Ru}_{0.8}\text{O}_2$ catalyst.

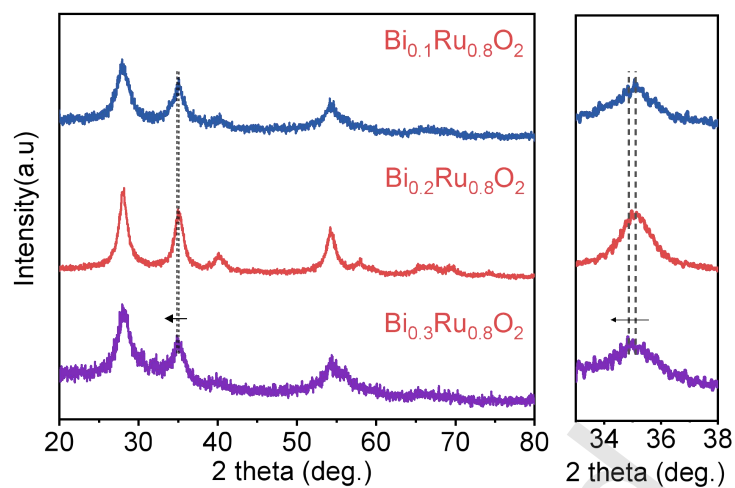


Fig. S5. The XRD pattern of $\text{Bi}_{0.1}\text{Ru}_{0.8}\text{O}_2$, $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$ and $\text{Bi}_{0.3}\text{Ru}_{0.8}\text{O}_2$ catalyst.

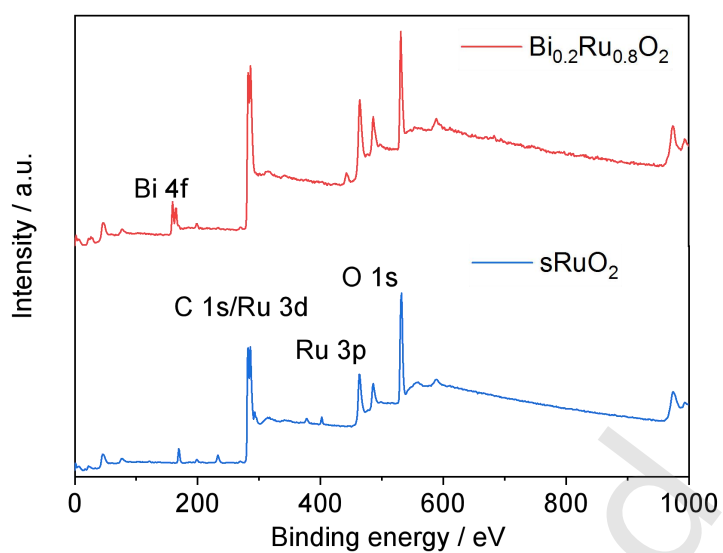


Fig. S6. The XPS survey spectra of $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$ and sRuO_2 catalysts.

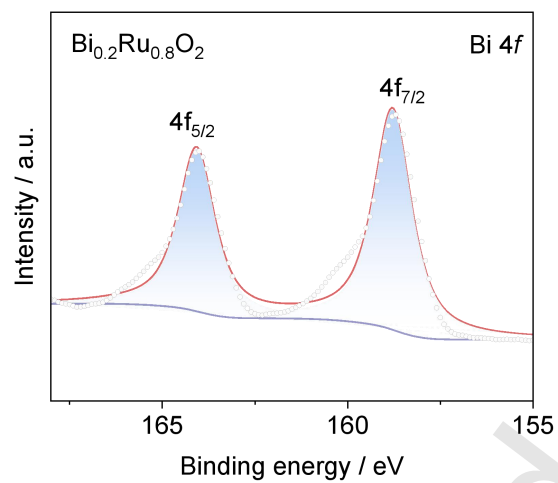


Fig. S7. The Bi 4fXPS spectrum of $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$ catalyst.

