Supplementary Information (SI) for ChemComm.

Supplementary Information

Synergistic zinc and tantalum doping of RuO_2 boosts acidic water oxidation activity and stability

Experimental section

Methods

Reagents

$RuCl_3 \cdot xH_2O$ was purchased from Shaanxi Kaida Chemical Co., Ltd. Tantalum pentachloride ($TaCl_5$) was purchased from Annaiqi (Shanghai) Pharmaceutical Chemistry Co., Ltd. $ZnCl_2$, H_2SO_4 (98 wt%) and HCl (98 wt%)) were purchased from Macklin. Ethanol was purchased from Chengdu Kelong Chemical Co., Ltd. $H_2{}^{18}O$ (99%) was purchased from xx. Carbon paper (CP GDL) was purchased from the Fuel Cell Store. All chemicals were used as received without further purification. The water used in all experiments was purified using a Millipore system.

Samples synthesis

Preparation of RuO_2 catalyst. Weigh 3.1 mg of hydrated ruthenium(III) chloride ($RuCl_3 \cdot xH_2O$) into a 2 mL centrifuge tube; the precious metal loading of the catalyst was uniformly controlled at 0.43 mg cm^{-2}. Add 500 μL of deionized water and 500 μL of anhydrous ethanol to each tube, and sonicate for several hours to thoroughly mix the solution. Subsequently, 500 μL of the mixed solution was dispensed onto each of two 1×2 cm^2 carbon paper sheets. The sheets were dried on a 250 °C hot plate and then placed in a muffle furnace for calcination. The calcination was conducted at 350 °C for 3 hours with a heating rate of 5 °C/min, followed by natural cooling to room temperature. The resulting catalyst was designated RuO_2.

Preparation of Catalysts with Different Zn:Ru Ratios (Ru_xZn_{1-x}). To control the final catalyst loading on the carbon paper at 1 mg cm^{-2}, 1.1 mg, 2.1 mg, 3.0 mg, 3.8 mg, 4.5 mg, 5.2 mg, 5.8 mg, 6.4 mg, and 7.0 mg of hydrated ruthenium trichloride ($RuCl_3 \cdot xH_2O$) were weighed out, and sequentially added 7.1 mg, 6.0 mg, 5.0 mg, 4.1 mg, 3.3 mg, 2.5 mg, 1.8 mg, 1.2 mg, and 0.6 mg of zinc chloride ($ZnCl_2$) to 2 mL centrifuge tubes, denoted as $n_{Ru}:n_{Zn}$ = 1:9, 2:8, 3:7, 4:6, 5:5, 6:4, 7:3, 8:2and 9:1, respectively. To each tube, 500 μL of deionized water and 500 μL of anhydrous ethanol were added, followed by high-power ultrasonication for several hours to ensure the solution was highly dispersed and homogeneous. Subsequently, 500 μL of each mixed solution was dropped onto two 1×2 cm^2 carbon paper sheets, dried on a 250 °C hot plate, and finally calcined in a muffle furnace at 350 °C, calcination time of 3 hours, and a heating rate of 5 °C/min. The samples were then allowed to cool naturally to room temperature. The resulting catalysts were named $Ru_{0.1}Zn_{0.9}$, $Ru_{0.2}Zn_{0.8}$, $Ru_{0.3}Zn_{0.7}$, $Ru_{0.4}Zn_{0.6}$, $Ru_{0.5}Zn_{0.5}$, $Ru_{0.6}Zn_{0.4}$, $Ru_{0.7}Zn_{0.3}$, $Ru_{0.8}Zn_{0.2}$ and $Ru_{0.9}Zn_{0.1}$.

Preparation of RuO_2 catalysts with different ratios of Zn and Ta co-doping ($Ru_{0.5}Zn_xTa_{0.5-x}$). To control the final catalyst loading on the carbon paper at 1 mg cm^{-2}, 2.9 mg, 3.2 mg, 3.5 mg, and 4.0 mg of hydrated ruthenium (III) chloride ($RuCl_3 \cdot xH_2O$) were weighed out, respectively, and 0.4

