

Supplementary Information for

Stabilizing ruthenium dioxide with cation-anchored sulfate for durable oxygen evolution in proton-exchange membrane water electrolyzers

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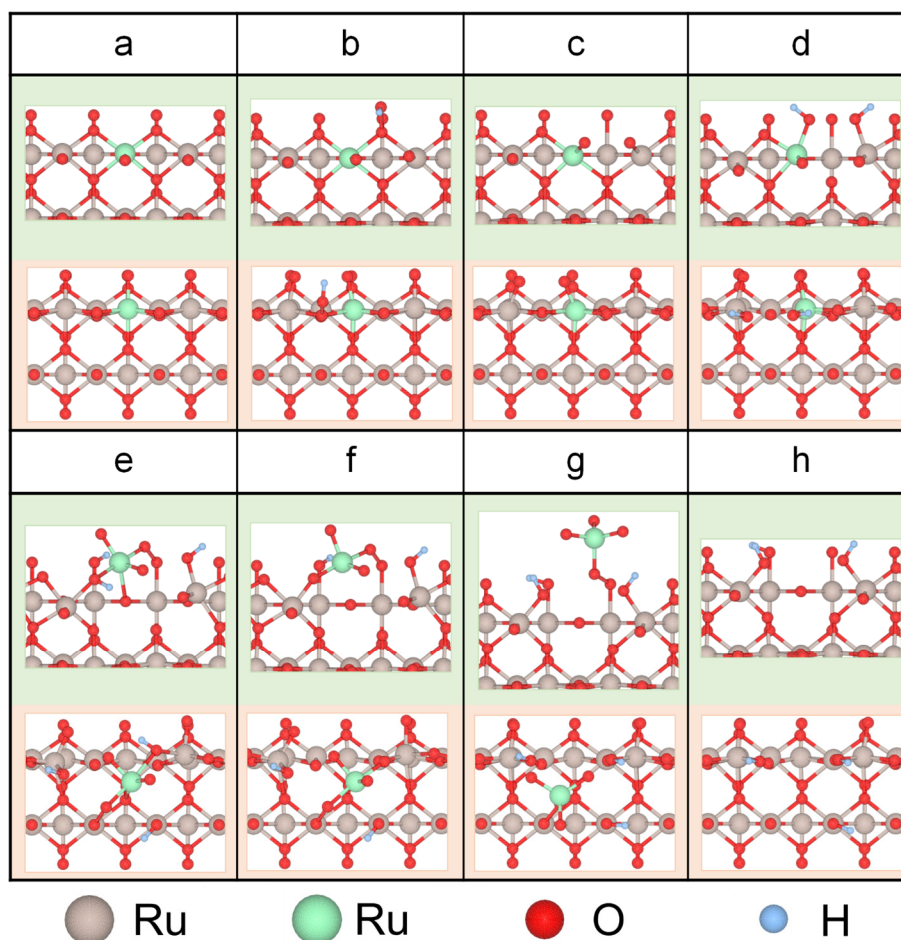
⁷These authors contributed equally.

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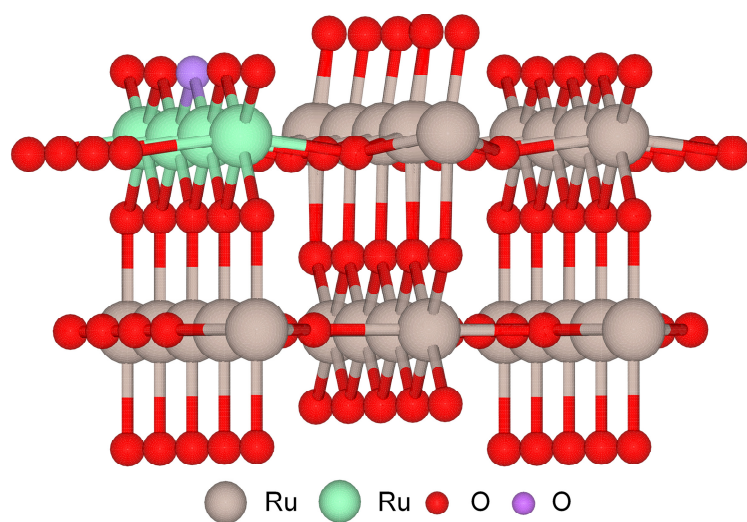
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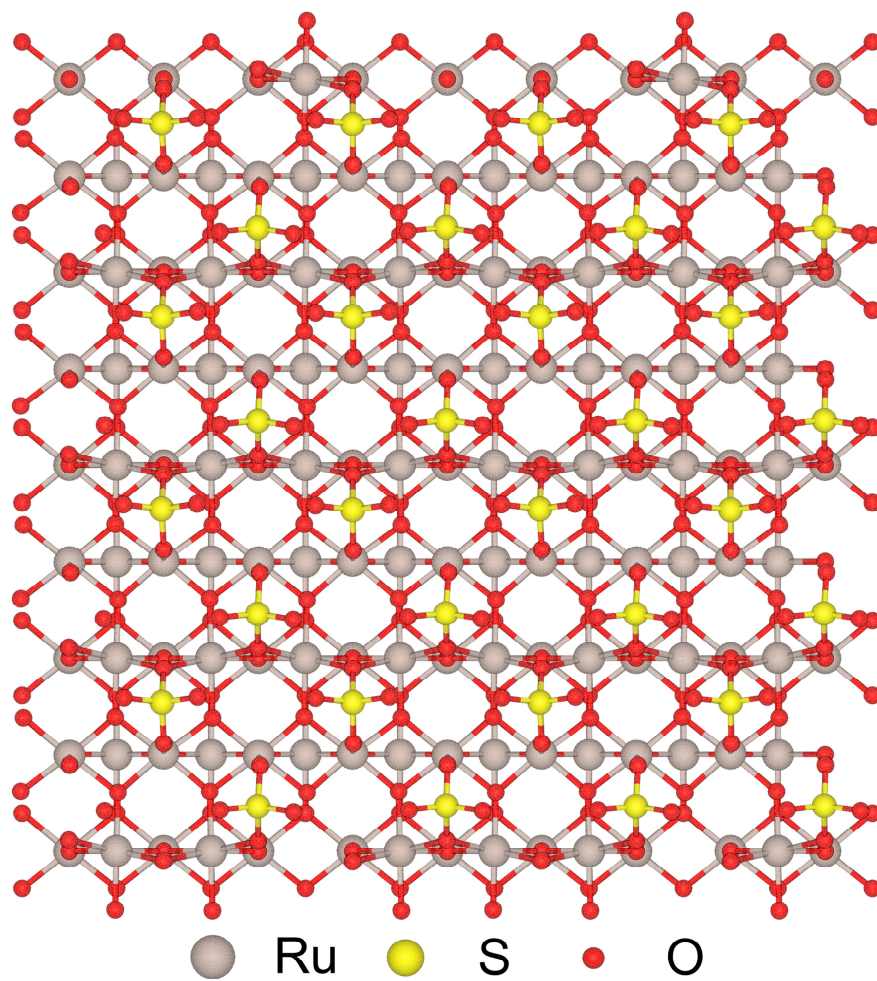
Supplementary Figure 1 Atomic structure of RuO_2 and intermediates during Ru dissolution. Of note, the green ball represents the Ru atom on the grain edge.

Supplementary Notes

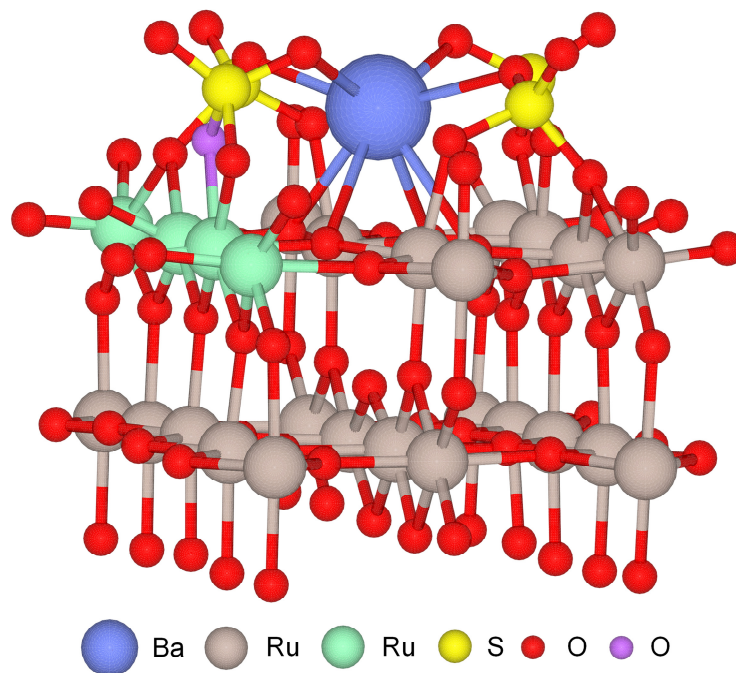
Supplementary Note 1: In this work, we use the boundary between RuO_2 (110) and RuO_2 (-110) planes as our model. At first, an H_2O molecule is adsorbed onto a bridging O site on the grain edges and deprotonated to form $^*\text{OH}$ (a to b). Then, the $^*\text{OH}$ and a lattice O connected to it are deprotonated to release an O_2 molecule (b to c). In parallel, two H_2O molecules are separately adsorbed on two Ru atoms and deprotonated to form two $^*\text{OH}$ (c to d). Then, an H_2O molecule is adsorbed onto a new Ru atom adjacent to the Ru atom (green ball) and deprotonated to form $^*\text{OH}$. At this time, the Ru-O-Ru (green ball) bond is broken, and the unstable Ru (green ball) group starts to rotate, resulting in the formation of Ru-O-O-Ru (green ball), Ru-O-Ru (the O atom from $^*\text{OH}$), and proton transfer process (d to e). Afterward, the Ru-O-Ru (the O atom from $^*\text{OH}$) is deprotonated to form Ru-O-Ru (e to f). Next, an H_2O molecule is adsorbed to the Ru atom and deprotonated to form $^*\text{OH}$, accompanied by the breaking of a Ru-O-Ru bond (f to g). Finally, the RuO_4 leaves the crystal (g to h).



