Supporting Information

Reversible lattice oxygen participation in Ru_{1-x}O_{2-x} for superior acidic

oxygen evolution reaction

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Experimental Section

1. Synthesis and Characterizations

Chemicals and materials

Ruthenium chloride hydrate (RuCl₃·xH₂O, 99%, Adamas), urea (NH₂CONH₂, \geq 99.0%, Greagent), ruthenium dioxide (RuO₂·xH₂O, \geq 99%, Adamas), commercial rutile-type IrO₂ (IrO₂·xH₂O, 99.9%, Adamas), Nafion perfluorinated resin (20 wt%, Adamas), sulfuric acid (H₂SO₄, 95–98%, Greagent), ethanol (EtOH, \geq 99.7%, Greagent), water-¹⁸O (98 atom% ¹⁸O, Adamas), and isopropanol (IPA, 70%, Adamas) were used in this study. The commercial Pt/C (40 wt% Pt) catalyst was obtained from SCI Materials Hub. Carbon paper was purchased from Toray Industries, Inc. Nafion 117 membrane was purchased from DuPont Co. The L-shaped glassy carbon electrode (GCE), platinum electrodes, and saturated calomel electrode (SCE) were obtained from Gaossunion (Tianjin) Optoelectronic Technology Co. All chemicals were of analytical grade and used as received without any further purification. Ultrapure water (DIW, 18.2 MΩ·cm⁻¹) used in the experiments was supplied by HHitech Master Touch.

Synthesis of EtOH-RuO₂

EtOH-RuO₂ was synthesized through a normal pressure heating process and subsequent calcination. Typically, 264 mg RuCl₃·xH₂O and 3.9 g urea were dissolved in 200 mL ethanol under stirring, and the solution was heated at 65 °C for 3.5 h in a three-necked flask. To obtain the precuror, abbreviated as EtOH-RuO₂-pre, the precipitate resulted, was then washed and separated by suction filtration, dried at 60 °C under vacuum for 12 h. After carefully grinding, the precursor was annealed in air at 300 °C for 3 h, with a ramping rate of 3 °C/min, to obtain the final RuO₂-EtOH sample.

Synthesis of DI-RuO₂

DI-RuO₂ was prepared by the similar synthetic procedure, except that the precursor solution was made by RuCl₃·xH₂O and urea dissolving in deionised water, and the former solution was heated at 90 °C.

Characterizations

Electrochemical Characterization

The electrochemical performance was carried out using a typical three-electrode setup on a Gamry electrochemical workstation (Gamry, Interface 1010E). L shape glassy carbon electrode (and platinum sheet electrode clamp), Platinum electrode and saturated calomel electrode (SCE) were used as working electrode, counter electrode and reference electrode, respectively. The ink was prepared by 5 mg catalyst dispersing in a mixture of 0.980 mL isopropanol (70%) and 20 µL 5wt% Nafion solution, followed by ultrasonication for 30 min. For activity tests, 20 µL ink was dropped on a prepolished L shape glassy carbon electrode (GCE, 5 mm diameter, 0.19625 cm²) and dried under an infrared heat lamp to serve as working electrode. The resulting loading of the catalyst can be calculated to be 0.51 mg cm⁻². All the electrochemical tests in a three-electrode setup are conducted in 0.5 M H₂SO₄ solution at room temperature. The initial working electrode was activated by Cyclic voltammetry (CV) scans scanning at a sweep rate of 50 mV s⁻¹ for 20 cycles from 1.0 to 2 V. Liner sweep voltammetry (LSV) tests were conducted at a sweep rate of 10 mV s⁻¹ from 0.95 to 1.5 V. The polarization curve was determined by the coincident curves obtained from repeated tests. The iR compensation was automatically applied during the tests. The LSV curve was fitted accordingly, and the Tafel slope was derived from the Tafel equation (1).

$$\eta = a + b \log j \tag{1}$$

where *b* is the Tafel slope, the slope obtained from the linear fit, and η , *j*, and *a* represent the overpotential, current density, and a constant, respectively.

