## Supporting Information

Tetragonal ZrO<sub>2</sub> supported low-iridium catalyst activating oxygen spillover stabilized lattice oxygen for proton exchange membrane water electrolysis

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## Methods

Chemicals. All chemicals were used as received without further purification. N,Ndimethylformamide (DMF) was purchased from Shanghai Macklin Biochemical Co., Ltd. Terephthalic acid (BDC) was purchased from Shanghai D&B Biological Science and Technology Co., Ltd. Nano zirconium dioxide (m-ZrO<sub>2</sub>, ≤100 nm), tetrahydrofuran (THF), benzoic acid and Water-18O (H218O, 97 at% 18O) were purchased from Aladdin Industrial Corporation, Shanghai. Sodium nitrate (NaNO<sub>3</sub>), potassium nitrate (KNO<sub>3</sub>), hydrochloric acid (HCl) and perchloric acid (HClO<sub>4</sub>) were purchased from Sinopharm Chemical Reagent Co., Ltd. Zirconium chloride (ZrCl<sub>4</sub>) and Nafion solution (5 wt%) were purchased from Sigma-Aldrich. Iridium (III) Chloride Trihydrate (IrCl<sub>3</sub>·3H<sub>2</sub>O) was purchased from Adamas beta. Platinum on graphitized carbon (Pt/C, 40 wt%) was purchased from Shanghai Hesen Electric Co., Ltd. Platinum on graphitized carbon (Pt/C, 75 wt%) was purchased from Anhui Contango New Energy Technology Co., Ltd. Ir black (Ir) was purchased from Ningbo Zhongkeke Innovation Energy Technology Co., Ltd. Sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) was purchased from Shanghai Titan Technology Co., Ltd. Nafion 212 and 115 proton exchange membrane were purchased from Suzhou Shengeruo Technology Co., Ltd. Platinum-plated titanium felt was purchased from Bekaert New Materials. The chemicals were used without further purification. Deionized (DI) water (>18.25 M $\Omega$  cm) used in our experiments was supplied by Millipore System (Millipore, Billerica, MA).

**Synthesis of UIO-66.** UiO-66 was synthesized according to a previous report<sup>1</sup>. Typically, ZrCl<sub>4</sub> (466 mg, 2 mmol), benzoic acid (2.44 g, 20 mmol) and BDC (57 mg, 0.343 mmol), were dissolved in 36 mL DMF by an ultrasonic cleaner. Then, the bottle was sealed and increased temperature to 120 °C and maintained that temperature for 24 h. After cooling to room temperature, the liquid was exchanged in DMF for 3 hours for

three days and then washed with EtOH for three hours for three days, and finally activated by suction.

Synthesis of the mixture of Ir@UIO-66 and corresponding dry salts. Ir@UIO-66 was prepared through a continually stir. Typically,  $IrCl_3 \cdot 3H_2O$  (60 mg) was dissolved in 30 mL (THF: H<sub>2</sub>O=1:1). After the UIO-66 (96.6 mg) was added, the mixture was stirred for 24 h, and the Ir@UIO-66 was obtained. Then the solution was transformed into a florence flask with NaNO<sub>3</sub> (600 mg) and KNO<sub>3</sub> (400 mg) were further added, and the solution was stirred for another 30 min. Afterwards, the solvent was removed by means of a rotary evaporator (120 rpm, 60 °C), and the mixture of Ir@UIO-66 and salts was obtained.

Synthesis of the mixture of  $Ir@m-ZrO_2$  and corresponding dry salts. The preparation of the mixture of  $Ir@m-ZrO_2$  and salts was similar to that of the mixture of Ir@UIO-66 and salts, except that  $m-ZrO_2$  was used as the support.

**Synthesis of IrO**<sub>x</sub>/t-**ZrO**<sub>2</sub>. IrO<sub>x</sub>/t-ZrO<sub>2</sub> was prepared through a molten salt method. Typically, the mixture of Ir@UIO-66 and salts was grinded and placed in a muffle furnace preheated to 450 °C in advance, held for 30 min and then quickly removed and cooled to room temperature in air. Then the products were washed by the mixture of DI water and EtOH for three times. Afterwards, the products were immersed in 1 M HCl for 24 h and were further washed by the mixture of DI water and EtOH for three times. After dried under vacuum at 60 °C for 12 h, the IrO<sub>x</sub>/t-ZrO<sub>2</sub> was obtained.

Synthesis of  $IrO_x/t$ - $ZrO_2$  with different Ir content. The preparation of  $IrO_x/t$ - $ZrO_2$  with Ir content was similar to that of  $IrO_x/t$ - $ZrO_2$ , except different amount of UIO-66 was used (48.3 mg for 30 wt% and 24.2 mg for 50 wt%).