Supplementary Figure 2 Ball-and-stick model of the RuO₂ (110) plane. Of note, the green and purple balls represent Ru and O atoms, respectively, on the grain edges.

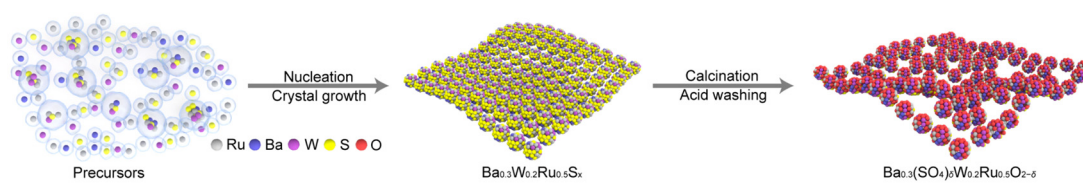


Supplementary Figure 3 Ball-and-stick model of sulfate bound with RuO₂ (110) plane.

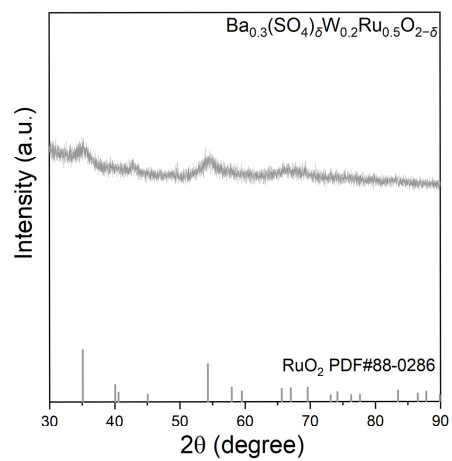


Supplementary Figure 4 Ball-and-stick model of Ba-anchored sulfate on the RuO₂ (110) plane. Of note, the green and purple balls represent Ru and O atoms, respectively, on the grain edges.

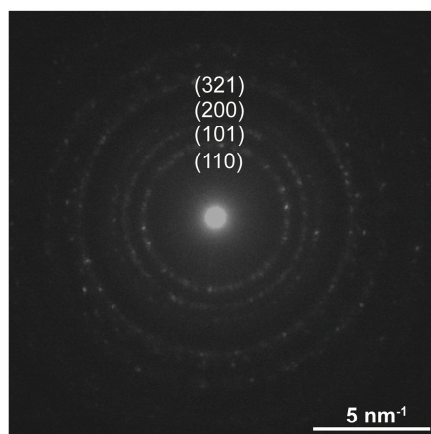
Supplementary Note 2: In this model, two O atoms of a sulfate bond to Ru atoms, and Ba atom bonds with one O atom of sulfate to fix the sulfate on the RuO₂ (110) plane. When calculating the binding energy of sulfate with other metal cations, Ba was replaced by other elements.



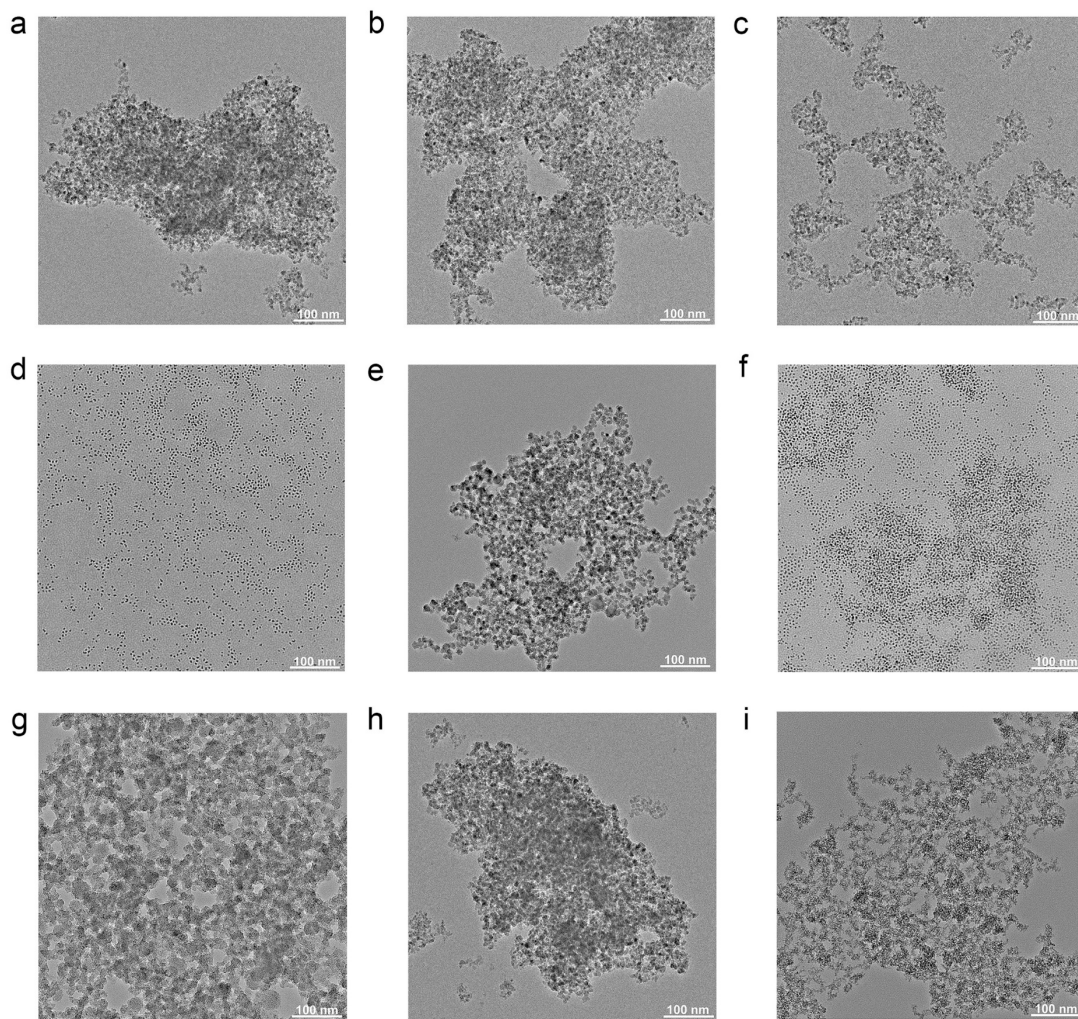
Supplementary Figure 5 Schematic illustrating the synthesis process of $\text{Ba}_{0.3}(\text{SO}_4)_\delta\text{W}_{0.2}\text{Ru}_{0.5}\text{O}_{2-\delta}$.



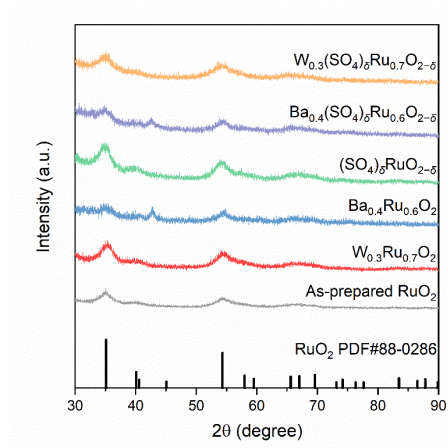
Supplementary Figure 6 XRD pattern of $\text{Ba}_{0.3}(\text{SO}_4)_\delta\text{W}_{0.2}\text{Ru}_{0.5}\text{O}_{2-\delta}$.