The electrochemical double-layer capacitance (C_{dl}) of the electrocatalyst surface was determined by measuring the non-Faradaic capacitive current associated with double-layer charging. Cyclic voltammetry was performed at evenly spaced scan rates in the non-Faradaic potential range of 0.75 to 0.85 V (vs. SCE), and the C_{dl} was calculated according to Equation (2):

$$j = v C_{dl} \tag{2}$$

where j is the non-Faradaic capacitive current, and v is the scan rate. The C_{dl} was obtained by fitting the variation of current density with scan rate at 0.80 V (vs. SCE). The electrochemical active surface area (ECSA) of the catalyst sample was calculated from the double-layer capacitance according to Equation 3:

$$ECSA = \frac{c_{dl}}{c_s} \tag{3}$$

where C_S is the specific capacitance of the sample. According to previous reports, the value for smooth oxide surfaces is 0.035 mF cm⁻². The normalized ECSA was then calculated by dividing the LSV curve by the ECSA. For chronopotentiometry (CP) tests, the catalyst ink (200 µL) was added dropwise onto a 1 cm² carbon paper in multiple steps and dried under an infrared lamp, corresponding to a calculated catalyst loading of 1 mg/cm². Chronopotentiometry measurements were performed at a constant current density of 10 mA cm⁻². The carbon paper was subsequently secured onto the platinum sheet electrode clamp, serving as the working electrode. The voltage data from CP tests were not corrected for iR compensation

Potential was calibrated with respect to the reversible hydrogen electrode (RHE) using the Nernst equation (4):

$$E_{corr} = E_{measured} + 0.241 V + 0.0592 * pH$$
(4)

where E_{corr} is the potential relative to the reversible hydrogen electrode (RHE), $E_{measured}$ is the potential measured with respect to the reference electrode, and 0.241 V is the potential difference between the reference electrode (SCE) and the standard hydrogen electrode.

PEMWE test

MEA Fabrication

For the anode catalyst, 10 mg of EtOH-RuO₂ was dispersed in 2 mL of 70% isopropanol and 50 μ L of 20 wt% Nafion solution. The mixture was ultrasonicated to prepare a homogeneous ink, which was then uniformly deposited onto the surface of a Nafion-117 membrane using ultrasonic spray coating. Similarly, a commercial Pt/C catalyst was used as the cathode material and was sprayed ultrasonically onto the opposite side of the same membrane. The loading of the anode catalyst was 1.96 mg cm⁻², corresponding to a noble metal loading of 1.5 mg_{Ru} cm⁻². For the cathode, the commercial Pt/C catalyst had a total loading of 1 mg cm⁻², equivalent to 0.4 mg_{Pt} cm⁻².

Commercial IrO_2 was used to prepare membrane electrodes with identical noble metal loadings (1.5 mg_{Ir} cm⁻².) following the same fabrication protocol for comparative studies.

Electrochemical Testing of PEMWE

The proton exchange membrane water electrolysis (PEMWE) device was assembled by first placing the end plates for structural support and electrical connections. Then, the gas diffusion layers (GDL) were added, followed by the catalyst layers. The fabricated MEA was positioned in the center of the stack, with the flow field plates added on both sides. Current collectors were placed next to the flow field plates, and finally, seals and gaskets were installed to ensure proper sealing and prevent gas leakage. Electrochemical testing of the PEMWE was conducted using ultrapure water as the electrolyte at 60 °C. Prior to I-V and stability tests, the PEMWE was activated at a current density of 300 mA cm⁻² for 30 minutes. Steady-state polarization curves were obtained by gradually increasing the current density in steps, collecting the corresponding potential responses within the range of 0.01 to 2.0 A cm⁻². Stability testing was carried out at a constant current density of 100 mA cm⁻², the cell voltage was measured as the function of time.