**Synthesis of IrO<sub>x</sub>/m-ZrO<sub>2</sub>.** The preparation of  $IrO_x/m-ZrO_2$  was similar to that of  $IrO_x/t-ZrO_2$ , except that the mixture of  $Ir@m-ZrO_2$  and salts was used as precursor.

Characterization. The crystal structure of the samples was recorded by X-ray diffraction (XRD, D/max2550V). The morphology of the samples was characterized by scanning electron microscopy (SEM, Hitachi S4800, Thermo Fisher Helios G4 UC), and transmission electron microscopy (TEM, JEOL JEM 2010, operated at 200 kV). Scanning transmission electron microscopy (STEM) characterization was performed using Thermo Fisher Talos F200X. Aberration-corrected scanning transmission electron microscopy (AC-STEM) operated on a ThermoFisher Themis Z transmission electron microscope equipped with two aberration correctors. High angle annular dark field (HAADF)-STEM images were recorded using a convergence semi angle of 11 mrad, and inner- and outer collection angles of 59 and 200 mrad, respectively. Energy dispersive X-ray spectroscopy (EDS) was carried out using 4 in-column Super-X detectors. More detailed chemical compositions were collected on X-ray photoelectron spectroscopy (XPS, Thermo Escalab 250) with Al Ka X-ray beam (1,486.6 eV), and all binding energies were calibrated using the C 1s peak at 284.8 eV as the reference. Inductively coupled plasma optical emission spectroscopy (ICP-OES) was carried out on an Agilent 725 to determine the Ir and Zr concentration, to dissolve the catalyst completely, 1 mg catalyst was dissolved in 8 ml aqua regia and ultrasoniced at 60 °C for 4 h. Hard XAFS measurement and data analysis: XAFS spectra at the Ir L<sub>3</sub>-edge and Zr K-edge were recorded at the 1W1B beamline of the Beijing Synchrotron Radiation Facility (BSRF), China. Ir foil, IrO<sub>2</sub>, Zr foil and ZrO<sub>2</sub> were used as references. The sample were collected several times to obtain high-quality data. The acquired EXAFS data were processed according to the standard procedures using the ATHENA module implemented in the IFEFFIT software packages.<sup>2</sup> Brunauer-Emmett-Teller (BET) surface area was performed on a Micromeritics ASAP 2460.

*In-situ* SEIRAS was recorded in the home-built reflection accessory with external reflection configuration using an FTIR spectrometer equipped with a PerkinElmer spectrum 100 detector, and spectra were obtained from an average of 16 scans with a resolution of 8 cm<sup>-1</sup>. The thin Au film with a thickness of ~10 nm is prepared on a Si prism using electroless deposition described previously<sup>3</sup>. The sample ink was prepared as above mentioned on GDE. 25  $\mu$ L ink was dropped on the Au underlayer and dried in the air for 2 times. For spectroelectrochemical measurements, the catalyst-coated Si ATR crystal is placed in a three-electrode spectroelectrochemical cell as the working electrole, and platinum wire and Ag/AgCl electrode (3.5 M KCl) were used as the counter and reference electrodes, respectively. Prior to electrochemical measurements, the electrolyte (0.1 M HClO<sub>4</sub>) was injected into the cells. A CHI 760E electrochemical station was employed to record the electrochemical response. Spectra are presented in absorbance, with positive and negative peaks showing an increase and decrease in signal, respectively. The spectra were collected for every minute at 0.1 V with a dwell time of 20 min.

The *operando* Raman measurement was performed on the Raman spectrometer (LabRAM HR) utilizing an excitation laser with a wavelength of 514 nm. Before the experiments, calibration was carried out based on the peak at 520 cm<sup>-1</sup> of a silicon wafer standard.  $IrO_x/t$ - $ZrO_2$  was taken as the working electrodes. Platinum wire and Ag/AgCl were used as the counter electrode and reference electrode, respectively. During the *operando* experiment, the electrodes were submerged in the corresponding electrolyte. For each specified potential, the system was allowed to undergo a reaction for approximately 200 s to facilitate a steady-state environment before the acquisition of Raman signals.