mg, 0.9 mg, 1.5 mg, and 2.3 mg of zinc chloride ($ZnCl_2$) were added, respectively. 4.4 mg, 3.6 mg, 2.7 mg, and 1.5 mg of tantalum pentachloride ($TaCl_5$) were sequentially added to 2 mL centrifuge tubes, designated as n_{Ru}:n_{Zn}:n_{Ta} = 5:1:4, 5:2:3, 5:3:2and 5:4:1, respectively. Add 500 μL of deionized water and 500 μL of anhydrous ethanol to each mixture, and sonicate for several hours to homogenize the solutions. Subsequently, dispense 500 μL of each mixture onto two 1×2 cm^2 carbon paper sheets, dry them on a 250 °C hot plate, and finally calcine them in a muffle furnace at 350 °C, for 3 hours at a heating rate of 5 °C/min, and allowed to cool naturally to room temperature. The resulting catalysts were named $Ru_{0.5}Zn_{0.1}T_{0.4}$, $Ru_{0.5}Zn_{0.2}Ta_{0.3}$, $Ru_{0.5}Zn_{0.3}Ta_{0.2}$, and $Ru_{0.5}Zn_{0.4}Ta_{0.1}$.

Preparation of $Ru_{0.5}Ta_{0.5}$ catalyst.

Weigh 3.1 mg of hydrated ruthenium (III) chloride ($RuCl_3 \cdot xH_2O$) and 6.0 mg of tantalum(V) chloride ($TaCl_5$) into a 2 mL centrifuge tube, with a Ru:Ta ratio of 5:5. The precious metal loading of the catalyst was uniformly controlled at 0.43 mg cm^{-2}, to ensure consistent precious metal loading across different catalysts at the optimal ratio. Add 500 μL of deionized water and 500 μL of anhydrous ethanol to each, and sonicate for several hours to thoroughly mix the solutions. Subsequently, dispense 500 μL of each mixed solution onto two 1× 2 cm^2 carbon paper sheets, dry them on a 250 °C hot plate, and finally calcine them in a muffle furnace at 350 °C, for 3 hours at a heating rate of 5 °C/min, and allowed to cool naturally to room temperature. The resulting catalyst was designated $Ru_{0.5}Ta_{0.5}$.

Materials characterization. Powder X-ray diffraction (XRD) patterns were collected on a Rigaku D/max 2500 X-ray generator Cu Kα radiation at a scanning rate of 5^{o} min^{-1} from 10 to 90^{o}. Transmission electron microscope (TEM) and high resolution TEM (HRTEM) characterization studies were carried out on a Talos F200s instrument at an acceleration voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) data was recorded on a PHI-5702 instrument.

Electrochemical tests. All electrochemical measurements were carried out with a CHI 760E electrochemistry workstation under room temperature in a typical three-electrode system. The working electrode was carbon paper coated with a thin layer of catalyst. Graphite rod electrode and Hg/Hg_2SO_4 were used as the counter and reference electrode, respectively. Unless otherwise stated, all the mentioned potentials were reported relative to the reversible hydrogen electrode (RHE). Polarization data was collected at a sweep rate of 5 mV s^{-1}. Data recorded in the whole electrochemical section was iR corrected. Electrochemical impedance spectra (EIS) was carried out from 10 mHz to 100 kHz with an AC voltage amplitude of 5 mV. The double-layer capacitance (C_{dl}) was collected by cyclic voltammetry (CV) with scan rates of 20 to 100 mV s^{-1} in the potential range of 0.876 V to 0.976 V. Chronopentionmetry analysis was measured under a constant current density of 10 mA cm^{-2} in 0.5 M H_2SO_4 solution. TMA^+ was applied to detected the O_2^{2-} species.

Online DEMS with isotope labeling. The ^{18}O isotope labelled experiments were monitored with an online different electrochemical mass spectrometer (Linglu Instrument). The working electrode was the catalyst loaded porous Au/PTFE film. The Pt wire and an Ag/AgCl electrode were used as the counter and reference electrode, respectively, in a three-electrode cell. The lattice oxygen exchange experiments of all catalysts were carried out by cyclic voltammetry (CV) cycling in 0.5 M H_2SO_4 ($H_2{}^{18}O$) solution. Before the DEMS tests, the treated working electrodes were washed with $H_2{}^{16}O$ for tens of times to purge residual $H_2{}^{18}O$. Afterwards, the system of ^{18}O isotope labelled experiment was detected by online DEMS through cyclic voltammetry measurement from 1.2-1.8

V for 5 cycles in 0.5 M H_2SO_4 ($H_2{}^{16}O$) solution.

In-situ ATR-FTIR measurements. The in-situ ATR-FTIR measurements in an electrochemical ATR-FTIR cell were monitored by a Bruker FTIR spectrometer equipped with an MCT detector (32 scans at a spectral resolution of 4 cm^{-1}). The catalysts loaded on single crystal silicon coated with Au (Au/Si) was used as the working electrodes. The Pt wire and an Hg/Hg_2SO_4 electrode were used as the counter and reference electrode, respectively. The measurements were conducted using 0.5 M H_2SO_4 as the electrolyte. The potential window from OCP to 1.8 V was chosen to conduct line-sweep voltammetry tests with 1 mV s^{-1} scan rate.