Structural characterizations

Scanning electron microscopy (SEM) imaging were performed on a Zeiss Gemini 300 field emission scanning electron microscopy. Transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), and elemental mapping characterizations were performed on a FEI Tecnai F20 electron microscope with an operating voltage of 200 kV. Powder X-ray diffraction (XRD) patterns were collected using a X'Pert PRO MPD with Cu K α radiation (λ = 1.5418 Å), covering a scan range of 20° to 80° at a scan rate of 2°/min. X-ray photoelectron spectroscopy (XPS) characterizations were conducted on a Thermo Scientific K-Alpha instrument, utilizing Al-Ka (1486.6 eV) as the X-ray source. Fourier Transform Infrared Spectrometer (FTIR) was performed on a Thermo Fisher Scientific Nicolet iS20. Thermogravimetric analysis (TGA) measurement was performed on a TA TGA 55. The heating program involved heating the precursor from room temperature to 500°C at a rate of 5°C/min under an air atmosphere. BET surface area analysis was conducted using a Micromeritics 3Flex surface area analyzer, with nitrogen (77 K) as the adsorptive gas. The sample was pre-treated by vacuum drying at 200 °C for 6 hours to remove adsorbed moisture and impurities. UV-vis diffuse reflectance spectroscopy measurements were performed on a Shimadzu UV-3600i (DRS) Plus spectrophotometer in reflectance mode (R%), scanning from 200 to 1200 nm. In-situ infrared spectroscopy (In-situ IR) measurements were performed using a Thermo IS 50. The applied potential ranged from 1.2 V to 1.7 V (vs. RHE), with data collected at 0.5 V intervals. In-situ Raman spectroscopy measurements were performed using a HORIBA LabRAM HR Evolution instrument. The applied potential ranged from 1.2 V to 1.6 V (vs. RHE), with data collected at 0.5 V intervals. Differential Electrochemical Mass Spectrometry (DEMS) measurements were conducted using the Linglu QAS 100 instrument. Before testing, the electrolyte was purged with high-purity argon to remove dissolved oxygen. The catalyst was applied to the working electrode (loading: 0.95-1.45 mg/cm²) and dried, and testing was performed using a three-electrode system with H₂¹⁸O electrolyte. In the potential range of 0.6–1.2 V vs. RHE, five cyclic voltammetry (CV) cycles were carried out at 50 mV/s to remove adsorbed ¹⁶O from the electrode surface. Subsequently, five additional CV cycles were performed (1.192–1.692 V vs. RHE, 10 mV/s, 110 s per cycle) and signals for ³²O₂, ³⁴O₂, and ³⁶O₂ were recorded. The electrode was then cleaned with H₂¹⁶O to remove physically adsorbed H₂¹⁸O molecules, ensuring the catalyst remained intact. The same electrode (now labeled with ¹⁸O) was placed in H₂¹⁶O electrolyte for repeated testing, with the corresponding signals recorded. The electrolyte used for all these in-situ experiments was 0.5 M H₂SO₄.

XAFS

The Ru K-edge XAFS measurements were performed at BL14W1 station in Shanghai Synchrotron Radiation Facility (SSRF, 3.5 GeV, 220 mA maximum, Si (111) double crystals). The Ru K-edge spectra of the samples were collected in transmission mode using a Lytle detector. The original XAFS data were background-corrected and normalized using the ATHENA software. The EXAFS $\chi(k)$ data were subjected to leastsquares curve-fitting analysis, considering various coordination shells in R-space (1.0– 3.0 Å) and Fourier transforms in k-space (3.1–11.0 Å⁻¹), using the ARTEMIS program. The data in R-space were analyzed by fitting them to theoretical models based on the crystal structure obtained from XRD.

2. Computational detail

All the first principle calculations were performed using spin-polarized DFT as implemented in Vienna Ab initio Simulation Package (VASP 6.4),¹ Generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) functional was selected to describe the exchange-correlation interaction.² The ion-electron interaction was described by projector augmented-wave (PAW) method with a kinetic energy cutoff of 450 eV. Van de Waals (v dW) interactions were considered using the Grimme's DFT-D3 method.³ For sampling the Brillouin zone, Monkhorst-Pack grid of $2 \times 2 \times 1$ and $5 \times 5 \times 1$ k-point was used to optimize the configurations and investigate the electronic properties, respectively. All the calculations were carried out until the total energy and force were less than 10⁻⁵ eV per atom and 10⁻² eV Å⁻¹, respectively. Based on XRD results, two crystal planes RuO₂ (101) and (110) were built. For RuO₂ (101), the simulation model was based on a three-layers $2 \times 2 \operatorname{RuO}_2$ (101) slab with a = 8.98 Å and b = 10.92 Å, respectively. For RuO₂ (110), the simulation model was based on a three-layers $3 \times 2 \operatorname{RuO}_2$ (110) slab with a = 9.32 Å and b = 12.69 Å, respectively. The bottom layer was fixed during the relaxation. In addition, a sufficiently vacuum slab of 15 Å along the *z* axis was added to eliminate the interaction between the periodically repeated unit cells. In addition, the VASPKIT was used to post-process the numerical results of VASP.⁴