**Electrochemical measurements.** All electrochemical measurements were carried in a three-electrode system with an electrochemical station (CHI 760E) in an H-type cell at room temperature. The electrocatalyst powder (2.5 mg) was dispersed in a mixture of

960 µL isopropanol and 40 µL Nafion® solution (5 wt%). After 30 min of sonication, 5 µL of homogeneous ink was dropped onto a 3 mm diameter GC electrode (area 0.07065 cm<sup>-2</sup>), dried in air for 30 min, and then used as the working electrode. For the Ag/AgCl (3.5 M KCl) electrode, it was used as the reference electrode, and the Pt mesh was used as the counter electrode. The Ag/AgCl (3.5 M KCl) reference electrode was calibrated relative to the RHE. Calibration was performed in a high-purity H<sub>2</sub> saturated 0.1 M HClO<sub>4</sub> electrolyte.CV was performed at a scan rate of 1 mV s<sup>-1</sup>, assuming that the average of the two potentials at which the current exceeded zero was the thermodynamic potential for the hydrogen electrode reaction (0.2005 V in 0.1 M HClO<sub>4</sub>) (Fig. S6). All potentials were referenced to RHE by the following calculation:  $E_{RHE} =$  $E_{Ag/AgCl}$  + 0.0592 pH + 0.2005 V. For LSV and CV, the scan rate was set to 5 mV/s, unless otherwise specified. And all LSV curves were corrected (100%) using the iRcompensation method. When performing LSV, CV tests, the electrolyte was rotated by external magnetic stirring at 800 rpm, sufficient to remove visible bubbles formed on the electrode surfaces. EIS measurements were performed at frequencies from 0.01 Hz to 100 kHz with an amplitude of 5 mV. The magnetic stirring was not performed when the CVs were collected for ECSA calculations and EIS measurements. Stability tests were performed using a Chronopotentiometry (CP) test with a current density of 10 mA  $cm^{-2}$  in 0.1 M HClO<sub>4</sub> with 1 cm<sup>2</sup> carbon paper (catalyst loading: 1 mg cm<sup>-2</sup>). The dissolve rates of Ir and Zr during the CP test were determined by inductively coupled plasma mass spectrometry (ICP-MS) on a NexION 2000-(A-10). To study the mechanism of the water oxidation reaction, 0.5 M H<sub>2</sub>SO<sub>4</sub> fixed with (CH<sub>3</sub>)<sub>4</sub>NCl  $(c[(CH_3)_4NCl] = 0.1 \text{ M})$  was used.

Mass activity (MA). MA = J/m

Where J is the current (A); m is all metal load (mg).

The ECSAs were obtained from the electrochemical double-layer capacitance of the catalytic surface. The electrical double-layer capacitors ( $C_{dl}$ ) were measured from double-layer charging curves using cyclic voltammograms in a non-Faradaic region with scan rate from 1 to 5 mV s<sup>-1</sup>.

The ECSA is calculated from the double layer capacitance according to:  $ECSA = C_{dl}/C_S$ Where CS is the specific capacitance of the sample (set as 0.035 mF cm<sup>-2</sup>).

The stability number (S\_number): S number =  $n_{O2}/n_{Ir}$ 

where  $n_{O2}$  is the molar number of oxygen produced during a time and  $n_{Ir}$  is the molar number of dissolved Ir in electrolyte determined via ICP-MS.

**Differential electrochemical mass spectrometric measurements.** *In situ* DEMS experiments was performed on an in situ differential electrochemical mass spectrometer provided by Linglu Instruments (Shanghai) Co. Ltd. A typical test was carried out in a three-electrode cell with N<sub>2</sub> saturated 0.1 M HClO<sub>4</sub> as electrolyte. Firstly, the pristine samples were labelled with <sup>18</sup>O isotopes in <sup>18</sup>O-labelled 0.1 M HClO<sub>4</sub> solution at 1.5 V for 10 min. The resultant electrodes were then rinsed with H<sub>2</sub><sup>16</sup>O for several times and dried in an oven to remove the residual H<sub>2</sub><sup>18</sup>O. Before the DEMS measurement, cyclic voltammetry was performed in the range of 0.6 - 1.2 V at 50 mV s<sup>-1</sup> to further purge the adsorbed <sup>18</sup>O species on the electrode. After these processes, the *in situ* DEMS measurement was carried out with applied potential on the samples. To get a reliable result, both LSV (0.8-1.5 V, 5 mV s<sup>-1</sup>) was performed on IrO<sub>x</sub>/t-ZrO<sub>2</sub> and IrO<sub>x</sub>/m-ZrO<sub>2</sub>. To exclude the influence from the nature abundance of <sup>18</sup>O, the mass signal of <sup>34</sup>O<sub>2</sub> was normalized by the total signal intensity of <sup>36</sup>O<sub>2</sub> obtained at the same test.