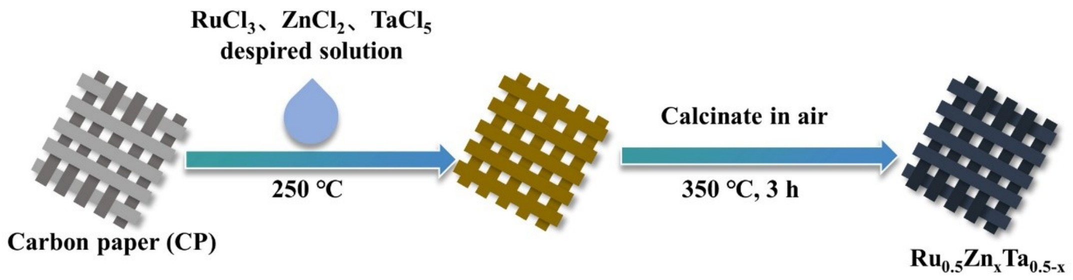
Kinetic isotope effect (KIE) measurements. To evaluate the KIE of the catalysts, electrochemical tests were conducted in both protonated (0.5 M H_2SO_4 in H_2O) and deuterated (0.5 M D_2SO_4 in D_2O) electrolytes. The overpotentials (η) in the protonated and deuterated electrolytes were calculated as follows:

η = E(RHE) – 1.23 V

η = E(RDE) – 1.263 V

The KIE was calculated using the following equation: $KIE=j_{H2O}/j_{D2O}$

where j_{H2O} and j_{D2O} are the catalytic current density in the protonic and deuteric solution, respectively, at the same η.



Scheme. S1. Schematic illustration for catalyst synthesis

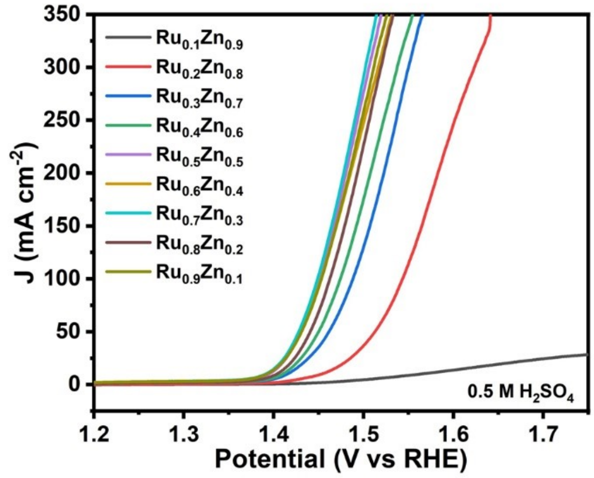


Fig. S1. LSV curves for $Ru_xZn_{1-x}O_2$ in acid solution.

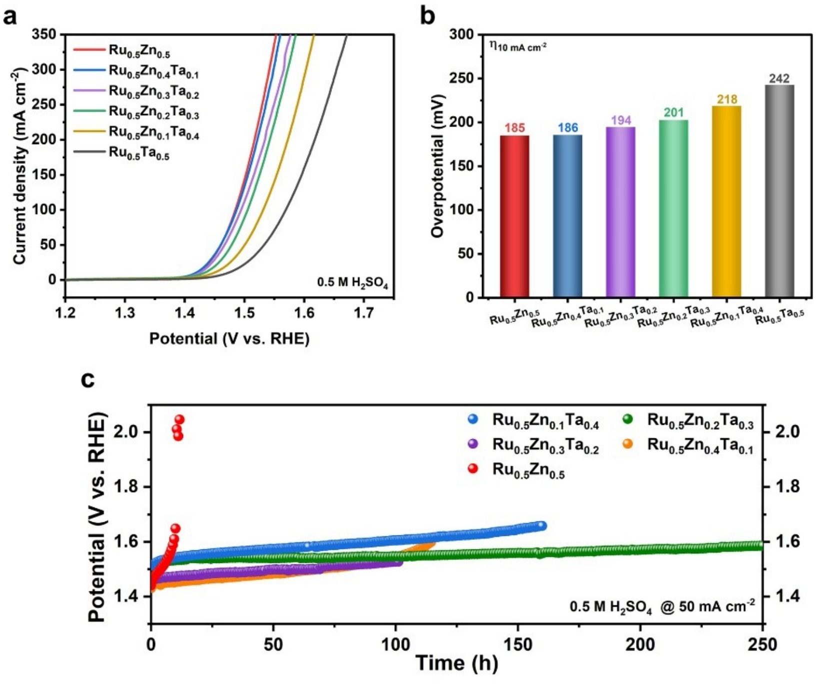


Fig. S2. OER performance in acid solution. a) LSV curves for $Ru_{0.5}Zn_{0.5}O_2$, $Ru_{0.5}Ta_{0.5}O_2$, and $Ru_{0.5}Zn_xTa_{0.5-x}O_2$ catalysts. b) Overpotential for different catalysts at 10 mA cm^{-2}. c)