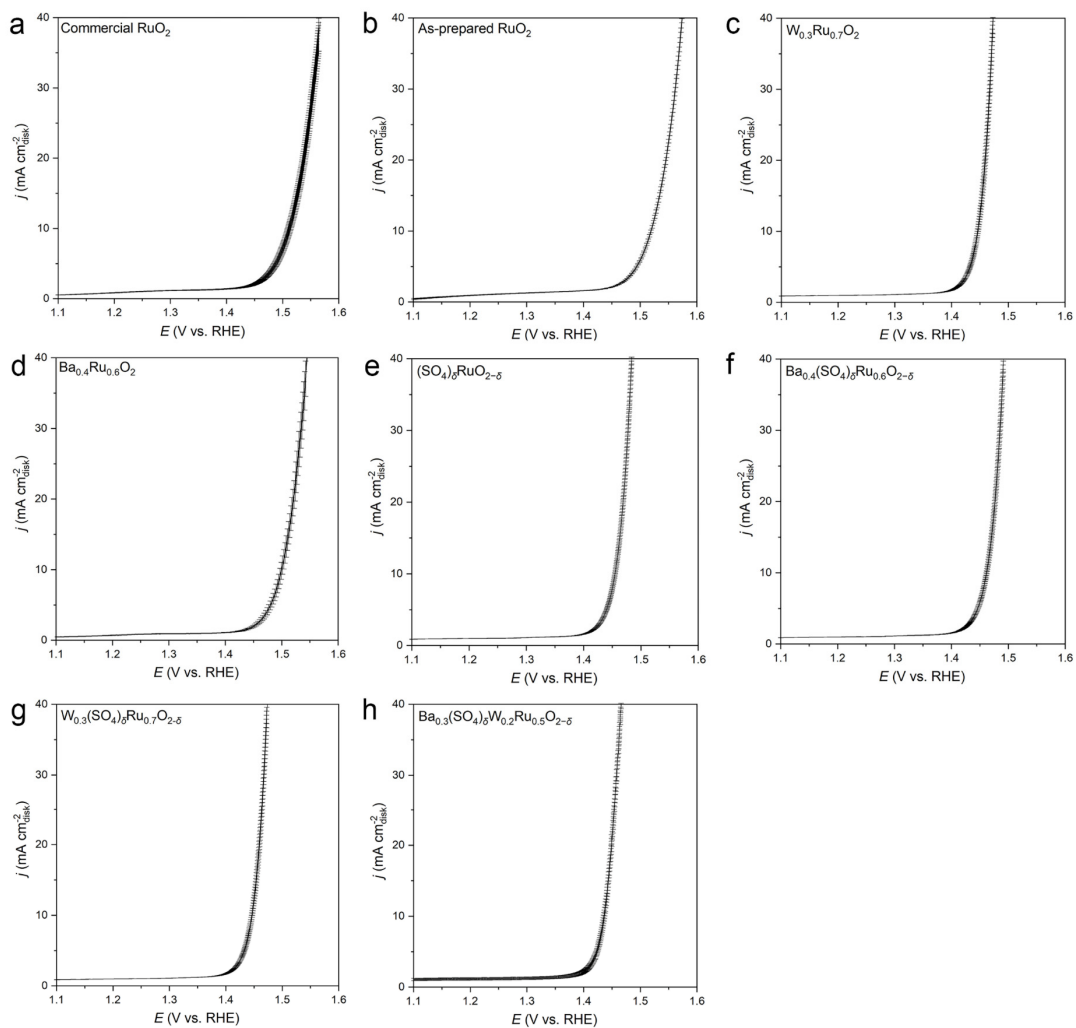
Supplementary Figure 7 SAED pattern of the $\text{Ba}_{0.3}(\text{SO}_4)_\delta\text{W}_{0.2}\text{Ru}_{0.5}\text{O}_{2-\delta}$.



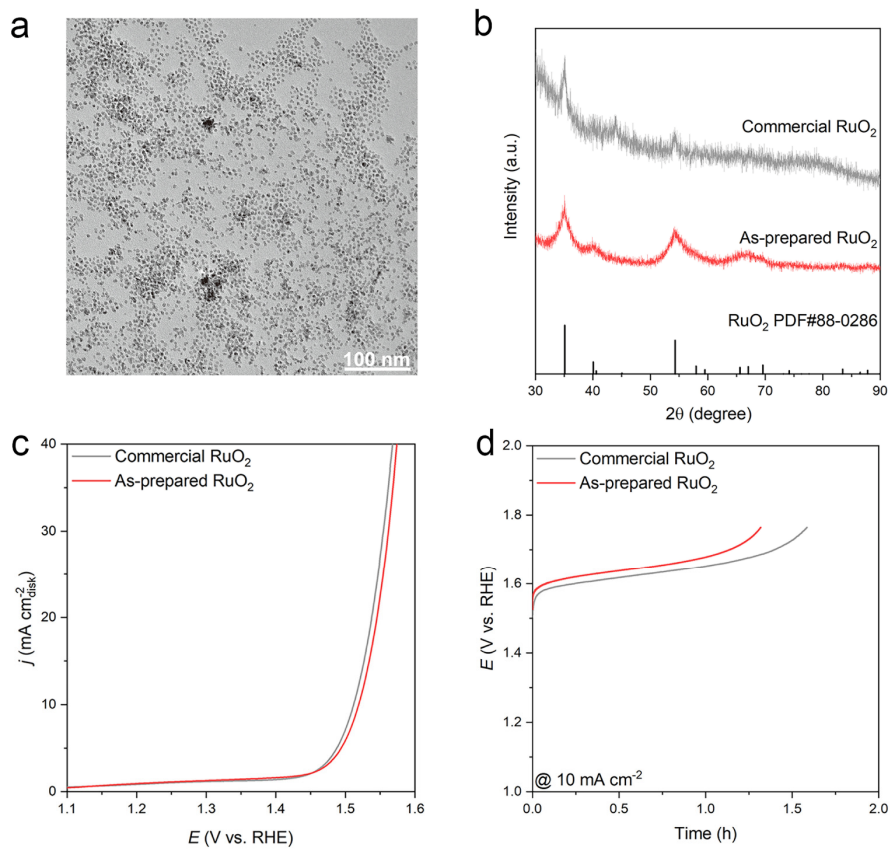
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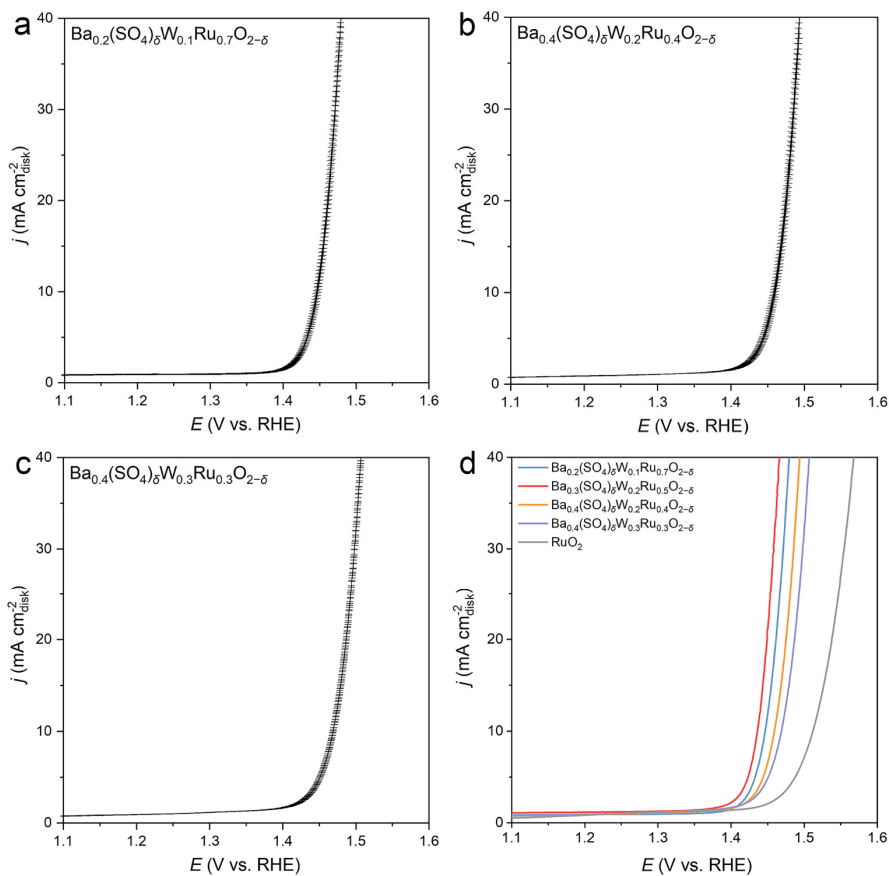
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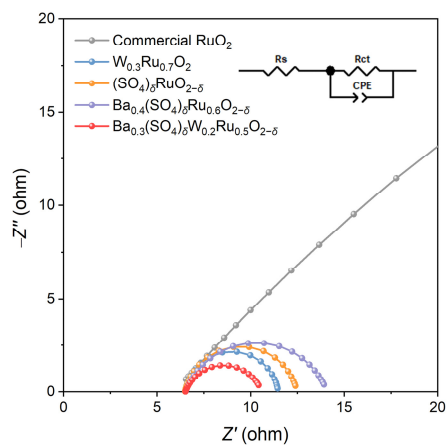
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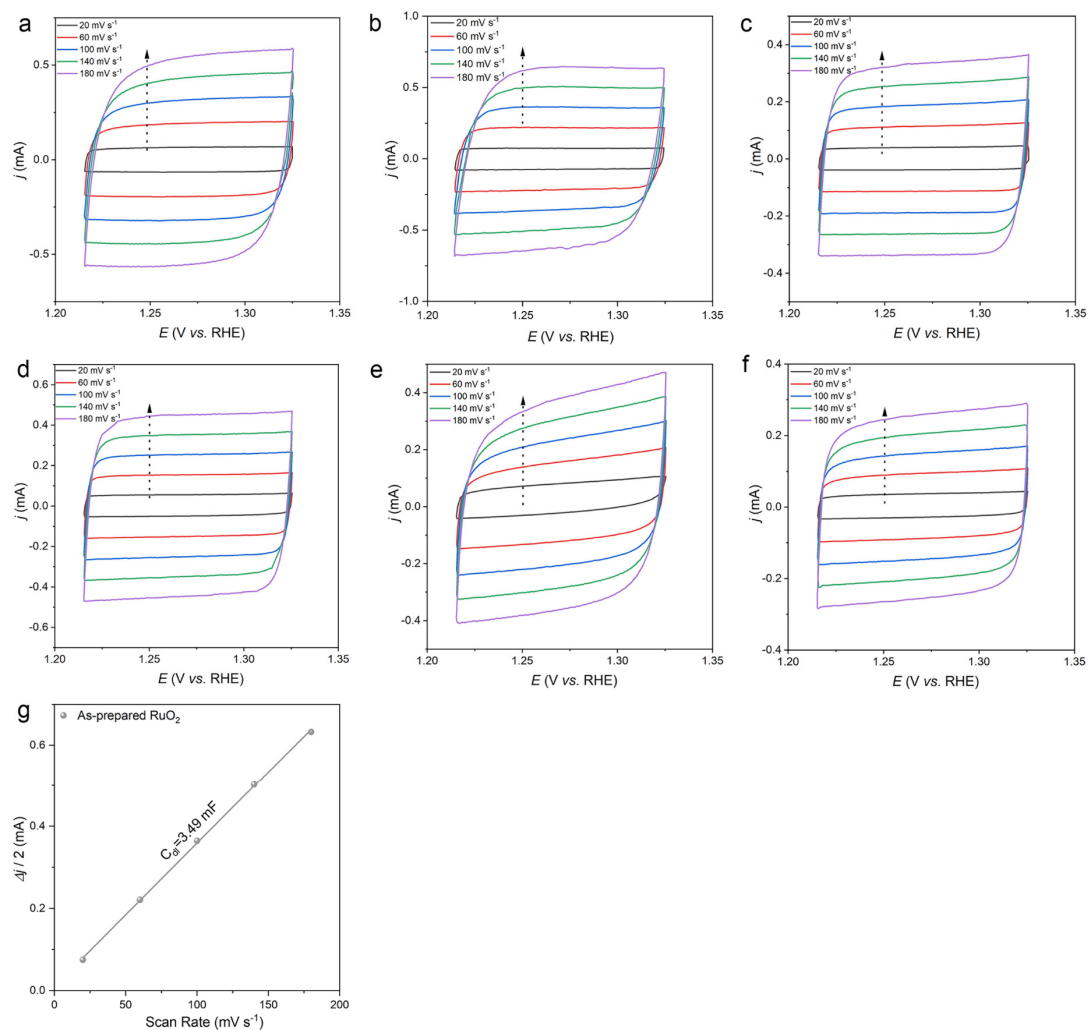
Supplementary Figure 11 **a** TEM images of commercial RuO₂. **b** XRD patterns of commercial RuO₂ and as-prepared RuO₂. **c** OER polarization curves of commercial RuO₂ and as-prepared RuO₂. **d** Chronopotentiogram of commercial RuO₂ and as-prepared RuO₂ at 10 mA cm⁻² in 0.5 M H₂SO₄.