Proton exchange membrane water electrolysis test. To fabricate the membrane electrode assembly (MEA), IrO<sub>x</sub>/t-ZrO<sub>2</sub> or commercial Ir black was used as the anode catalyst, commercial 40% Pt/C and 75% Pt/C was used as the cathode catalyst. For preparing the anode and cathode inks, the catalysts were proportionally dispersed into a combination of isopropanol and deionized water. Then, Nafion® solution (5 wt%) was added to obtain 30 wt% for the anode and 20 wt% for the cathode. Homogeneous catalyst inks were obtained after sonication in a low temperature water bath for at least 30 minutes. To prepare MEA with Nafion 115/212 membranes as electrolytes, the anode and cathode catalyst ink were first sprayed on polytetrafluoroethylene (PTFE) sheets. Then, PTFE-loaded Ir black, Nafion 115/212, and PTFE-loaded cathode catalyst were hot-pressed under a pressure of 2.5 MPa for 2 min at 140 °C. Cooling peeled off the PTFE on the surface to obtain a catalyst-coated membrane (CCM). The prepared CCM was stored in distilled water for further measurements. To build the PEM electrolyzer for performance evaluation, titanium felt and carbon paper were used as different porous transport layers (PTL) on the anode and cathode, respectively. The assembly pressure of the fixture was set to 2.5 N·m. The effective working area of this electrode was measured to be 5 cm<sup>2</sup>. The PEM electrolyzer was operated at 80 °C with deionized water as the reactant. The current-voltage polarization curves were collected in the range of 0.01 to 4 A cm<sup>-2</sup> when the flow rate was 40 mL min<sup>-1</sup>. The stability of the PEM electrolyzer was also measured by electrolyzing water at 1 A cm<sup>-2</sup> at a flow rate of 40 mL min<sup>-1</sup>.

**Density functional theory (DFT) calculations.** DFT calculations are carried out in using periodic calculation software Vienna Ab-initio Simulation Package (VASP)<sup>4, 5</sup>, using the generalized gradient approximation (GGA) functional of the Perdew-Burke-Ernzerhof (PBE)<sup>6</sup>. The project-augmented wave (PAW) is added to describe the interaction between the atomic nucleus and electron<sup>7</sup>. Bader charge analysis was used to determine the atomic charge<sup>8</sup>. On the plane wave basis, an energy cutoff of 450 eV was employed. DFT-D3 (BJ) is used to correct Van der Waals force in our system<sup>9, 10</sup>.

The Broyden method was employed for geometric relaxation until the maximal force on each relaxed atom was less than 0.05 eV/Å. m-  $ZrO_2$  (111) surface and t- $ZrO_2$  (101) surface were molded with four layers with a vacuum of 15 Å. During optimization, the bottom two layers of the slab were fixed, and the top three layers were fully relaxed. A  $p(3\times3) ZrO_2$  (101) surface and m-  $ZrO_2$  (111) slab with a corresponding  $2\times2\times1$  k-point mesh was used. The constrained optimization method was used to search the transition state, which has been widely verified<sup>11, 12</sup>.



**Figure S1.** Schematic illustration of (a) AEM pathway, (b) LOM pathway and (c) oxygen spillover stabilized LOM pathway.

Notes: In oxygen spillover stabilized LOM pathway, the vacancies formed during the LOM pathway can be filled by diffusing the absorbed oxygen on the Zr to the Ir sites, thus stabilizing the structure.



**Figure S2.** Structures and Surface Active Sites of (a) t-ZrO<sub>2</sub> and (b) m-ZrO<sub>2</sub> after DFT optimization, with Zr in t-ZrO<sub>2</sub> being 8-coordinated and in m-ZrO<sub>2</sub> being 7-coordinated.



Figure S3. Free energy changes of water dissociation in  $IrO_x/t$ - $ZrO_2$  and  $IrO_x/m$ - $ZrO_2$ .



Figure S4. (a, b) SEM images of UIO-66 at different magnifications, showing its octahedral architecture.



Figure S5. XRD pattern of UIO-66 (Zr) compared with the simulated UIO-66.



Figure S6. XRD patterns of m-ZrO<sub>2</sub> and  $IrO_x/m$ -ZrO<sub>2</sub>. The PDF cards of m-ZrO<sub>2</sub> (PDF#97-018-7207) and  $IrO_2$  (PDF#97-064-0887) are marked green and orange, respectively.



**Figure S7.** BET adsorption-desorption isotherm of UIO-66. The BET results shows that the catalysts remain its large surface area after molten salt.



**Figure S8.** (a) TEM images of  $IrO_x/t$ -ZrO<sub>2</sub>, 100  $IrO_x$  nanoparticles were measured and marked by red lines. (b) Size statistics of the  $IrO_x$  nanoparticles.



**Figure S9.** (a, b) Atomic-resolution aberration-corrected HAADF-STEM image of  $IrO_x/t$ -ZrO<sub>2</sub> in which the bright spots highlighted by the circles are ascribed to  $IrO_x$  clusters and lattice distances of 0.296 and 0.294 nm are ascribed to the (101) plane of t-ZrO<sub>2</sub>.