Chronopotentiometry curves for different catalysts at 50 mA cm^{-2}.

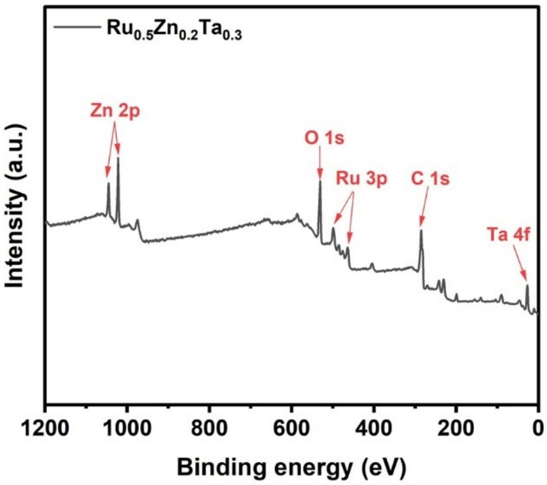


Fig. S3. Full XPS spectrum of the $Ru_{0.5}Zn_{0.2}Ta_{0.3}O_2$ catalyst.

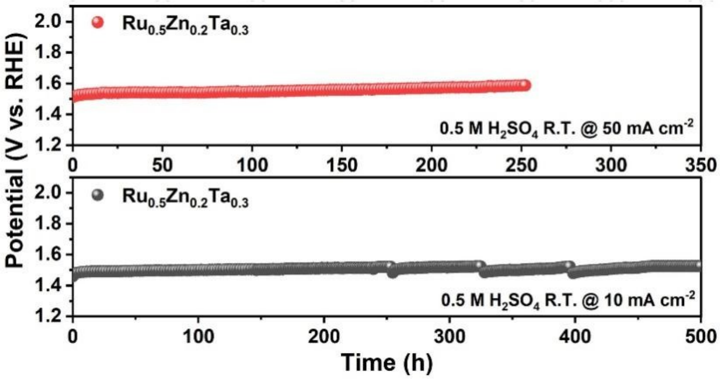


Fig. S4. Chronopotentiometry curves for $Ru_{0.5}Zn_{0.2}Ta_{0.3}O_2$ catalysts at 50 mA cm^{-2} and 10 mA^{-2}.

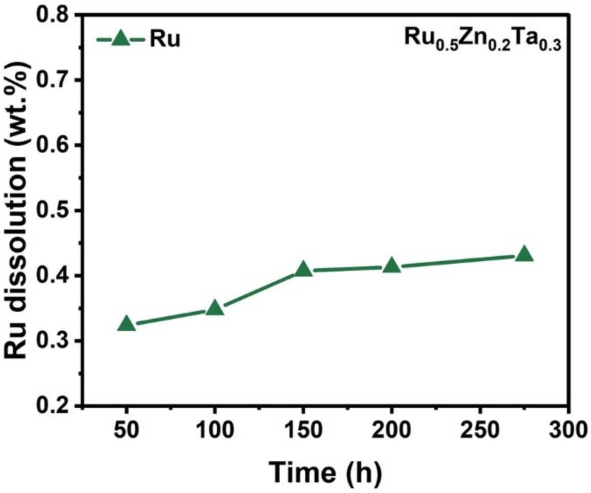


Fig. S5. Accumulative total dissolved ions for $Ru_{0.5}Zn_{0.2}Ta_{0.3}O_2$ in the 0.5 M H_2SO_4 electrolyte.

