# Supporting Information

# Oxygen Evolution on Well-Characterized Mass-Selected Ru and RuO<sub>2</sub> Nanoparticles

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#### Preparation of mass-selected Ru nanoparticles.

The nanoparticles were prepared using a magnetron sputter gas aggregation source (Birmingham Instruments Inc.), combined with time-of-flight mass filtering<sup>1</sup>, and deposited onto either electrodes (glassy carbon or Au(111)) for electrochemical measurement or Si<sub>3</sub>N<sub>4</sub> grid for TEM analysis. The substrates were mounted in a multi-chamber ultrahigh vacuum (UHV) system (Omicron, Multiscan Lab) with a base pressure in the low  $10^{-10}$  mbar region. The gas aggregation technique involves Ar<sup>+</sup> sputtering of a metallic target (in this study a Ru target from Kurt J. Lesker Inc.), to produce an atomic vapor that is condensed into nanoparticles through collisions with cooled Ar and He gas. Many of the nanoparticles produced via Ar<sup>+</sup> sputtering are ionized; thus the particles can be filtered based on their mass-to-charge ratio, which in turn allows the deposition of particles with a narrow size distribution.

Following the particle production and filtering stages, the ionized nanoparticles are directed using Einzel lenses onto the support mounted in the vacuum chamber. The Einzel lenses can be used to control the breadth and position of the particle beam, which gives control of the total number of particles that are deposited on the surface, as well as the density of the nanoparticles. The combination of particle counting and mass selection allow us to accurately estimate the amount of catalyst deposited onto the glassy carbon. The total deposited mass was calculated with the formula:

$$M_{dep} = m_p I_{dep} t$$

Where  $m_p$  is the single particle mass, set using the mass filter, assuming singly charged particles,  $I_{dep}$  is the deposition current and t is the deposition time.

### X-Ray Photoelectron Spectroscopy (XPS) Characterization.

Elemental characterization of the supported Ru nanoparticles was performed in-situ for each deposition, i.e. without breaking the vacuum, using X-ray Photoemission Spectroscopy (XPS).

Post-oxidation and post-electrochemistry (EC) XPS measurements were performed with the same apparatus after re-introducing the sample in the UHV system.

The XPS measurements of the as-prepared nanoparticles were directly taken under UHV after each deposition. The analysis chamber base pressure was 2 x  $10^{-11}$  mbar. The X-ray source XR-50 was a non-monochromatized Al K $\alpha$  (1486.7 eV), manufactured by SPECS GmbH. The employed pass energy was 25 eV. The atomic concentrations were quantified by integration of the Ru 3d, C 1s peaks after background removal. A Shirley-type background was chosen for this purpose. The intensities were corrected for the relative sensitivity factors.

Fitting of the XPS spectra was performed with Gaussian-Lorentzian functions mixed with exponential tail, using CASA XPS software. Carbon was fitted using three different features, which we attribute to carbon and to its surface oxides. Ruthenium was fitted using two peaks for metallic ruthenium, two peaks for ruthenium dioxide (oxide at low B.E.) and another couple of peaks for the satellite features at higher binding energy (oxide at high B.E. in figure 1 and in figure S1). <sup>2–5</sup>



**Figure S1.** XPS spectra of the Ru 3d core level region for 2.9  $10^6$  u (a) *as-deposited* Ru, (b) thermally oxidized RuO<sub>2</sub> and (c) RuO<sub>2</sub> after electrochemistry (EC) nanoparticles on Glassy Carbon disk.

In order to independently estimate the total mass deposited, XPS measurements were used. To do this, we calculated the XPS Ru3d-to-C1s ratio, which is an estimate of the Ru nanoparticle projected coverage.

$$X_{Ru} = \frac{I_{Ru3d}}{I_{Ru3d} + I_{C1s}}$$

Where Ru3d represents the total ruthenium contribution normalized with the sensitivity factor and C1s the total corrected contribution from the carbon

$$I_{Ru3d} = \frac{I_{Ru3d\ 3/2} + I_{Ru3d\ 5/2}}{S_{Ru}}$$

Where  $\text{Ru}3d_{3/2}$  and  $\text{Ru}3d_{5/2}$  represent the integration of the Ru 3d peaks and  $S_{\text{Ru}}$  is the Scofield cross section factor for Ru  $\alpha$  is the angle between the detector and the normal to the surface of the sample.

$$I_{Corrected C1s} = I_{C1s} \left( 1 - \left( \frac{\pi \left( r_{electrode}^2 - r_{dep}^2 \right)}{\pi r_{electrode}^2} \right) \right) - I_{Ru3d} \left( exp \left( -\frac{d}{\lambda cos(\alpha_{detector})} \right) \right)$$

Where C1s is the integration of C1s XPS peak,  $r_{electrode}$  is the radius of the electrode, and  $r_{dep}$  is the radius of the deposited area and  $\lambda$  is the mean free path.