**Figure S10.** (a) TEM image and particle size distribution of as-synthesized  $IrO_x/m$ -ZrO<sub>2</sub>. (b) HAADF-STEM image of  $IrO_x/m$ -ZrO<sub>2</sub> and corresponding elemental maps for (c) Ir, (d) O, and (e) Zr, respectively. The results indicate that the  $IrO_x$  clusters with an average diameter of 1.39 nm are uniformly supported on m-ZrO<sub>2</sub>.



**Figure S11.** (a) TEM images of  $IrO_x/m$ -ZrO<sub>2</sub>, 100 IrO<sub>x</sub> nanoparticles were measured and marked by red lines. (b) Size statistics of the  $IrO_x$  nanoparticles.



**Figure S12.** CV curves of Ag/AgCl (3.5 M KCl) electrode calibration in H<sub>2</sub>-saturated 0.1 M HClO<sub>4</sub>.



Figure S13. LSV curves of  $IrO_x/t$ -ZrO<sub>2</sub> with different Ir content (quantified by ICP) recorded at a scan rate of 5 mV s<sup>-1</sup>.



Figure S14. CV test with scan rate from 1 to 5 mV s<sup>-1</sup> for (a)  $IrO_x/t$ -ZrO<sub>2</sub> and (b)  $IrO_x/m$ -ZrO<sub>2</sub>.



Figure S15. Electrochemical active area (ECSA) analyses. (a) Double-layer capacitance  $(C_{dl})$  represented by curve slope and (b) ECSA comparison.



**Figure S16.** Comparison of XRD patterns of  $IrO_x/t$ - $ZrO_2$  before and after reaction (1000 h @ 10 mA cm<sup>-2</sup> in 0.1 M HClO<sub>4</sub>). The PDF cards of t- $ZrO_2$  (PDF#97-009-7004) and  $IrO_2$  (PDF#97-064-0887) are marked green and orange, respectively. Notes: The triangles represent the diffraction peaks of the carbon paper, and the green and yellow arrows represent the diffraction peaks of  $ZrO_2$  and  $IrO_2$  respectively.



**Figure S17.** (a) TEM image  $IrO_x/t$ -ZrO<sub>2</sub> after reaction (1000 h @ 10 mA cm<sup>-2</sup> in 0.1 M HClO<sub>4</sub>). (b) HAADF-STEM image of  $IrO_x/t$ -ZrO<sub>2</sub> and corresponding elemental maps for (c) Ir, (d) O, and (e) Zr, respectively.

Notes: The results indicate that the morphology  $IrO_x/t$ - $ZrO_2$  has not changed and no aggregated Ir were found after OER test.



**Figure S18.** (a-c) Atomic-resolution aberration-corrected HAADF-STEM images of  $IrO_x/t$ -ZrO<sub>2</sub> after stability test (100 h @ 10 mA cm<sup>-2</sup> in 0.1 M HClO<sub>4</sub>). (d) HAADF-STEM image of  $IrO_x/t$ -ZrO<sub>2</sub> after stability test (100 h @ 10 mA cm<sup>-2</sup> in 0.1 M HClO<sub>4</sub>) and corresponding elemental maps of Ir, Zr and O, showing the homogenous dispersion within the catalyst.



**Figure S19.** (a) Atomic-resolution aberration-corrected HAADF-STEM image of  $IrO_x/t$ -ZrO<sub>2</sub> after stability test (100 h @ 10 mA cm<sup>-2</sup> in 0.1 M HClO<sub>4</sub>), 80 IrO<sub>x</sub> nanoparticles were measured and marked by wight circles. (b) Size statistics of the IrO<sub>x</sub> nanoparticles.



Figure S20. LSV curve of (a)  $IrO_x/t$ -ZrO<sub>2</sub>, (b) commercial RuO<sub>2</sub>, (c)  $IrO_x/m$ -ZrO<sub>2</sub> and (d) commercial  $IrO_2$  with/without adding TMA<sup>+</sup>.

Notes: When TMA<sup>+</sup> is added, the LOM pathway will be inhibited. The commercial RuO<sub>2</sub> follows LOM pathway during the OER process. Thus, the decreased OER performance in (a) and (b) reveals that similar to commercial RuO<sub>2</sub>, the IrO<sub>x</sub>/t-ZrO<sub>2</sub> follows a LOM pathway during the OER process. However, when TMA<sup>+</sup> is added, the AEM pathway will not be affected. Thus, in Figure S20c and S20d, the similar OER performance of IrO<sub>x</sub>/m-ZrO<sub>2</sub> and commercial IrO<sub>2</sub> reveals that the IrO<sub>x</sub>/m-ZrO<sub>2</sub> follows a AEM pathway during the OER process.



Figure S21. pH independent OER activity of  $IrO_x/t$ -ZrO<sub>2</sub> on RHE scale with varying pH.