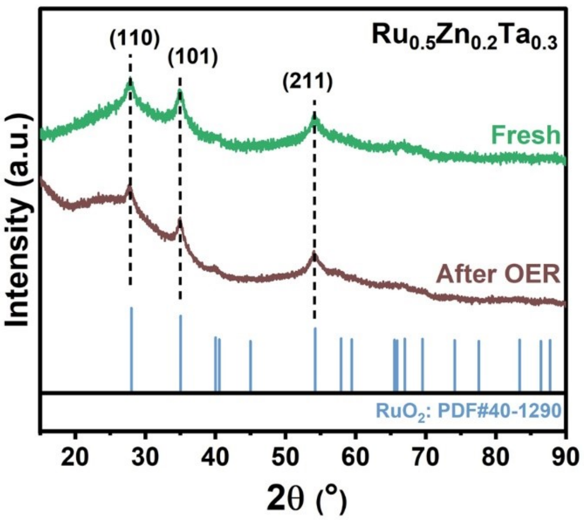


Fig. S6. The XRD patterns of $Ru_{0.5}Zn_{0.2}Ta_{0.3}O_2$ sample after the stability test.

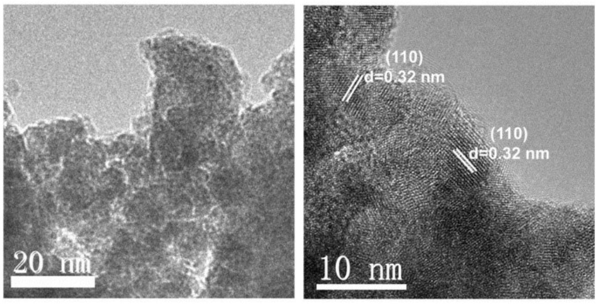


Fig. S7. The TEM images of $Ru_{0.5}Zn_{0.2}Ta_{0.3}O_2$ sample after the stability test.

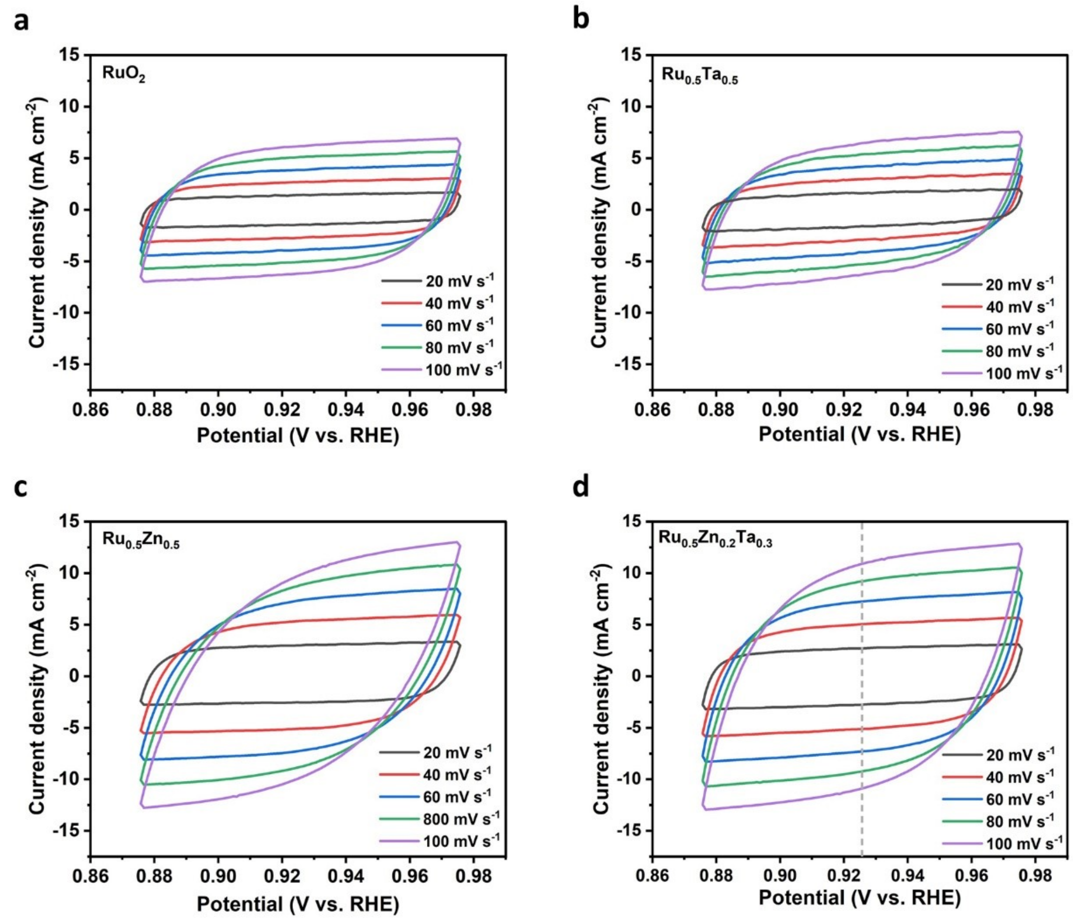


Fig. S8. CV curves at scan rates of 20, 40, 60, 80, 100 mV s^{-1} for a) RuO_2, b) $Ru_{0.5}Ta_{0.5}O_2$, c) $Ru_{0.5}Zn_{0.5}O_2$, and d) $Ru_{0.5}Zn_{0.2}Ta_{0.3}O_2$ catalysts.