The calculation of Gibbs free energy change (ΔG) for OER was based on the computational hydrogen electrode (CHE) model,⁵ which can be expressed by:

$$\Delta G = \Delta E + \Delta E_{\text{ZPE}} - T\Delta S + eU + \Delta G_{\text{pH}}$$
(1)

where ΔE is the electronic energy difference between the free standing and adsorption states of reaction intermediates; ΔE_{ZPE} and ΔS are the changes in zero-point energies and entropy, respectively, which are obtained from the vibrational frequency calculations; T is the temperature, and is set to be 298.15 K in this work; *e* and *U* are the number of electrons transferred and the electrode potential applied, respectively. ΔG_{pH} is the free energy correction of pH, which can be obtained from: $\Delta G_{pH} = K_BT \times$ pH × ln10. In this work, H₂ and H₂O were used as the reference states, hence a set of equivalent reactions for the OER mechanism are used to determine ΔG . The OER catalytic process via AEM in acid condition includes the following four elementary steps:

* + H₂O
$$\rightarrow$$
 OH^{*} + H⁺ + e⁻(i)
OH^{*} \rightarrow O^{*} + H⁺ + e⁻(ii)
O^{*} + H₂O \rightarrow OOH^{*} + H⁺ + e⁻(iii)
OOH^{*} \rightarrow * + O₂(g) + H⁺ + e⁻(iv)

The LOM in acid condition includes the following six elementary steps:

* + H₂O
$$\rightarrow$$
 OH^{*} + H⁺ + e (v)
OH^{*} \rightarrow O^{*} + H⁺ + e⁻ (vi)
O^{*} + O_{lat} \rightarrow OO_{lat}^{*} + O_V (vii)
OO_{lat}^{*} + O_V \rightarrow O₂(g) + O_V (viii)
O_V + H₂O \rightarrow H^{*} + H⁺ + e⁻ (ix)
H^{*} \rightarrow H⁺ + e⁻ (x)
OOH^{*} + OH⁻ \rightarrow * + O₂(g) + H₂O + e⁻ (iv)

where * indicates the adsorption site. The step with the greatest increasing energy of OER is defined as the potential-determining step (PDS). And the overpotential (V vs. RHE) is calculated by:

$$\eta = \frac{\max\{\Delta G_1, \dots, \Delta G_i\}}{e} - 1.23 \tag{2}$$

The lower value of $\boldsymbol{\eta}$ indicates the better OER activity.



Fig. S1. (a, b) SEM images of EtOH-RuO₂-pre.



Fig. S2. SEM images of EtOH-RuO₂-pre annealed at (a) 150 °C, (b) 200 °C, (c) 250 °C, (d) 300 °C, (e) 400 °C.



Fig. S3. The thermogravimetric analysis (TGA, 25-500 °C with a ramping rate of 5 °C/min) curve of (a) EtOH-RuO₂-pre and (b) DI-RuO₂-pre

The thermogravimetric analysis (TGA) reveals distinct mass retention percentages (post-annealed/pre-annealed mass ratio) of 41.4% for EtOH-RuO₂ and 68.2% for DI-RuO₂, indicating a higher organic residue content on the EtOH-RuO₂-pre surface. Differential decomposition behaviors are observed through their onset temperatures and maximum DTG rates: DI-RuO₂ exhibits a primary decomposition stage at 253°C (mass loss: 31.4%), whereas EtOH-RuO₂ demonstrates delayed decomposition at 388°C (mass loss: 58.3%).



Fig. S4. (a, b) SEM images of DI-RuO₂-pre and (c, d) DI-RuO₂.



Fig. S5. N₂ adsorption-desorption isotherms of EtOH-RuO₂ and DI-RuO₂. The inset is the corresponding nanoparticle size distribution



Fig. S6. (a) TEM and (b) high resolution-TEM (HR-TEM) images of DI-RuO₂.



Fig. S7. (a) HAADF-STEM image and (b, c) corresponding elemental maps of DI-RuO₂.



Fig. S8 Rietveld refinement results for (a) EtOH-RuO₂ and (b)DI-RuO₂.