**Figure S22.** pH dependent OER activity of IrO<sub>x</sub>/m-ZrO<sub>2</sub> on RHE scale with varying pH.



**Figure S23.** (a) XANES spectra at the Ir L<sub>3</sub>-edge and (b) FT-EXAFS of IrO<sub>x</sub>/t-ZrO<sub>2</sub>, Ir foil, IrO<sub>2</sub> and IrO<sub>x</sub>/t-ZrO<sub>2</sub> after reaction. (10 h @ 10 mA cm<sup>-2</sup> in 0.1 M HClO<sub>4</sub>)



Figure S24. (a) XANES spectra at Zr K-edge and.(b) FT-EXAFS of  $IrO_x/t$ -ZrO<sub>2</sub>, Zr foil, and ZrO<sub>2</sub>.



**Figure S25.** The operando XAS electrochemical OER measurement system, in which the fluorescence model was adopted for collecting spectra.



**Figure S26.** *Operando* SEIRAS spectra of the (a)  $IrO_x/t$ -ZrO<sub>2</sub> and (b)  $IrO_x/m$ -ZrO<sub>2</sub> sample in 0.1 M HClO<sub>4</sub> electrolyte at different applied bias (from 1.1 V vs. RHE to 1.6 V vs. RHE).



**Figure S27.** *Operando* Raman spectra of the  $IrO_x/t$ -ZrO<sub>2</sub> sample in 0.1 M HClO<sub>4</sub> electrolyte at different applied bias (from OCP to 1.7 V vs. RHE).



**Figure S28.** Digital photograph of the (a) PEM electrolyzer and (b) a 5 cm<sup>2</sup> catalyst coated membrane (CCM).



**Figure S29.** EIS of the PEM electrolyzer using  $IrO_x/t$ -ZrO<sub>2</sub> (0.5 mg cm<sup>-2</sup>, 0.1 mg<sub>Ir</sub> cm<sup>-2</sup>),  $IrO_x/m$ -ZrO<sub>2</sub> (0.5 mg cm<sup>-2</sup>, 0.12 mg<sub>Ir</sub> cm<sup>-2</sup>), commercial Ir black (2 mg cm<sup>-2</sup>, 2 mg<sub>Ir</sub> cm<sup>-2</sup>) and commercial  $IrO_2$  (1 mg cm<sup>-2</sup>, 0.8 mg<sub>Ir</sub> cm<sup>-2</sup>) as anodic catalysts and 75% Pt/C (0.5 mg cm<sup>-2</sup>, 0.375 mg<sub>Pt</sub> cm<sup>-2</sup>) as cathodic catalyst obtained at 1 A cm<sup>-2</sup> 80 °C with Nafion 212 membrane.



**Figure S30.** Polarization curve of the PEM electrolyzer using  $IrO_x/t$ -ZrO<sub>2</sub> (0.5 mg cm<sup>-2</sup>, 0.1 mg<sub>Ir</sub> cm<sup>-2</sup>),  $IrO_x/m$ -ZrO<sub>2</sub> (0.5 mg cm<sup>-2</sup>, 0.12 mg<sub>Ir</sub> cm<sup>-2</sup>), commercial Ir black (2 mg cm<sup>-2</sup>, 2 mg<sub>Ir</sub> cm<sup>-2</sup>) and commercial  $IrO_2$  (1 mg cm<sup>-2</sup>, 0.8 mg<sub>Ir</sub> cm<sup>-2</sup>) as anodic catalysts and 75% Pt/C (0.5 mg cm<sup>-2</sup>, 0.375 mg<sub>Pt</sub> cm<sup>-2</sup>) as cathodic catalyst obtained at 80 °C with Nafion 212 membrane.



**Figure S31.** Polarization curve of the PEM electrolyzer using  $IrO_x/t$ -ZrO<sub>2</sub> (0.5 mg cm<sup>-2</sup>, 0.1 mg<sub>Ir</sub> cm<sup>-2</sup>),  $IrO_x/m$ -ZrO<sub>2</sub> (0.5 mg cm<sup>-2</sup>, 0.12 mg<sub>Ir</sub> cm<sup>-2</sup>), commercial Ir black (2 mg cm<sup>-2</sup>, 2 mg<sub>Ir</sub> cm<sup>-2</sup>) and commercial  $IrO_2$  (1 mg cm<sup>-2</sup>, 0.8 mg<sub>Ir</sub> cm<sup>-2</sup>) as anodic catalysts and 75% Pt/C (0.5 mg cm<sup>-2</sup>, 0.375 mg<sub>Pt</sub> cm<sup>-2</sup>) as cathodic catalyst obtained at 80 °C with Nafion 115 membrane.