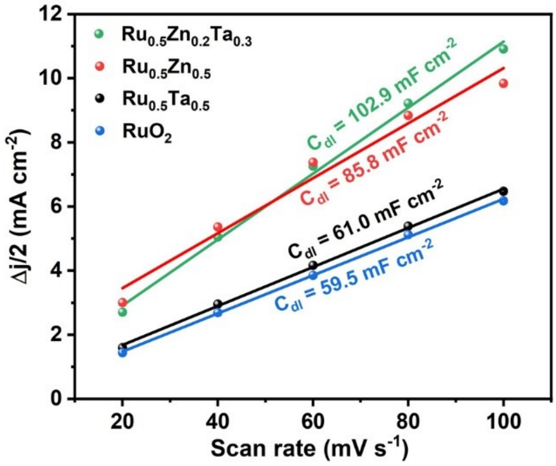


Fig. S9. The electrochemical double-layer capacitances of RuO_2, $Ru_{0.5}Zn_{0.5}O_2$, $Ru_{0.5}Ta_{0.5}O_2$, and $Ru_{0.5}Zn_{0.2}Ta_{0.3}O_2$ catalysts according to CV curves at scan rates of 20, 40, 60, 80, 100 mV s^{-1}.

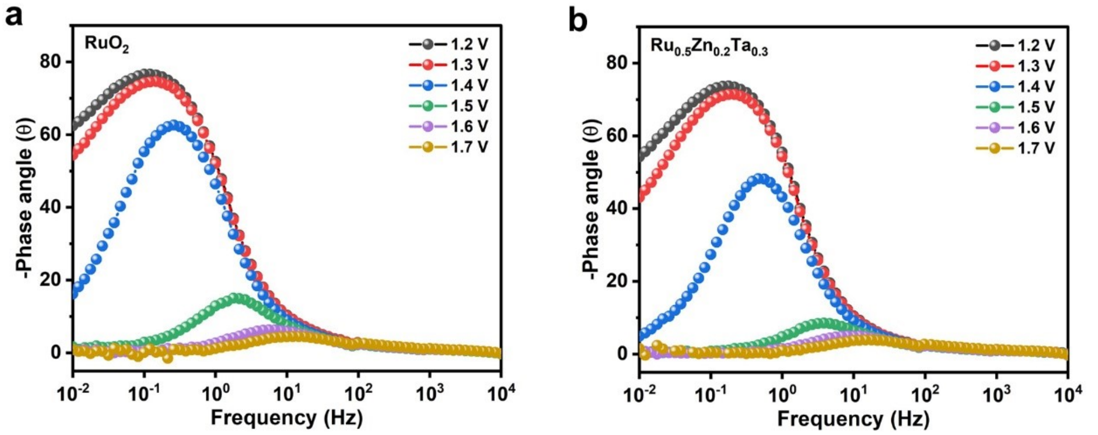


Fig. S10. Bode phase plots of a) RuO_2 and b) $Ru_{0.5}Zn_{0.2}Ta_{0.3}O_2$ catalysts.