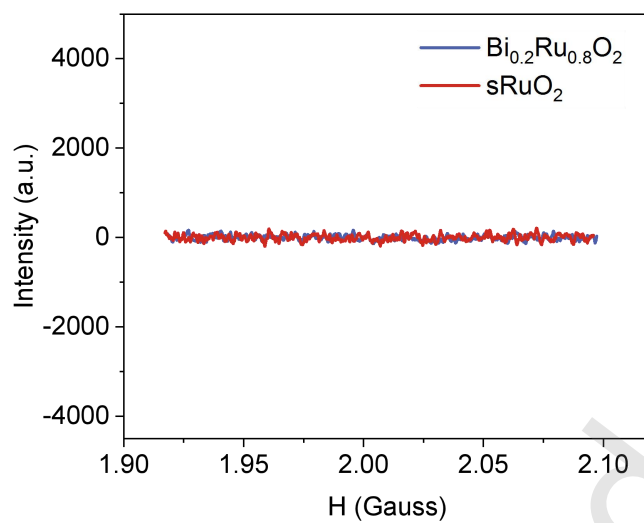


Fig. S8. Electron paramagnetic resonance spectra of $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$ and sRuO_2 .

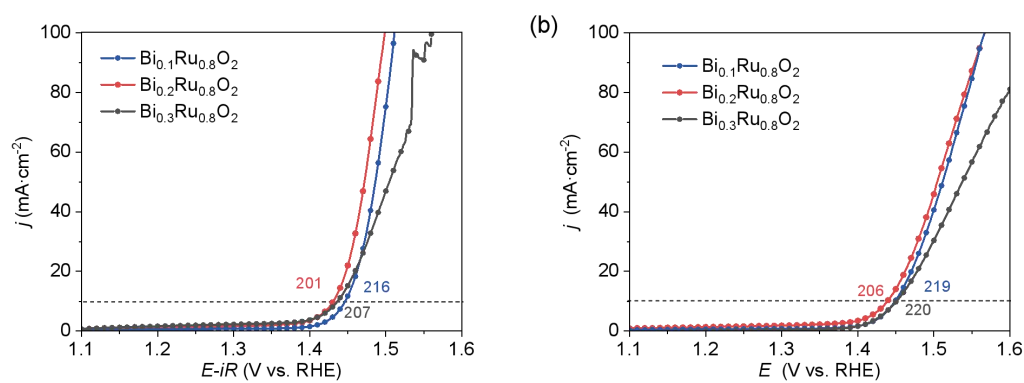


Fig. S9. (a) The LSV curves with iR correction, and (b) LSV curves without iR correction of $\text{Bi}_{0.1}\text{Ru}_{0.8}\text{O}_2$, $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$, and $\text{Bi}_{0.3}\text{Ru}_{0.8}\text{O}_2$ catalysts.

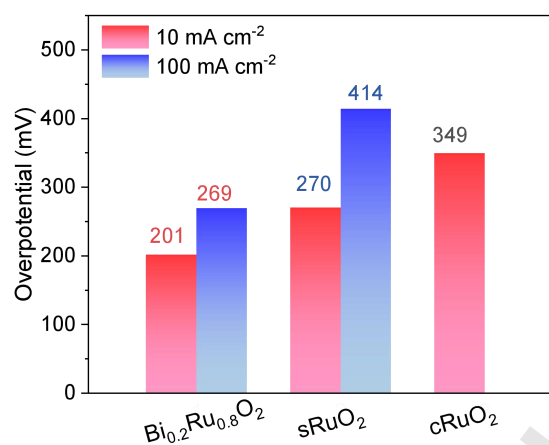


Fig. S10. The overpotentials at current densities of 10 and 100 mA cm^{-2} of $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$, sRuO_2 and cRuO_2 electrocatalysts in the $0.5 \text{ M H}_2\text{SO}_4$ aqueous electrolyte.