Fig. S9 The residuals of the XPS O 1s spectral fitting for (a) EtOH-RuO₂ and (b)DI-RuO₂.



Fig. S10. Normalized (a) Ru $3p_{3/2}$ and (b) O 1s XPS spectra of EtOH-RuO₂ and DI-RuO₂.



Revised **Fig. S11** (a) UV-vis DRS spectra and (b) Tauc plot derived from UV-vis diffuse reflectance spectra for EtOH-RuO₂ and DI-RuO₂;

In the UV-vis DRS analysis, where R represents the measured reflectance and F(R) corresponds to the Kubelka-Munk (K-M) transformed function $(F(R) = \frac{(1-R)^2}{2R})$ proportional to the absorption coefficient.



Fig. S12. (a) N 1s spectra and (b) O 1s spectra of EtOH-RuO₂-pre and DI-RuO₂-pre.

The XPS results of the precursors were used to further elucidate the solvent effect. In EtOH-RuO₂-pre, the N 1s peak, as shown in the Fig.S12 (a), exhibits a peak at 399.3 eV, which can be attributed to N-H bonding. In contrast, DI-RuO₂-pre shows a noticeable shift, with a new peak at 397.9 eV corresponding to the Ru-N bond.

This shift is due to N atoms in urea forming hydrogen bonds with water, increasing electron density and enhancing nitrogen's nucleophilicity for stronger metal ion coordination, further supported by the Fourier Transform Infrared Spectrometer (FTIR) shown in Fig. S13.

EtOH-RuO₂-pre displays higher O1s binding energy, suggesting oxygen species dominated by hydroxyl groups, adsorbed water, or organic-coordinated oxygen rather than stable lattice oxygen (e.g., Ru-O-Ru bridge oxygen). These weakly bonded oxygen species readily desorb as H₂O or CO₂ during annealing, directly inducing oxygen vacancies.⁶



Fig. S13. FTIR spectrum of EtOH-RuO₂-pre and DI-RuO₂-pre.

EtOH-RuO₂-pre exhibits distinct features of a primary amide: the absorption bands at 3340 and 3220 cm⁻¹ can be attributed to the stretching vibrations of NH₂ (v_{NH}), while the peaks at 1640, 1560, and 1400 cm⁻¹ correspond to the stretching vibrations of C=O, in-plane bending of NH₂ (δ_{NH}), and C-N stretching vibrations (v_{C-N}). The band at approximately 1150 cm⁻¹ is assigned to the rocking vibrations of NH₂.

The FTIR spectrum of DI-RuO₂-pre exhibits clear secondary amide features; however, the v_{NH} stretching vibration is not split into two distinct absorption bands. The coupling of δ_{NH} and v_{C-N} results in the formation of amide II and amide III bands, located at 1510 cm⁻¹ and 1270 cm⁻¹, respectively.

The absence of organic functional group peaks in the annealed sample confirms the effective synthesis of the oxide phase. The characteristic peaks observed at 1630 and 3450 cm⁻¹ are attributed to the bending vibration of adsorbed water (H–O–H) and the O–H stretching vibration of surface hydroxyl groups, respectively, consistent with the hydration and hydroxylation of the oxide surface.



Fig. S14. Experimental and fitting results for the EXAFS spectra of (a) EtOH-RuO₂ and (b) DI-RuO₂.



Fig. S15. X-ray diffraction (XRD) spectra of EtOH-RuO₂-pre, EtOH-RuO₂ (1h), EtOH-RuO₂ (2h), EtOH-RuO₂ (3h), "time" in the parentheses represents the annealing time at 300 °C.

During the initial stage of annealing, high-surface-energy facets (101) and (211) preferentially form, indicating that crystal growth at this stage is primarily kinetically driven. As annealing time extends, the proportion of low-surface-energy facets begins to increase.



Fig. S16. Simulated equivalent circuits for electrochemical impedance spectroscopy (EIS).



Fig. S17. CV profiles of (a) EtOH-RuO₂, (b) DI-RuO₂, (c) Com-RuO₂ and (d) Com-IrO₂ in the non-Faradaic region of 0.99-1.09 V vs. RHE with equally spaced scan rates.