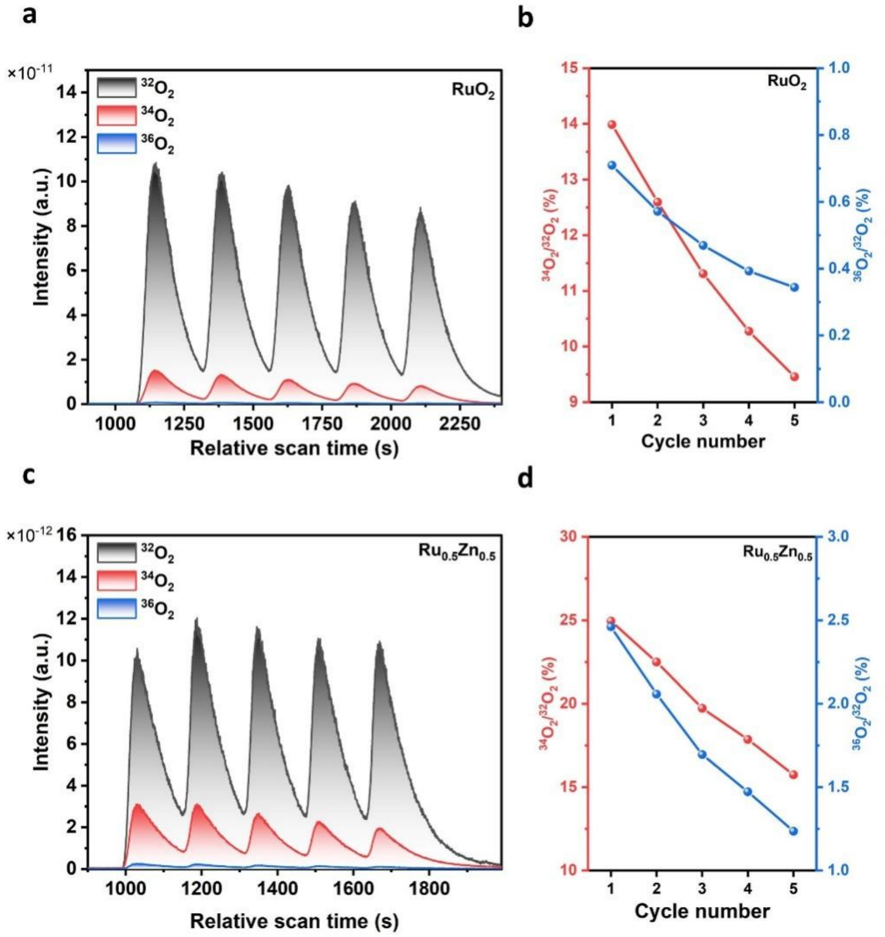


Fig. S11. DEMS signals of $^{36}O_2$ ($^{18}O^{18}O$), $^{34}O_2$ (^{16}O in the electrolyte + ^{18}O in the lattice) and $^{32}O_2$ (^{16}O in the electrolyte + ^{16}O in the electrolyte) from the reaction products for ^{18}O-labelled a) RuO_2 and c) $Ru_{0.5}Zn_{0.5}O_2$ catalysts in $H_2{}^{16}O$/0.5 M H_2SO_4 electrolyte. Ratio of relative abundances of $^{34}O_2/^{32}O_2$ and $^{36}O_2/^{32}O_2$ for b) RuO_2 and d) $Ru_{0.5}Zn_{0.5}O_2$ catalysts.

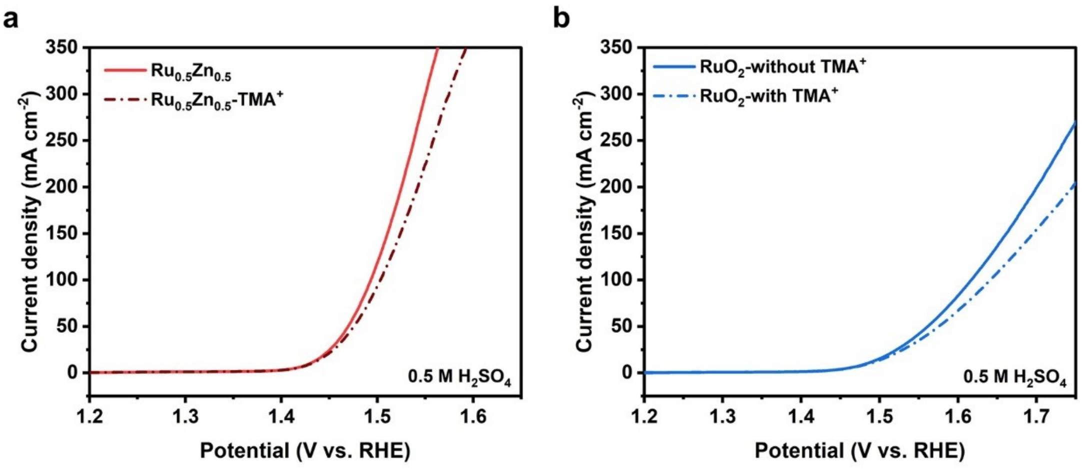


Fig. S12. OER polarization curves of a) $Ru_{0.5}Zn_{0.5}O_2$ and b) RuO_2 catalysts in 0.5 M H_2SO_4 electrolyte with and without TMA^+.