Supplementary Figure 12 a-c The mean OER polarization curves with error bars for (a) $\text{Ba}_{0.2}(\text{SO}_4)_\delta\text{W}_{0.1}\text{Ru}_{0.7}\text{O}_{2-\delta}$, (b) $\text{Ba}_{0.4}(\text{SO}_4)_\delta\text{W}_{0.2}\text{Ru}_{0.4}\text{O}_{2-\delta}$, (c) $\text{Ba}_{0.4}(\text{SO}_4)_\delta\text{W}_{0.3}\text{Ru}_{0.3}\text{O}_{2-\delta}$ based on three independent tests. **d** OER polarization curves of RuO_2 , $\text{Ba}_{0.2}(\text{SO}_4)_\delta\text{W}_{0.1}\text{Ru}_{0.7}\text{O}_{2-\delta}$, $\text{Ba}_{0.3}(\text{SO}_4)_\delta\text{W}_{0.2}\text{Ru}_{0.5}\text{O}_{2-\delta}$, $\text{Ba}_{0.4}(\text{SO}_4)_\delta\text{W}_{0.2}\text{Ru}_{0.4}\text{O}_{2-\delta}$, and $\text{Ba}_{0.4}(\text{SO}_4)_\delta\text{W}_{0.3}\text{Ru}_{0.3}\text{O}_{2-\delta}$.

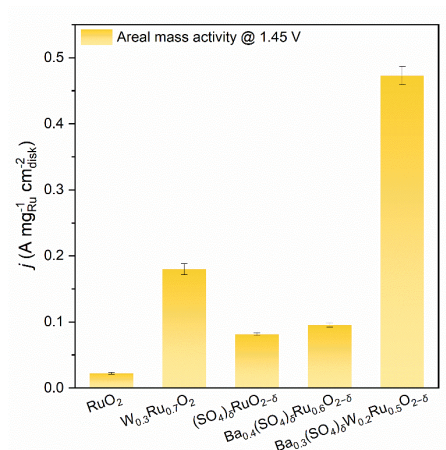


Supplementary Figure 13 Nyquist plots of commercial RuO₂, W_{0.3}Ru_{0.7}O₂, (SO₄)_δRuO_{2-δ}, Ba_{0.4}(SO₄)_δRu_{0.6}O_{2-δ}, and Ba_{0.3}(SO₄)_δW_{0.2}Ru_{0.5}O_{2-δ}.

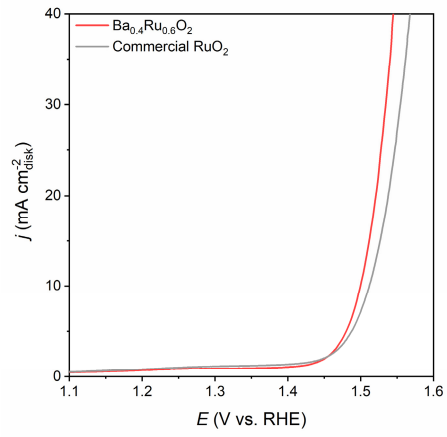


Supplementary Figure 14 a-f Cyclic voltammograms of (a) commercial RuO_2 , (b) as-prepared RuO_2 , (c) $\text{W}_{0.3}\text{Ru}_{0.7}\text{O}_2$, (d) $(\text{SO}_4)_\delta\text{RuO}_{2-\delta}$, (e) $\text{Ba}_{0.4}(\text{SO}_4)_\delta\text{Ru}_{0.6}\text{O}_{2-\delta}$, and (f) $\text{Ba}_{0.3}(\text{SO}_4)_\delta\text{W}_{0.2}\text{Ru}_{0.5}\text{O}_{2-\delta}$ at scan rates of 20, 60, 100, 140, and 180 mV s^{-1} . **g** C_{dl} plots of as-prepared RuO_2 at 1.25 V.

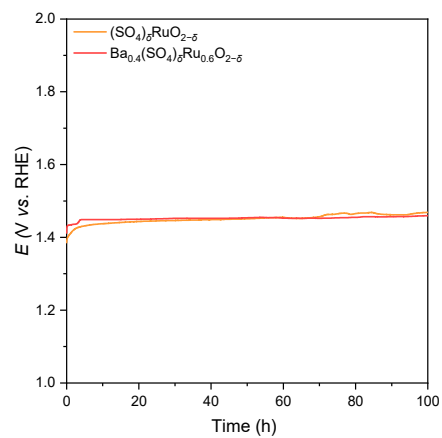
Supplementary Note 3: For particles, both the specific surface area and the ECSA increase with the decrease of the size. In comparison to commercial RuO_2 , the size of as-prepared RuO_2 is smaller, resulting in a larger C_{dl} and ECSA (Supplementary Fig. 14g). After the formation of Ru alloys with Ba or W, the particle size becomes larger, leading to a smaller ECSA. Additionally, Ru coordinates with sulfate to easily form a large nanosheet-like structure, which can also reduce the ECSA.