Fig. S18. SEM images of EtOH-RuO₂ after OER



Fig. S19. Comparison between the XRD spectra of (a) $EtOH-RuO_2$ and (b) $DI-RuO_2$ before and after OER.



Fig. S20. Comparison between the normalized Ru 3p XPS spectra of a) EtOH-RuO₂ and b)DI-RuO₂ before and after OER. (c) Ru $3p_{3/2}$ XPS spectra of EtOH-RuO₂ and DI-RuO₂ before and after OER.



Fig. S21. Comparison between the normalized O 1s XPS spectra of a) EtOH-RuO₂ and b)DI-RuO₂ before and after the OER.



Fig. S22. O 1s XPS spectra of (a) EtOH-RuO₂ and (b) DI-RuO₂ before and after OER.



Fig. S23. Band structure for crystal planes (101) and (110) of RuO₂, RuO_{2-x} and Ru_{1-x}O₂.



Fig. S24. Charge density difference for crystal planes (101) of RuO₂, RuO_{2-x} and Ru_{1-x}O₂. (yellow and cyan clouds indicating charge density accumulation and depletion, and isosurface values are set at $\pm 3.0 \times 10^{-2}$ e/Å³)



Fig. S25. Charge density difference for crystal planes (110) of RuO₂, RuO_{2-x} and Ru_{1-x}O₂. (yellow and cyan clouds indicating charge density accumulation and depletion, and isosurface values are set at $\pm 3.0 \times 10^{-2}$ e/Å³)

	EtOH-RuO ₂ -	DI-RuO ₂
BET specific surface area	20.6360 m ² /g	35.6351 m²/g
Total pore volume	0.092470 cm ³ /g	0.084643 cm ³ /g
Average mesopore diameter	24.6463 nm	8.2108 nm

 Table S1: BET Analysis Data for EtOH-RuO2 and DI-RuO2

Sample	а	b	c	Volume (Å ³)	R_{wp} (%)	R _p (%)	χ^2
EtOH-RuO ₂	4.517	4.517	3.112	63.500	5.99	4.70	1.40
DI -RuO ₂	4.499	4.499	3.086	62.449	9.82	7.37	1.93
Standard Rutile-RuO ₂	4.491	4.491	3.107	62.665	/	/	/

Table S2: Refined unit cell parameters for EtOH-RuO₂ and DI-RuO₂ obtained from XRD Rietveld refinement

Sample	Peak	Position (eV)	FWHM (eV)	Area	Area ratio (%)	L/G
	O_L	529.1	0.89	220654.99	52.1	79.1
EtOH- RuO2	Ov	530.4	1.5	155766.22	37.0	80
	\mathbf{O}_{ad}	532.1	1.5	45734.50	10.9	80
DI -RuO ₂	O_L	529.1	0.92	140414.46	63.7	79.55
	\mathbf{O}_{V}	530.6	1.5	67004.65	30.6	80
	\mathbf{O}_{ad}	532.4	1.5	13067.08	5.7	80

Table S3: Fitting results of O 1s XPS spectra for EtOH-RuO₂ and DI-RuO₂ before OER

Sample	Path	C.N	R(Å)	σ ² (×10 ⁻³ Å ²)	$\Delta E (eV)$	R factor
EtOH- RuO ₂	Ru-O	5.48±0.58	1.973	4.05	2.21	0.00831
DI -RuO ₂	Ru-O	5.95±0.18	1.968	2.48	-5.04	0.017
Ru foil	Ru-Ru	12	2.672	2.96	3.35	0.011

Table S4. EXAFS fitting parameters of EtOH-RuO₂ and DI-RuO₂ at the Ru K-edge $(S_0^2=0.75)$

Sample	Peak	Position (eV)	FWHM (eV)	Area	Area ratio (%)
	O_L	529.1	0.93	136333.19	44.0
EtOH- RuO2	Ov	530.4	1.5	42389.03	30.1
11402	O_{ad}	531.9	1.5	22856.01	25.9
	O_{L}	529.2	0.94	46990.99	43.8
DI-RuO ₂	$O_{\rm V}$	530.6	1.5	37493.92	35.0
	Oad	531.9	1.5	22711.49	21.2

Table S5: Fitting results of O 1s XPS spectra for EtOH-RuO₂ and DI-RuO₂ after OER

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