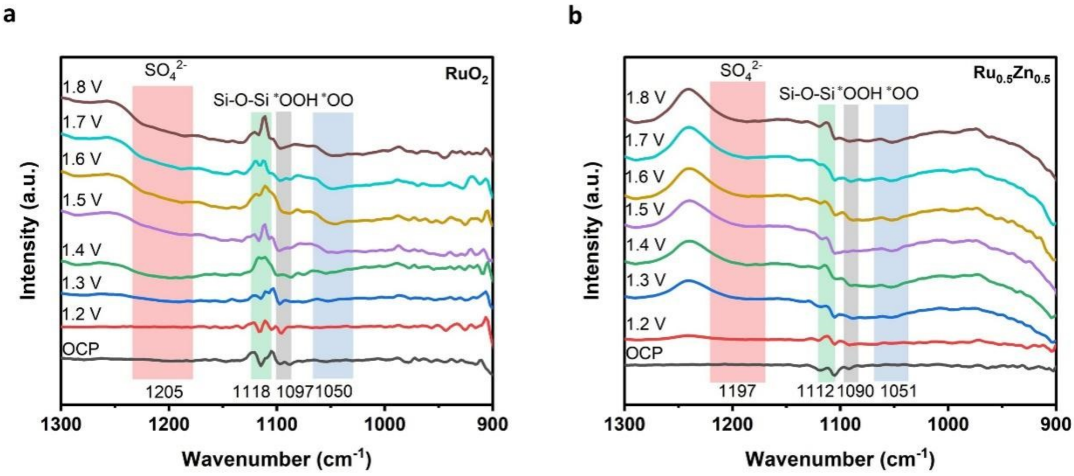


Fig. S13. In situ ATR-SEIRAS spectra for a) RuO_2 and b) $Ru_{0.5}Zn_{0.5}O_2$ catalysts.

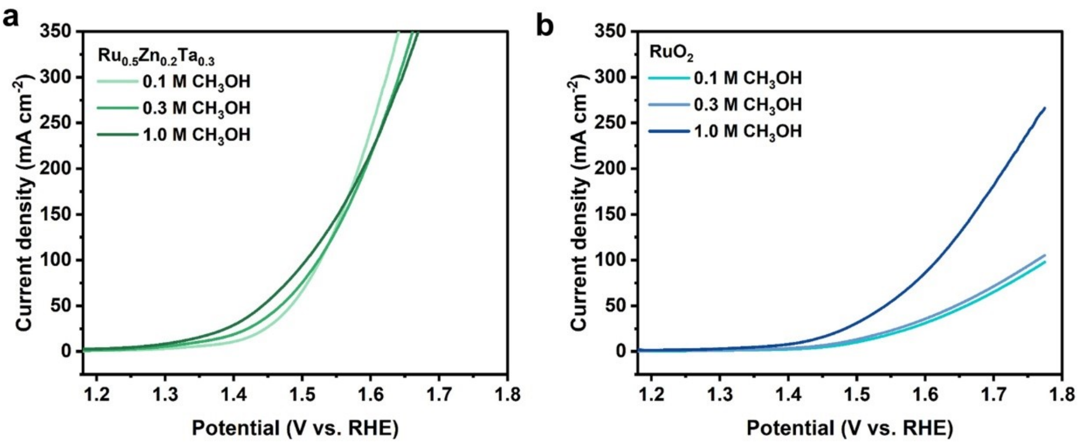


Fig. S14. OER polarization curves of a) $Ru_{0.5}Zn_{0.2}Ta_{0.3}O_2$ and b) RuO_2 catalysts in 0.5 M H_2SO_4 electrolyte with 0.1 M , 0.3 M, and 1.0 M CH_3OH.

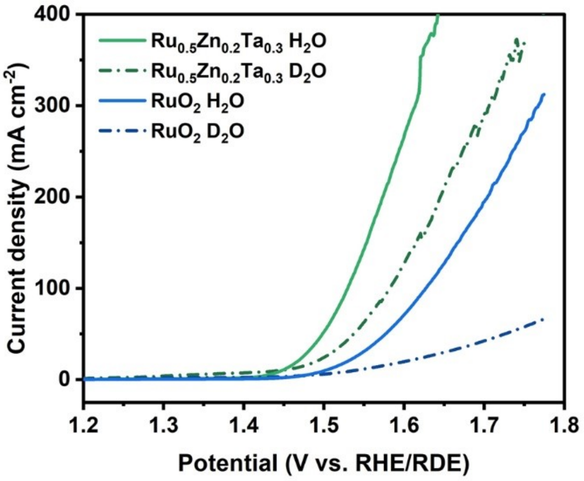


Fig. S15. LSV curves of $Ru_{0.5}Zn_{0.2}Ta_{0.3}O_2$ and RuO_2 catalysts in 0.5 M H_2SO_4/H_2O and 0.5 M D_2SO_4/D_2O electrolyte.