**Figure S32.** Chronopotentiometry curve of the PEM electrolyzer using  $IrO_x/t$ -ZrO<sub>2</sub> (0.5 mg cm<sup>-2</sup>, 0.1 mg<sub>Ir</sub> cm<sup>-2</sup>) as anodic catalyst and 75% Pt/C (0.5 mg cm<sup>-2</sup>, 0.375 mg<sub>Pt</sub> cm<sup>-2</sup>) as cathodic catalyst operated at 1 A cm<sup>-2</sup> at 80 °C with Nafion 115 membrane.



**Figure S33.** Chronopotentiometry curve of the PEM electrolyzer using  $IrO_x/t$ -ZrO<sub>2</sub> (0.5 mg cm<sup>-2</sup>, 0.1 mg<sub>Ir</sub> cm<sup>-2</sup>) as anodic catalyst and 75% Pt/C (0.5 mg cm<sup>-2</sup>, 0.375 mg<sub>Pt</sub> cm<sup>-2</sup>) as cathodic catalyst operated at 2 A cm<sup>-2</sup> at 80 °C with Nafion 115 membrane.



**Figure S34.** The dissolution rate of Ir and Zr derived from ICP-MS measurements after the stability tests at 1 A cm<sup>-2</sup> and 2 A cm<sup>-2</sup> in PEMWE for 150 hours. The results indicate 1 % Ir loss and 0.01% of Zr loss for  $IrO_x/t$ -ZrO<sub>2</sub> after 150 hours of working at 1 A cm<sup>-2</sup>, and 1.65 % Ir loss and 0.03% of Zr loss for  $IrO_x/t$ -ZrO<sub>2</sub> after 150 hours of working at 2 A cm<sup>-2</sup>.

Time	Dissolution amount	Dissolution rate of	Dissolution amount	Dissolution rate
(h)	of Ir ( $\mu g \ cm^{-2}$ )	Ir ( $\mu g h^{-1} cm^{-2}$ )	of Zr (µg cm <sup>-2</sup> )	of Zr ( $\mu$ g h <sup>-1</sup> cm <sup>-2</sup> )
2	2.68	1.34	0.52	0.26
24	4.13	0.17	0.86	0.036
48	4.92	0.10	1.04	0.022
100	4.60	0.046	0.93	0.0093
200	2.79	0.014	0.72	0.0036
300	1.76	0.0059	0.49	0.0016
400	1.59	0.0040	0.44	0.0011
500	1.15	0.0023	0.40	0.00080
600	1.06	0.0018	0.50	0.00084
700	1.63	0.0023	0.43	0.00062
800	1.65	0.0021	0.48	0.00060
900	1.22	0.0014	0.50	0.00055
1000	1.04	0.0010	0.49	0.00049

**Table S1.** ICP results of the dissolution rate of Ir and Zr during the 1000 h CP test in three electrodes system, the loading amount of the catalyst is 1 mg cm<sup>-2</sup>.

Table S2. Comparison of mass loading and stability of  $IrO_x/t$ - $ZrO_2$  with previously

reported Ir-based electrocatalysts in three electrodes system.	
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catalyst	loading amount of catalyst (mg cm <sup>-2</sup> )	loading amount ofloading amount of Ircatalyst (mg cm-2)(mg cm-2)		Reference	
IrO <sub>x</sub> /t-ZrO <sub>2</sub>	1	0.2	1000	this work	
Ti-IrO <sub>x</sub> /Ir <sup>13</sup>	1.4	1.286	100	Chem, 2023, <b>9</b> , 2931-2942	
DNP-IrNi <sup>14</sup>	/	0.67	50h @ 100mA cm <sup>-2</sup>	<i>Energy Environ. Sci.</i> , 2022, <b>15</b> , 3449-3461	
Ir-Sn PSC <sup>15</sup>	1	0.232	250 h @20 mA cm <sup>-2</sup>	Sci. Adv., 2023, 9, eadi8025	
KIr <sub>4</sub> O <sub>8</sub> <sup>16</sup>	0.281	0.225	100	<i>Adv. Mater.</i> , 2024, <b>36</b> , 2402643.	
p-L-IrO <sub>2</sub> <sup>17</sup>	0.28	0.224	200	CCS Chem., 2025, 7, 216-228.	
IrRu HNWs <sup>18</sup>	0.3	0.21	200	Joule, 2024, 8, 450-460	
$\mathrm{IrO}_{x}/\mathrm{Zr}_{2}\mathrm{ON}_{2}^{19}$	0.379	0.1516	5	Adv. Funct. Mater., 2023, <b>33</b> , 2301557	
HEA@Ir-MEO <sup>20</sup>	0.3	0.15	24 h @ 50 mA cm <sup>-2</sup>	<i>Adv. Mater.</i> , 2024, <b>36</b> , 2314049.	
$IrO_x \cdot nH_2O^{21}$	0.15	0.12	5700	<i>Sci. Adv.</i> , 2023, <b>9</b> , eadh1718	
$IrO_2 @TaB_2{}^{22}$	0.28	0.0448	130	Nat. Commun., 2023, 14, 5119	
Ir/D-ATO <sup>23</sup>	/	0.002023	18	Nat. Commun., 2023, 14, 5402.	