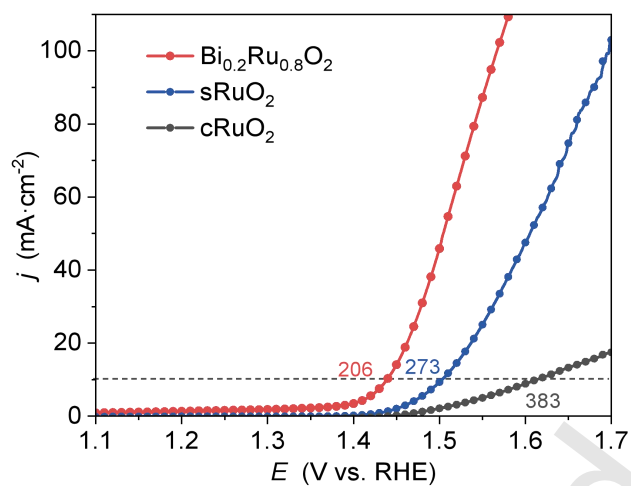


Fig. S11. The LSV curves without iR correction of $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$, sRuO_2 , and cRuO_2 catalysts.

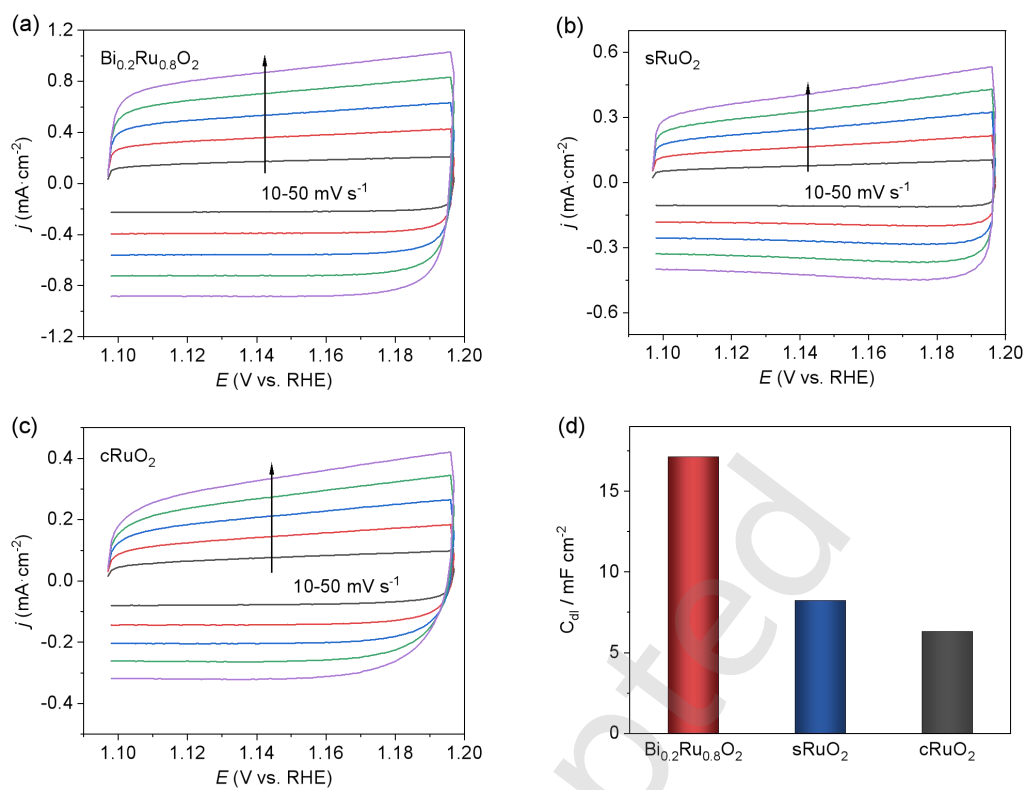


Fig. S12. The CV curves of (a) $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$, (b) sRuO_2 , and (c) cRuO_2 at different scan rates from 10 to 50 mV s^{-1} . (d) C_{dl} results for $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$, sRuO_2 , and cRuO_2 catalysts.