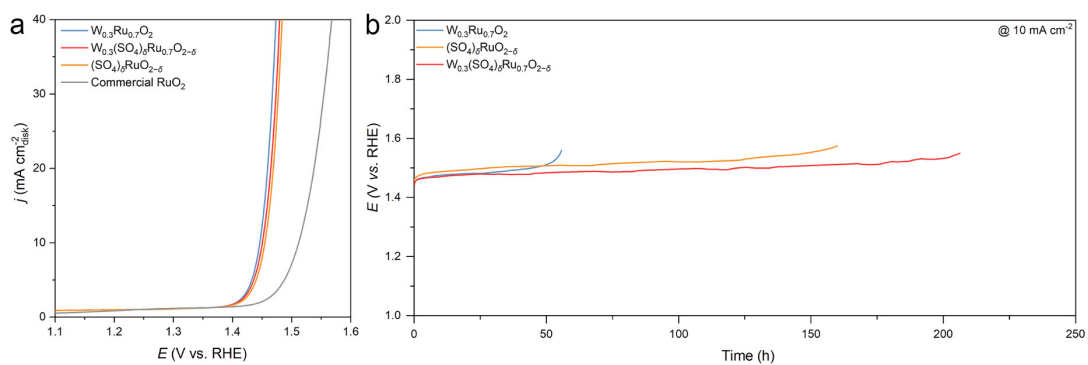
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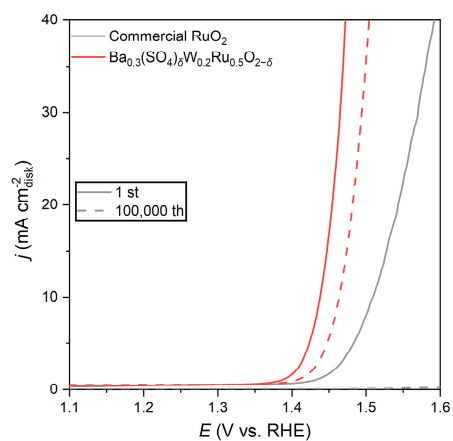
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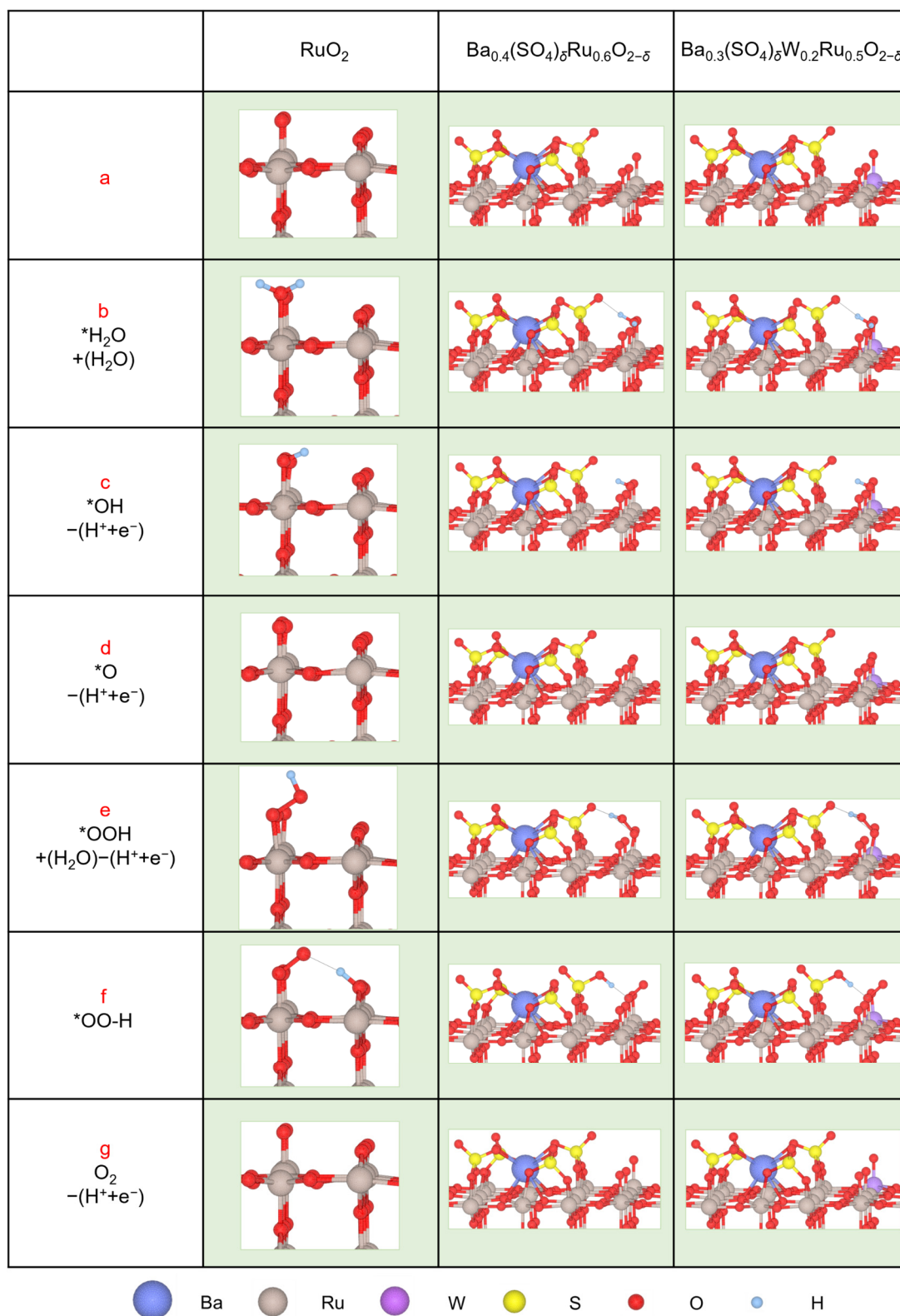
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Supplementary Figure 18 a OER polarization curves of commercial RuO_2 , $W_{0.3}Ru_{0.7}O_2$, $(SO_4)_\delta RuO_{2-\delta}$, and $W_{0.3}(SO_4)_\delta Ru_{0.7}O_{2-\delta}$. **b** Chronopotentiogram of $W_{0.3}Ru_{0.7}O_2$, $(SO_4)_\delta RuO_{2-\delta}$, and $W_{0.3}(SO_4)_\delta Ru_{0.7}O_{2-\delta}$ at 10 mA cm⁻² in 0.5 M H₂SO₄.



Supplementary Figure 19 OER polarization curves of commercial RuO₂ and Ba_{0.3}(SO₄)_δW_{0.2}Ru_{0.5}O_{2-δ} before and after 100,000 cycles.



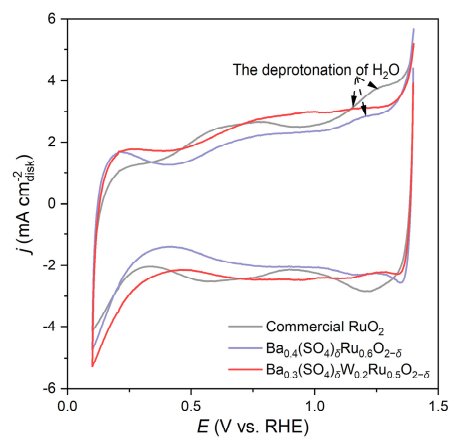
Supplementary Figure 20 Atomic structure of catalysts and intermediates during the OER process.

Supplementary Note 4: For RuO₂, an H₂O molecule is adsorbed on the 1f-cus Ru site of the RuO₂(110) plane (a to b) and undergoes continuous deprotonation, leading to the formation of *OH and *O on the same site (b to c, c to d). Subsequently, a second H₂O molecule is adsorbed onto the *O and deprotonates,

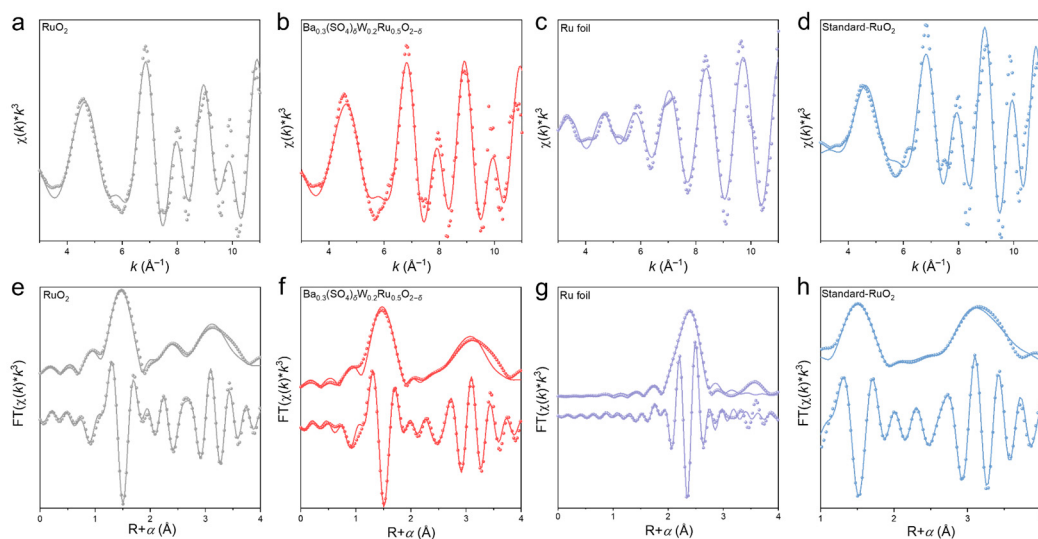
resulting in the formation of *OOH (d to e). Afterward, the *OOH donates a proton to an adjacent O site to form *OO-H (e to f). Finally, the *OO-H undergoes deprotonation, leading to the release of O₂ (f to g).

For Ba_{0.4}(SO₄)_δRu_{0.6}O_{2-δ}, the OER process is similar to RuO₂. An H₂O molecule is adsorbed on the 1f-cus Ru site (a to b), and deprotonated to form *OH and *O on this site (b to c, c to d). Then, a second H₂O molecule is adsorbed on *O and deprotonates to form *OOH (d to e). Here, the *OOH donates a proton to an adjacent O site, which belongs to a sulfate to form *OO-H (e to f). Finally, the *OO-H is deprotonated and an O₂ is released (f to g).