Anodic catalyst	$R_s (m\Omega cm^2)$	$R_{ct}(m\Omega \ cm^2)$		
IrO <sub>x</sub> /t-ZrO <sub>2</sub>	118	39.25		
IrO <sub>x</sub> /m-ZrO <sub>2</sub>	125	46.45		
Commercial Ir black	148	43.05		
Commercial IrO <sub>2</sub>	157.5	44.4		

 Table S3. Fitted parameters of the equivalent circuit model for different anodic catalysts in PEMWE.

Anode catalyst	Current density (A cm <sup>-2</sup> )	Anode PGM loading (mg cm <sup>-2</sup> )	Operation time (h)	Degradation rate <sup>a</sup> (mV h <sup>-1</sup> )	Reference
IrO <sub>x</sub> /t-ZrO <sub>2</sub>	3.10	0.1	1600	0.00625	This work
Ir <sub>VI</sub> -ado <sup>24</sup>	3.134	0.08	3740	/	Science, 2024, <b>384</b> , 666-670
$Ta_{0.1}Tm_{0.1}Ir_{0.8}O_{2\cdot\delta}{}^{25}$	1.73	0.154	500	0.152	Nat. Nanotechnol., 2021, <b>16</b> , 1371-1377
DNP-IrNi <sup>14</sup>	3.67	0.67	100	0.6	Energy Environ. Sci., 2022, <b>15</b> , 3449-3461
Ti-IrO <sub>x</sub> /Ir <sup>13</sup>	2.97	0.45	220	0.225	Chem, 2023, <b>9</b> , 2931- 2942
IrRu HNWs <sup>18</sup>	2.62	0.5	240	0.025	Joule, 2024, <b>8</b> , 450-460
KIr <sub>4</sub> O <sub>8</sub> <sup>16</sup>	2.00	1.6	1230	0.0935	<i>Adv. Mater.</i> , 2024, <b>36</b> , 2402643
HEA@Ir-MEO <sup>20</sup>	3.38	0.4	500	0.06	Adv. Mater., 2024, <b>36</b> , 2314049
Ir <sub>3</sub> Ni nanocages <sup>26</sup>	1.02	1	190	0.61	J. Am. Chem. Soc., 2024, <b>146</b> , 7858-7867
Ir/Nb <sub>2</sub> O <sub>5-x</sub> <sup>27</sup>	3.686	1.8	2000	/	Angew. Chem. Int. Ed., 2022, <b>61</b> , e202212341
Ir/D-ATO <sup>23</sup>	1.50	0.0475	250	0.624	Nat. Commun., 2023, 14, 5402
$IrO_2@TaB_2^{22}$	2.52	0.15	100	0.14	Nat. Commun., 2023, 14, 5119
Sr <sub>2</sub> CaIrO <sub>6</sub> <sup>28</sup>	2.45	0.4	450	/	Nat Commun., 2022, <b>13</b> , 7935

**Table S4.** Comparison on the PEM electrolyzer performance at 1.9 V, anode noble

 metal loading, stability and degradation rate with recent reported OER electrocatalysts.

Ir-ZrTaOx <sup>29</sup>	2.40	0.57	200	0.0047	<i>Chem Catal.</i> , 2023, <b>3</b> , 100667
$IrO_x \cdot nH_2O^{21}$	1.66	1.6	600	0.0059	<i>Sci. Adv.</i> , 2023, <b>9</b> , eadh1718
Ir-Sn PSC <sup>15</sup>	1.84	0.232	100	0.88	<i>Sci. Adv.</i> , 2023, <b>9</b> , eadi8025
p-L-IrO2 <sup>17</sup>	2.84	0.56	2300	0.0059	CCS Chem., 2025, <b>7</b> , 216-228
IrO <sub>x</sub> /Zr <sub>2</sub> ON <sub>2</sub> <sup>19</sup>	1.87	0.4	50	0.44	Adv. Funct. Mater., 2023, <b>33</b> , 2301557
$Ir/B_4C^{30}$	2.60	0.5	48	2.083	<i>J. Power Sources</i> , 2021, <b>512</b> , 230506
Ir@WO <sub>x</sub> NRs <sup>31</sup>	1.81	0.144	1030	0.049	ACS Appl. Mater. Interfaces, 2021, <b>13</b> , 15073-15082

<sup>a</sup>Some of the degradation rate values were manually extrapolated from their respective studies.

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