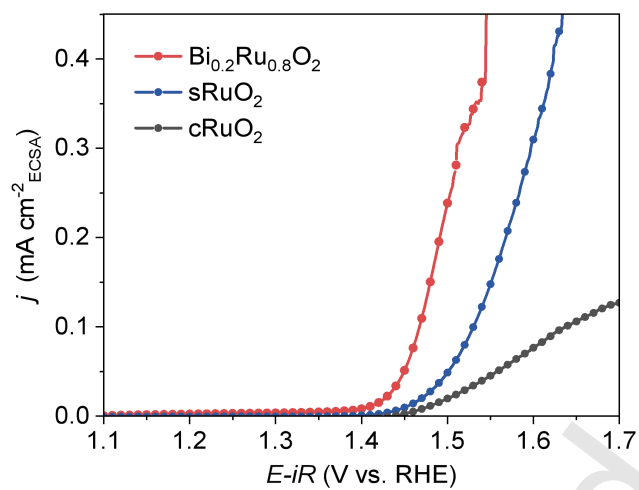


Fig. S13. The ECSA-normalized LSV curves of $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$, sRuO_2 , and cRuO_2 catalysts.

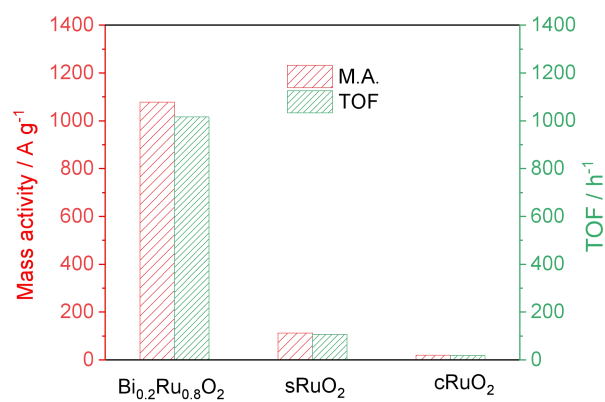


Fig. S14. M.A. and TOF at 1.53 V versus RHE of Bi_{0.2}Ru_{0.8}O₂, sRuO₂, and cRuO₂ catalysts.

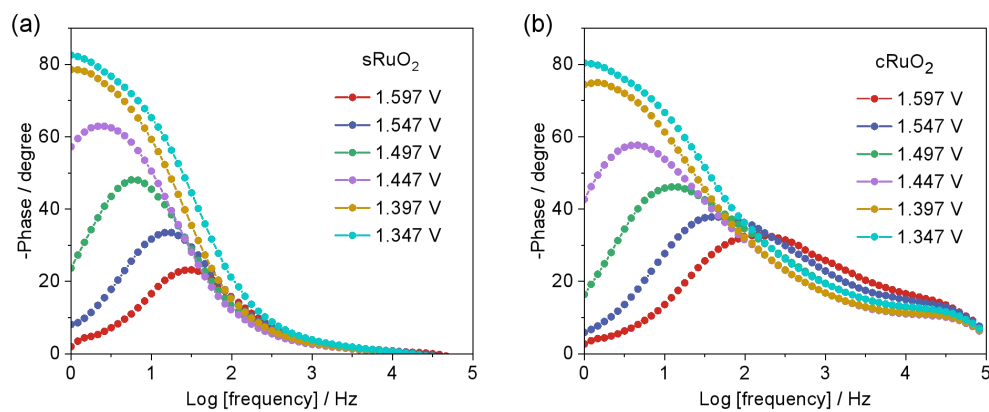


Fig. S15. Bode phase plots of sRuO₂ and cRuO₂ recorded in 0.5 M H₂SO₄ electrolyte at various OER potentials.