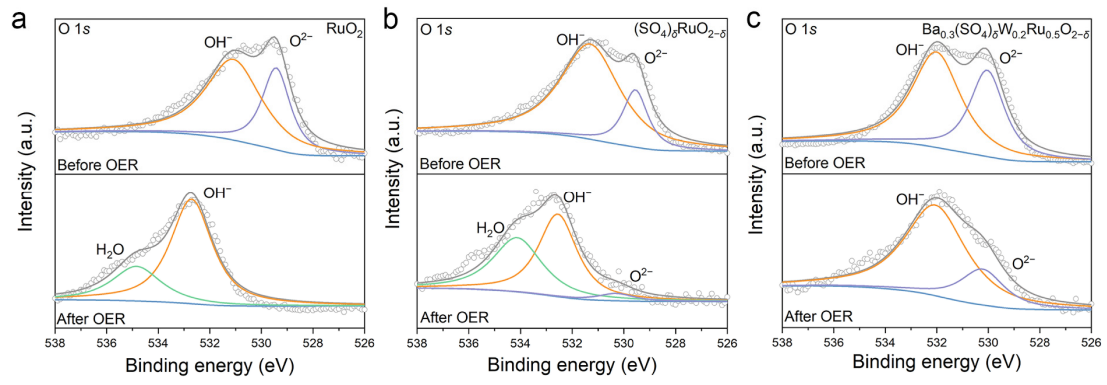
For Ba_{0.3}(SO₄)_δW_{0.2}Ru_{0.5}O_{2-δ}, the OER process is identical to that of Ba_{0.4}(SO₄)_δRu_{0.6}O_{2-δ}. In Ba_{0.3}(SO₄)_δW_{0.2}Ru_{0.5}O_{2-δ}, a Ru atom adjacent to the active site in the crystal is replaced with a W atom, forming Ru-O-W. This substitution allows W to modulate the electronic structure of the 1f-cus-Ru site, thereby adjusting the adsorption energy of the reaction intermediates.



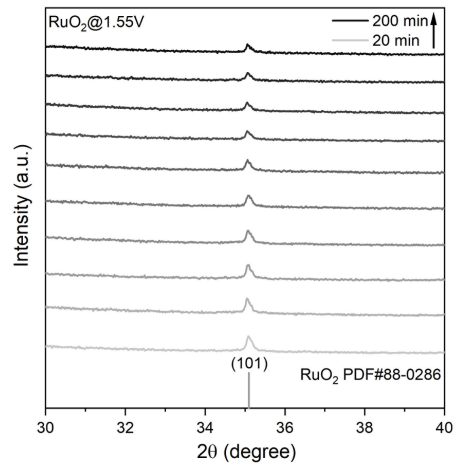
Supplementary Figure 21 Cyclic voltammograms of commercial RuO_2 , $\text{Ba}_{0.4}(\text{SO}_4)_\delta\text{Ru}_{0.6}\text{O}_{2-\delta}$, and $\text{Ba}_{0.3}(\text{SO}_4)_\delta\text{W}_{0.2}\text{Ru}_{0.5}\text{O}_{2-\delta}$ in Ar-saturated 0.5 M H_2SO_4 at a scan rate of 50 mV s^{-1} .



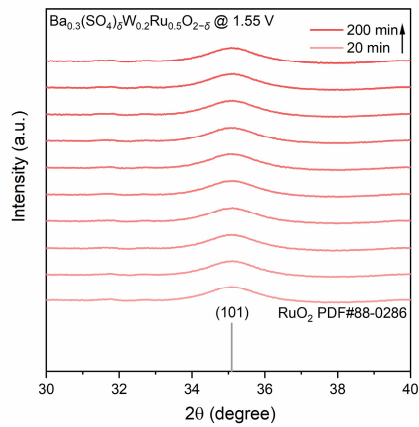
Supplementary Figure 22 a-d Ru K-edge EXAFS (points) and the curvefit (line) for (a) RuO₂, (b) Ba_{0.3}(SO₄)_δW_{0.2}Ru_{0.5}O_{2-δ}, (c) Ru foil, and (d) standard-RuO₂, shown in k^3 -weighted k -space. **e-h**, Ru K-edge EXAFS (points) and the curvefit (line) for (e) RuO₂, (f) Ba_{0.3}(SO₄)_δW_{0.2}Ru_{0.5}O_{2-δ}, (g) Ru foil, and (h) standard-RuO₂, shown in R -space (FT magnitude and imaginary component). The data are k^3 -weighted and not phase-corrected.



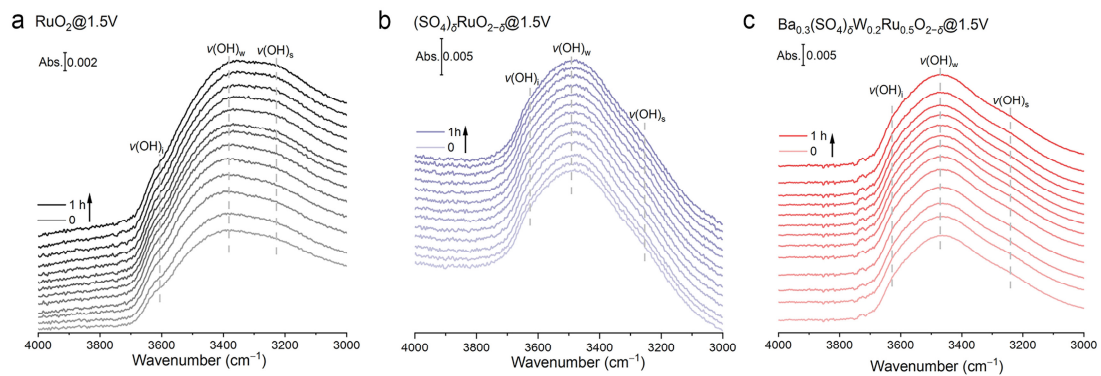
Supplementary Figure 23 a-c High-resolution O 1s XPS spectra of **(a)** RuO_2 , **(b)** $(\text{SO}_4)_\delta\text{RuO}_{2-\delta}$, and **(c)** $\text{Ba}_{0.3}(\text{SO}_4)_\delta\text{W}_{0.2}\text{Ru}_{0.5}\text{O}_{2-\delta}$ before and after OER.



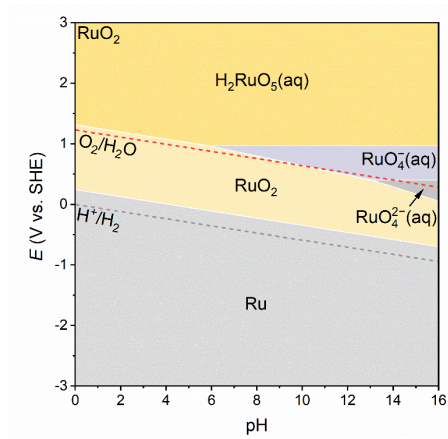
Supplementary Figure 24 Time-resolved *in-situ* XRD patterns of RuO₂ during 200 min acidic OER at 1.55 V.



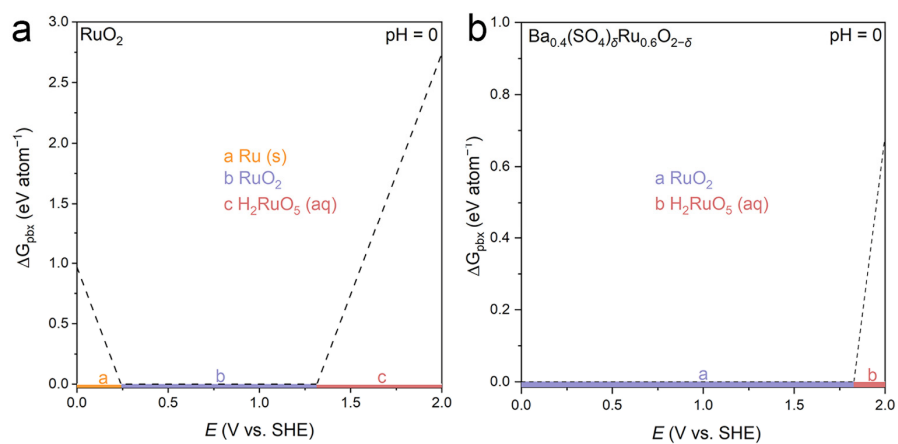
Supplementary Figure 25 Time-resolved *in-situ* XRD patterns of $\text{Ba}_{0.3}(\text{SO}_4)_\delta\text{W}_{0.2}\text{Ru}_{0.5}\text{O}_{2-\delta}$ during 200 min acidic OER at 1.55 V.



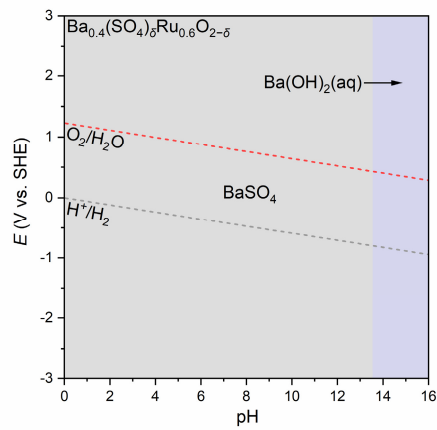
Supplementary Figure 26 a-c Time-resolved *in-situ* ATR-SEIRAS spectra of **(a)** RuO_2 , **(b)** $(\text{SO}_4)_\delta\text{RuO}_{2-\delta}$, and **(c)** $\text{Ba}_{0.3}(\text{SO}_4)_\delta\text{W}_{0.2}\text{Ru}_{0.5}\text{O}_{2-\delta}$ over the course of 1 h acidic OER at 1.5 V.