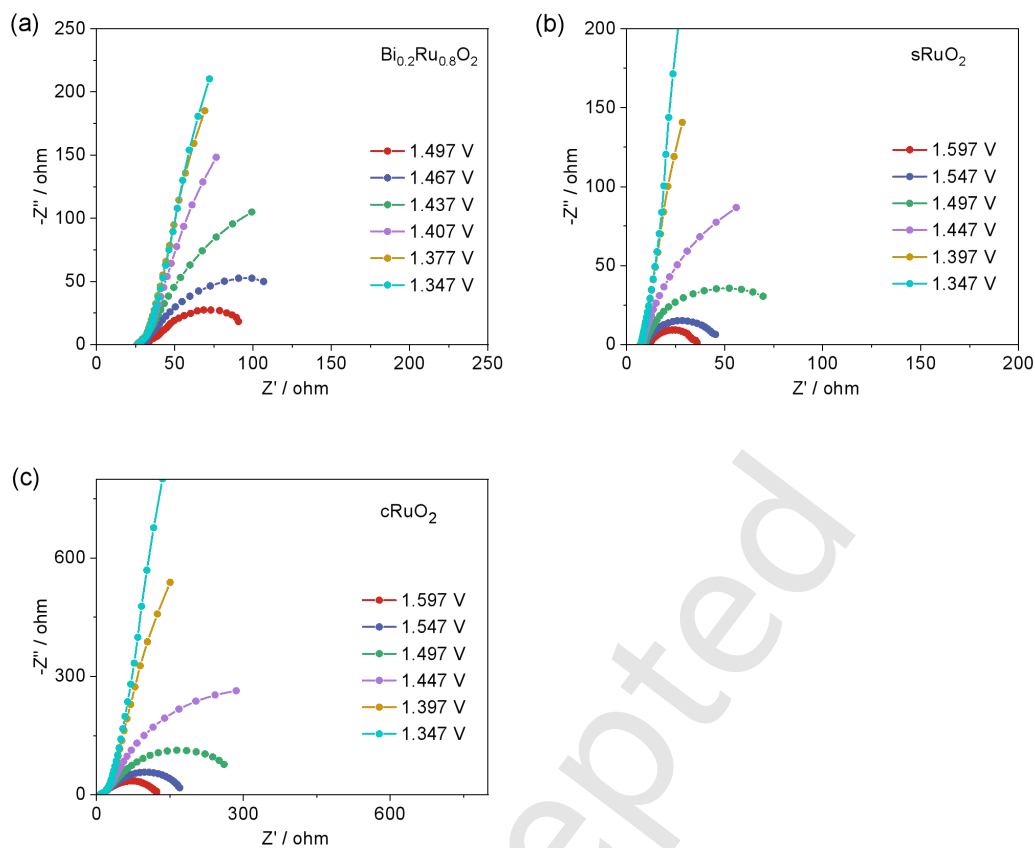


Fig. S16. EIS Nyquist plots for (a) $Bi_{0.2}Ru_{0.8}O_2$, (b) $sRuO_2$, and (c) $cRuO_2$ during various OER potentials in 0.5 M H_2SO_4 .

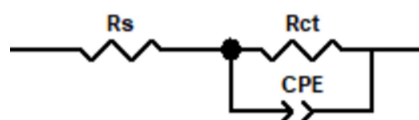


Fig. S17. Equivalent circuits of the OER.

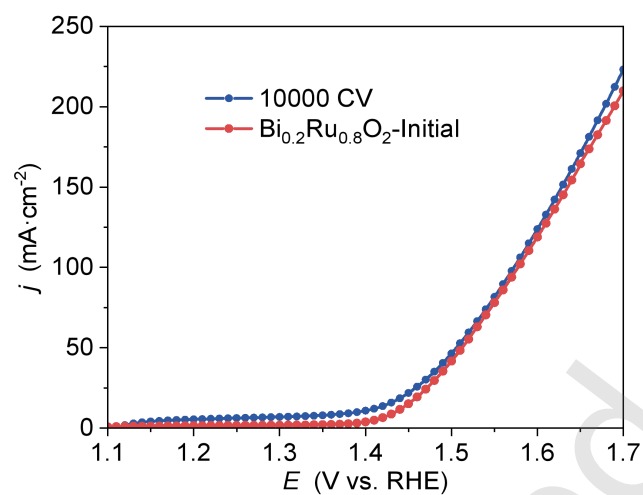


Fig. S18. LSV curves of Bi_{0.2}Ru_{0.8}O₂ before and after 10 000 CV cycles.

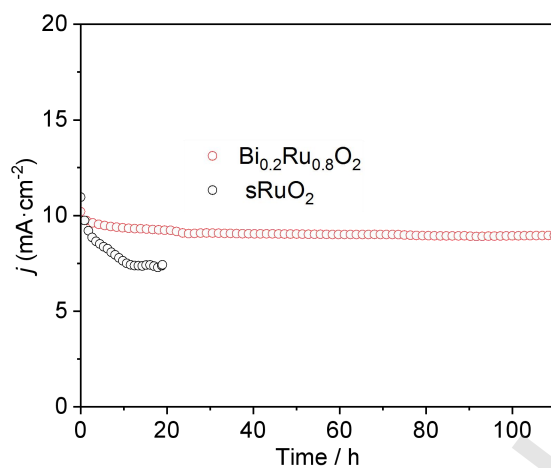


Fig. S19. Chronopotentiometry curves at 10 mA cm⁻² for $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$ and sRuO_2 catalysts.

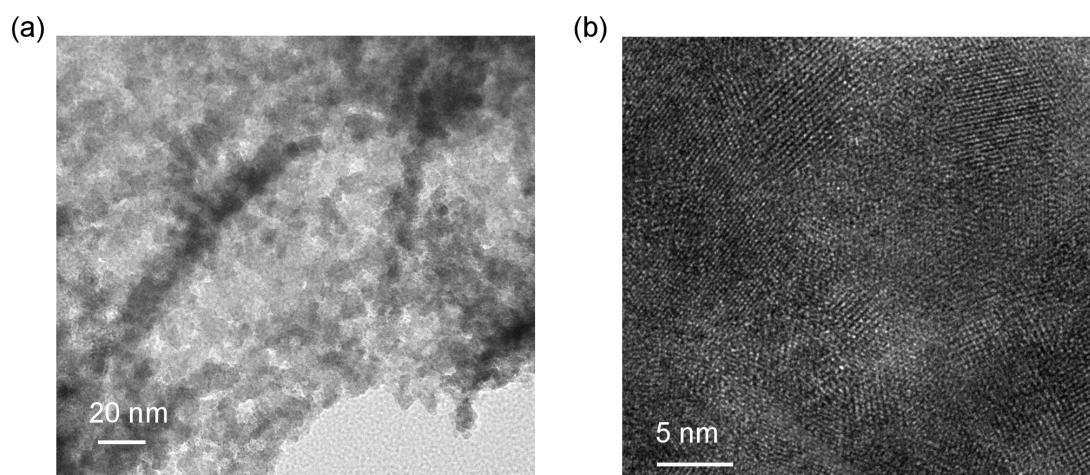


Fig. S20. (a) TEM, (b) HRTEM of $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$ after long-term stability test in 0.5 M H_2SO_4 .