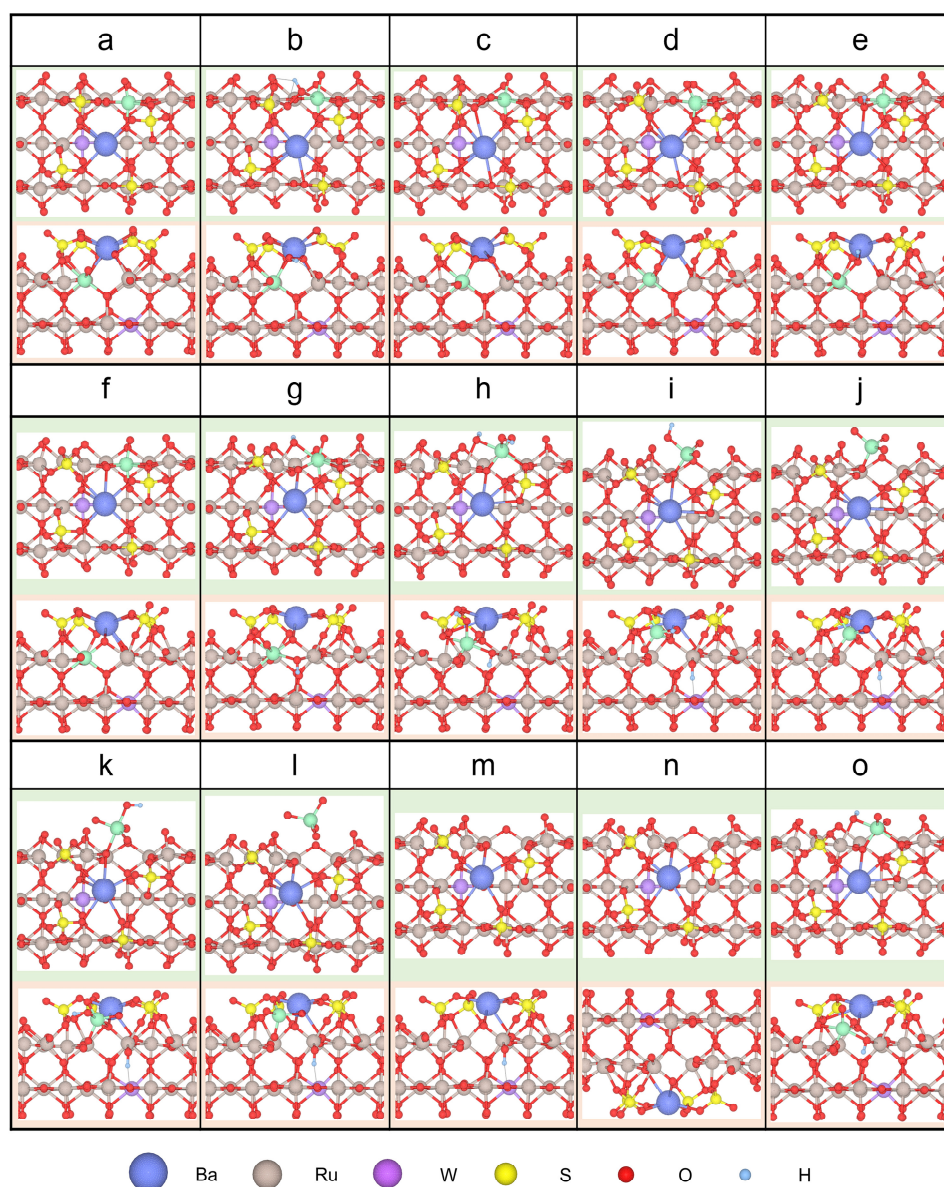
Supplementary Figure 27 Ru Pourbaix diagram for RuO₂ generated with an aqueous ion concentration of 10^{-6} M at 25 °C.



Supplementary Figure 28 a,b Pourbaix decomposition free energy (ΔG_{pbx}) of (a) RuO_2 and (b) $\text{Ba}_{0.4}(\text{SO}_4)_\delta\text{Ru}_{0.6}\text{O}_{2-\delta}$ at potentials between 0 and 2.0 V.

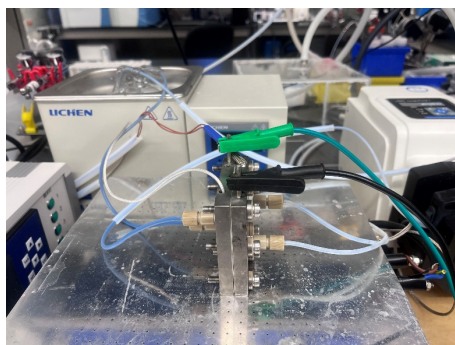


Supplementary Figure 29 Ba Pourbaix diagram for $\text{Ba}_{0.4}(\text{SO}_4)_\delta\text{Ru}_{0.6}\text{O}_{2-\delta}$ generated with an aqueous ion concentration of 10^{-6} M at 25 °C.

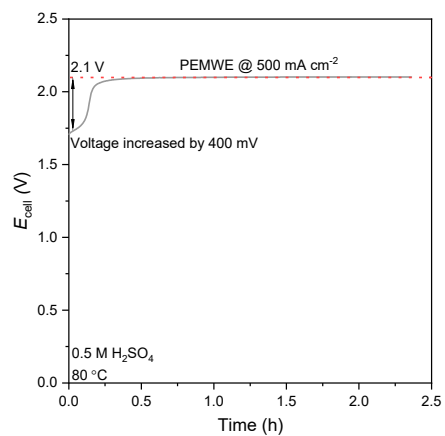


Supplementary Figure 30 Atomic structures of catalysts and intermediates during Ru dissolution on $\text{Ba}_{0.3}(\text{SO}_4)_\delta\text{W}_{0.2}\text{Ru}_{0.5}\text{O}_{2-\delta}$.

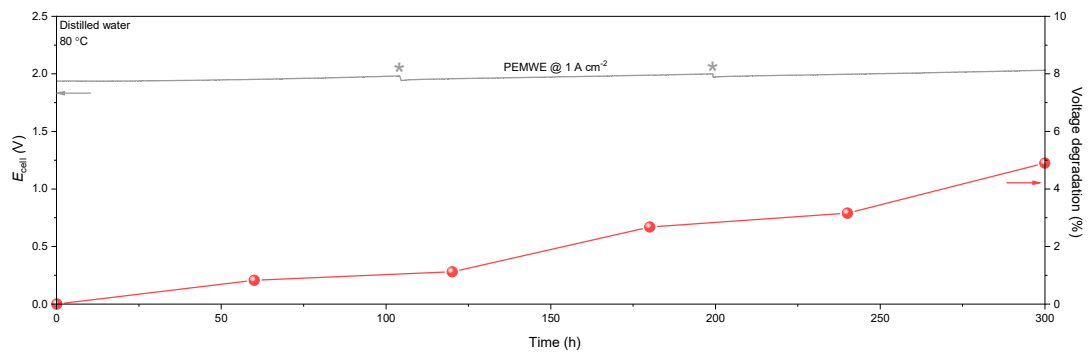
Supplementary Note 5: In the most possible thermodynamic deactivation pathway of $\text{Ba}_{0.3}(\text{SO}_4)_\delta\text{W}_{0.2}\text{Ru}_{0.5}\text{O}_{2-\delta}$, the adsorption and deprotonation of water are optimized on the most energetically favorable sites. Benefiting from the protection of Ba-anchored sulfate, the deactivation of $\text{Ba}_{0.3}(\text{SO}_4)_\delta\text{W}_{0.2}\text{Ru}_{0.5}\text{O}_{2-\delta}$ needs to overcome two positive free energy difference in the steps from *a* to *b* and *k* to *l*, respectively, while that of RuO_2 is almost spontaneous – that means, it is more difficult and sluggish for $\text{Ba}_{0.3}(\text{SO}_4)_\delta\text{W}_{0.2}\text{Ru}_{0.5}\text{O}_{2-\delta}$ to deactivate than RuO_2 .



Supplementary Figure 31 Photograph of the PEMWE.



Supplementary Figure 32 Chronopotentiogram of commercial RuO₂-based PEMWE operated at 500 mA cm⁻² in 0.5 M H₂SO₄ under 80 °C.



Supplementary Figure 33 Chronopotentiogram and voltage degradation of $\text{Ba}_{0.3}(\text{SO}_4)_\delta\text{W}_{0.2}\text{Ru}_{0.5}\text{O}_{2-\delta}$ -based PEMWE operated at 1 A cm^{-2} in distilled water under $80 \text{ }^\circ\text{C}$. Of note, the gray asterisks represent the replenishment of fresh electrolytes, and the difference in cell voltage between $0.5 \text{ M H}_2\text{SO}_4$ and distilled water results from the impedance difference between the electrolyte and the MEA.

Supplementary Tables

Supplementary Table 1. The binding energy of various metal cations with sulfate on the surface of RuO₂ (110) plane.