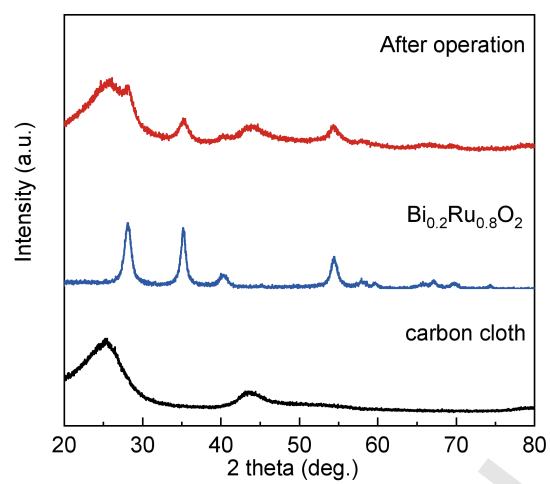


Fig. S21. XRD patterns of $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$ before and after OER test.

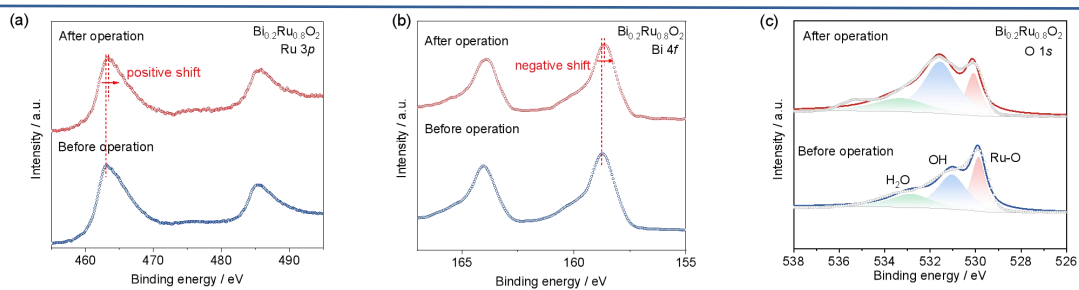


Fig. S22. The high-resolution XPS spectra of (a) Ru 3p (b) Bi 4f and (c) O 1s for $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$ before and after OER test.

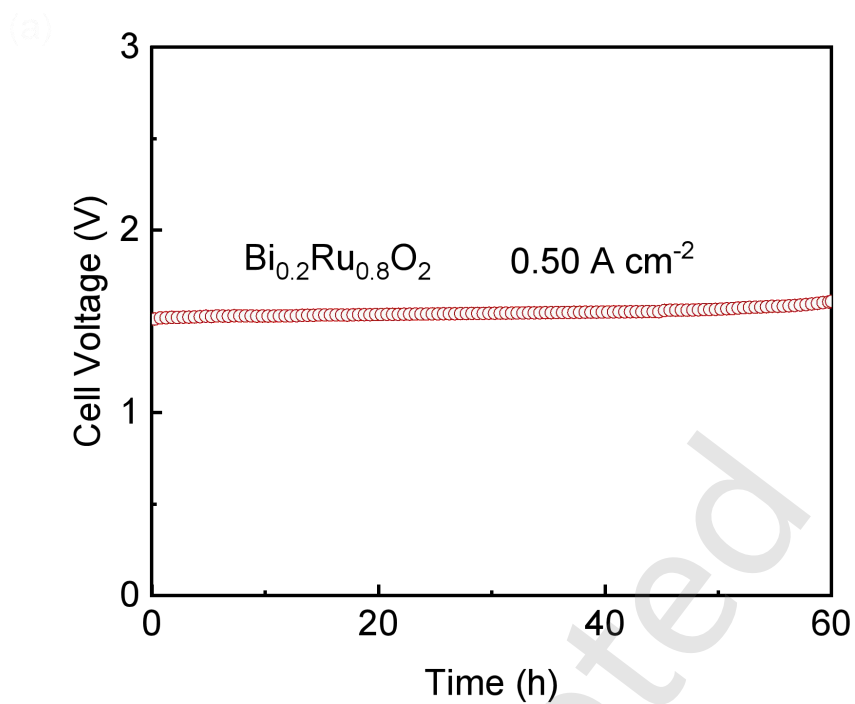


Fig. S23. The chronopotentiometry curve of the PEM device using Bi_{0.2}Ru_{0.8}O₂ catalyst at 0.50 A cm⁻².

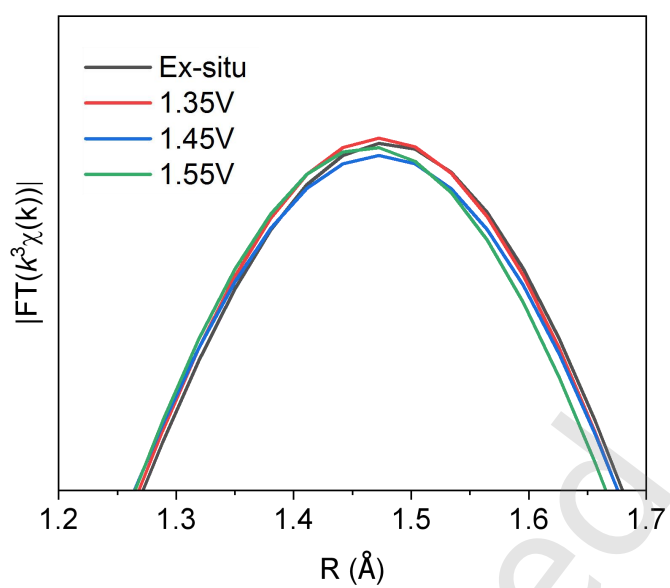


Fig. S24. In situ Ru *K*-edge FT-EXAFS spectra of $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$ during acidic OER.

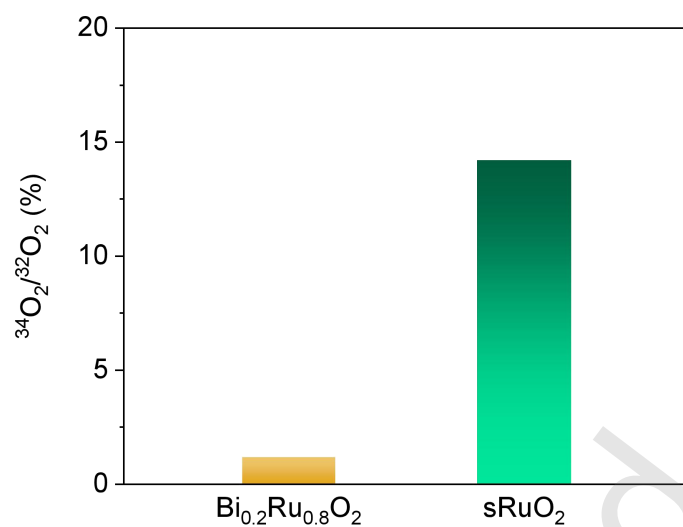


Fig. S25. Comparison of the ratio of $^{34}\text{O}_2/^{32}\text{O}_2$ between $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$ and sRuO_2 .

Table S1. The fitted parameters of the EIS data recorded at 1.497 V vs. RHE .

Catalyst	R_s (Ω)	R_{ct} (Ω)	CPE-T	CPE-P
$\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$	30.37	80.77	0.0018	0.687
sRuO ₂	8.76	88.87	0.0016	0.864
cRuO ₂	10.21	470.1	0.0006	0.620

Table S2. The concentration of dissolved Ru and Bi during acidic OER proces.

Reaction Time (h)	cRuO ₂	Bi _{0.2} Ru _{0.8} O ₂ Ru (mg L ⁻¹)	Bi _{0.2} Ru _{0.8} O ₂ Bi (mg L ⁻¹)
20	1.2398	0.0540	0.0605
120	-	0.1004	0.0649

Table S3. The S-number of $\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$ and cRuO_2 during the acidic OER process

Reaction Time (h)	cRuO_2	$\text{Bi}_{0.2}\text{Ru}_{0.8}\text{O}_2$
20	664	1.74×10^4
120	-	5.63×10^4