Metal	Binding Energy (eV)	Metal	Binding Energy (eV)	Metal	Binding Energy (eV)	Metal	Binding Energy (eV)
Au	-3.26	Te	-7.01	Al	-8.65	Re	-14.5
Ag	-4.03	Ni	-7.11	Fe	-8.82	V	-14.6
Cd	-4.8	Ge	-7.23	Mg	-8.94	Sc	-14.8
Se	-5.15	Pt	-7.33	Ir	-9.5	Ti	-15.3
Ga	-5.17	Sn	-7.36	Be	-10.2	Pr	-15.6
Zn	-5.49	Sb	-7.51	Sr	-10.4	Y	-15.9
Cu	-5.63	Pb	-7.56	Ca	-10.5	La	-16
Pd	-5.81	In	-7.78	Ru	-10.5	Mo	-16
Na	-5.92	Co	-7.85	Ba	-10.8	Ce	-17.1
K	-6.04	Bi	-7.93	Eu	-11.4	Gd	-17.1
Li	-6.52	Rh	-8.01	Cr	-12.1	Zr	-18.6
As	-6.87	Mn	-8.6	Nd	-14.5	Nb	-19
W	-19.19	Hf	-19.3	Ta	-20.2		

Supplementary Table 2. OER performances of the Ru-based catalysts in this work.

Catalysts	Loading ($\mu\text{g cm}^{-2}$)	ECSA ($\text{cm}^2_{\text{oxide}}$)	Overpotential (V) @ 10 mA cm^{-2}	j_m @ 1.45 V ($\text{A mg}^{-1}_{\text{oxide}}$)	j_s @ 1.45 V ($\text{mA cm}^{-2}_{\text{oxide}}$)
RuO_2	125	83.4	282	0.003	0.005
$\text{W}_{0.3}\text{Ru}_{0.7}\text{O}_2$	125	52.3	216	0.020	0.047
$(\text{SO}_4)_\delta\text{RuO}_{2-\delta}$	125	71.1	225	0.013	0.023
$\text{Ba}_{0.4}(\text{SO}_4)_\delta\text{Ru}_{0.6}\text{O}_{2-\delta}$	125	54.6	232	0.009	0.022
$\text{Ba}_{0.3}(\text{SO}_4)_\delta\text{W}_{0.2}\text{Ru}_{0.5}\text{O}_{2-\delta}$	125	39.7	206	0.034	0.105

Supplementary Table 3. The amount of dissolved Ru, Ba and W for various catalysts after OER.

Catalyst	Ru Loading (μg)	Ba Loading (μg)	W Loading (μg)	Dissolved Ru (μg)	Dissolved Ba (μg)	Dissolved W (μg)
RuO_2	95.05			33.84		
$\text{W}_{0.3}\text{Ru}_{0.7}\text{O}_2$	70.12		55.24	16.90		7.23
$(\text{SO}_4)_\delta\text{RuO}_{2-\delta}$	100.25			19.25		
$\text{Ba}_{0.4}(\text{SO}_4)_\delta\text{Ru}_{0.6}\text{O}_{2-\delta}$	62.54	46.93		7.19	1.59	
$\text{Ba}_{0.3}(\text{SO}_4)_\delta\text{W}_{0.2}\text{Ru}_{0.5}\text{O}_{2-\delta}$	45.12	33.82	34.76	3.20	0.81	3.22

Supplementary Table 4. The stability number (S-number) of various catalysts after OER stability test.

Catalyst	Ru loss (%)	Ba loss (%)	W loss (%)	Reaction time (h)	S-number
RuO_2	35.6			1.5	418
$\text{W}_{0.3}\text{Ru}_{0.7}\text{O}_2$	24.11		13.08	55	30682
$(\text{SO}_4)_\delta\text{RuO}_{2-\delta}$	19.19			160	78360
$\text{Ba}_{0.4}(\text{SO}_4)_\delta\text{Ru}_{0.6}\text{O}_{2-\delta}$	11.49	3.39		316	414346
$\text{Ba}_{0.3}(\text{SO}_4)_\delta\text{W}_{0.2}\text{Ru}_{0.5}\text{O}_{2-\delta}$	7.09	2.40	9.26	1000	2946151

Supplementary Table 5. Summary of the reported Ru-based OER catalysts under acidic conditions.

Catalyst	Loading ($\mu\text{g cm}^{-2}$)	Electrolyte	Overpotential @10 mA cm^{-2} (mV)	Overpotential increase @10 mA cm^{-2}	Ref.
Ni-RuO ₂	400	0.1 M HClO ₄	214	Stable for 200 h	1
Co-RuIr	50	0.1 M HClO ₄	235	Stable for 25 h	2
Faceted Ru	127	0.1 M HClO ₄	180	85 mV for 4 h	3
Ru ₁ -Pt ₃ Cu	21	0.1 M HClO ₄	220	30 mV for 28 h	4
Bi _x Er _{2-x} Ru ₂ O ₇	830	0.1 M HClO ₄	180	Stable for 100 h	5
Cu-doped RuO ₂	275	0.5 M H ₂ SO ₄	188	83 mV for 8 h	6
CaCu ₃ Ru ₄ O ₁₂	250	0.5 M H ₂ SO ₄	171	21 mV for 24 h	7
Cr _{0.6} Ru _{0.4} O ₂	283	0.5 M H ₂ SO ₄	178	Stable for 10 h	8
W _{0.2} Er _{0.1} Ru _{0.7} O _{2-δ}	330	0.5 M H ₂ SO ₄	168	83 mV for 500 h	9
Li _{0.52} RuO ₂	637	0.5 M H ₂ SO ₄	156	Stable for 70 h	10
Y _{1.7} Sr _{0.3} Ru ₂ O ₇	71	0.5 M H ₂ SO ₄	264	Stable for 28 h	11
RuNi ₂ @G-250	320	0.5 M H ₂ SO ₄	227	Stable for 3 h	12
Ba _{0.3} (SO ₄) _{δ} W _{0.2} Ru _{0.5} O _{2-δ}	125	0.5 M H ₂ SO ₄	206	43 mV for 1,000 h	This work

Supplementary Table 6. Curvefit parameters for Ru K-edge EXAFS for various samples ($S_0^2=0.9$).

Catalyst	Path	R(\AA) ^a	N ^b	σ^2 (10^{-3}\AA^2) ^c	ΔE_0 (eV) ^d	R factor
RuO ₂	Ru-O	1.97	4.4	2.4		
	Ru-Ru	2.7	1	1.2	-1.32	0.016
	Ru-O	3.16	2.5	3.5		
Ba _{0.3} (SO ₄) _{δ} W _{0.2} Ru _{0.5} O _{2-δ}	Ru-O	1.97	4	0.6		
	Ru-Ru	2.69	1	4.2	-1.71	0.019
	Ru-O	3.15	2	11.4		
Ru foil	Ru-Ru	2.67	12	3.6	3.59	0.013
Standard RuO ₂	Ru-O	1.96	6	-0.3		
	Ru-Ru	2.66	6	-1.5	-0.32	0.018
	Ru-O	3.17	2	4.9		

^aR: Bond distance; ^bN: coordination numbers; ^c σ^2 : Debye-Waller factors; ^d ΔE_0 : the inner potential correction; S_0^2 : the amplitude reduction factor, which was set to 0.9 in the fittings; R factor: goodness of fit.

Supplementary Table 7. Free energies of formation for DFT-computed phases in Pourbaix analysis.

RuO ₂		Ba _{0.4} (SO ₄) _δ Ru _{0.6} O _{2-δ}			
Ru	0	Ru	0	Ba	0
RuO ₂	-3.95	RuO ₂	-6.00	Ba ²⁺ (aq)	-6.17
RuO ₄ ²⁻ (aq)	-4.98	RuO ₄ ²⁻ (aq)	-4.98	BaOH ⁺ (aq)	-7.83
RuO ₄ ⁻ (aq)	-4.58	RuO ₄ ⁻ (aq)	-4.58	SO ₄ ²⁻ (aq)	-8.43
H ₂ RuO ₅ (aq)	-6.07	H ₂ RuO ₅ (aq)	-6.07	BaSO ₄	-14.60

Supplementary Table 8. Summary of the reported PEMWE stability using different Ru-based OER catalysts.

Anode catalyst	Mass loading (mg cm ⁻²)	PEM	Cell temperature (°C)	Electrolyte	Current density (A cm ⁻²)	Cell voltage increase	Ref.
PtCo–RuO ₂ /C	2.5	N212	80	Distilled water	1	11 mV for 24 h	13
RuO ₂ /SnO ₂	3	N115	30	Distilled water	0.25	~ 400 mV for 235 h	14
RuO ₂ NS	1.2	N212	90	Distilled water	1	Stable for 10 h	15
Ni-RuO ₂	~3.1	N117	Room temperature	0.1 M HClO ₄	0.2	Stable for 1,000 h	1
W _{0.2} Er _{0.1} Ru _{0.7} O _{2-δ}	Not given	N117	Room temperature	0.5 M H ₂ SO ₄	0.1	~ 100 mV for 120 h	9
Ba _{0.3} (SO ₄) _δ W _{0.2} Ru _{0.5} O _{2-δ}	3	N115	80	0.5 M H ₂ SO ₄	0.5	108 mV for 300 h	This work

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