We then computed the total mass ( $M_{XPS}$ ) and surface area ( $A_{XPS}$ ) by assuming Ru spherical particles, using the following formulas:

$$M_{XPS} = \left(\frac{A_{XPS}}{4\pi (\frac{d}{2})^2}\right) m_p 1.66 \times 10^{-18} \times 10^{12}$$
$$A_{XPS} = 4\pi X_{Ru} r^2_{dep}$$

Where  $X_{Ru}$  is the Ru signal fraction, d is the diameter of the nanoparticle,  $r_{dep}$  is the radius of the area where the particles are deposited on.



**Figure S2.** Comparison between the total deposited mass of ruthenium estimated from the XPS spectra assuming spherical particles vs. the total mass measured from the deposition current. The dashed line shows the theoretical correlation, if there were a 1:1 correspondence between the two measures of the deposited mass. Each color represents a different mass:  $0.1 \ 10^6$  u (red circle),  $0.5 \ 10^6$  u (black square),  $1.4 \ 10^6$  u (green triangle) and  $2.9 \ 10^6$  u (blue rhombus).

Figure S2 shows a good correlation between the mass from XPS and the mass from the deposition current for the particles with a mass up to  $1.4 \ 10^6$  u. The data from XPS are based on the assumption of spherical particles, which is not the case for big particles. The STEM images shown in Figure 1(c-f,) clearly show that, the largest particles have a very rough shape, which might explain the scatter for these particles in Figure S2. Consequently, for the plot of the mass activity, Figure 4 in the main text, the mass activity was calculated on the basis of the mass from the deposition current.

#### **Glancing Angle – X-Ray Diffraction (XRD)**

To identify the structure of the nanoparticles before and after thermal oxidation, Glancing Angle XRD was performed on 2.9  $10^6$  u nanoparticles deposited on a Au(111) disk. The glancing angle XRD technique limits the signal from the substrate making it easier to single out information from the particles. To further enhance the signal from the nanoparticles, the loading was increased up to ~20 µg/cm<sup>2</sup>. The measurements were conducted on PAN analytical X'pert Pro XRD equipment with X-ray wavelength at 1.54 Å for the CuK $\alpha$  line. Alignment of the sample was performed with reflectometry and the incident angle set to  $\omega = 0.5^{\circ}$ . The scan range used was  $2\theta = [35; 70]$ . Reference patterns for gold, metallic ruthenium and rutile RuO<sub>2</sub> were found in ref <sup>6</sup> ref. <sup>7</sup> and ref. <sup>8</sup>, respectively. In Figure 2 the measured pattern before and after oxidation can be seen together with the reference patterns. After thermal treatment, rutile RuO<sub>2</sub> peaks appear clearly, while the metallic peak at 43.5° disappears, indicating that the bulk of the particles are fully oxidized.

# Scanning Transmission Electron Microscopy (STEM) and Scanning Electron Microscopy (SEM) characterisation.

TEM analysis was performed on mass-selected RuO<sub>2</sub> nanoparticles deposited on Si<sub>3</sub>N<sub>4</sub> TEMwindows. The projected area distributions were obtained from high angle annular dark field (HAADF) STEM micrographs acquired in a FEI Titan Analytical 80-300 electron microscope equipped with a CEOS Cescor probe spherical aberration corrector and operated at 300 kV accelerating voltage. Within each specimen, the analysis was carried out with the same microscope condition, constant acquisition dwell time as well as the HAADF detector settings.

SEM images were obtained using a Helios EBS3 microscope, with an accelerating voltage of 5kV and using a secondary electron detector. In Figure S3 SEM images are shown. Identical Location (IL) SEM was not used and the difference in local particle distribution may be due to imaging of different areas of the electrode where the particles are randomly distributes. However, after thermal oxidation neither sintering nor aggregation was observed while, after electrochemistry, particles migrate forming agglomerates.<sup>9</sup>



**Figure S3.** SEM micrographs of the same sample 2.9  $10^6$  u (a) as deposited Ru Nps, (b) thermally oxidized RuO<sub>2</sub> Nps and (c) RuO<sub>2</sub> after electrochemical Nps (2 Cycles between 1.00 and 1.23 V at 20 mV/s and 4 hours at 1.5V). Magnification 125000x; accelerating voltage 5.00 kV.

#### **Electrochemical characterisation**

All the electrochemical measurements were performed in a Rotating Ring Disk Electrode (RRDE) assembly, provided by Pine Instruments Corporation, using a Bio-Logic Instruments VMP2 multichannel potentiostat/galvanostat with EIS analyzer, controlled by a computer. Data was acquired using the Bio-Logic EC-Lab software. The electrochemical cell was a standard three-compartment glass cell, equipped with a Luggin capillary. The auxiliary electrode was a carbon rod and the reference was a Hg/HgSO<sub>4</sub> electrode. All the potentials are expressed with respect to the reversible hydrogen electrode (RHE) and the reference electrode was calibrated against an actual hydrogen electrode for each measurement at room temperature in the same electrolyte. All the experiments were performed in a nitrogen saturated 0.05M sulfuric acid at 1600 rpm and at room temperature. The acid electrolyte was prepared from 98% sulfuric acid (Merck Suprapur) and diluted with Millipore water (18 MΩ cm).

All the CVs were corrected for Ohmic losses (~50  $\Omega$  on Glassy Carbon and ~40  $\Omega$  on Au(111)). The Ohmic compensated current is then capacitance-corrected by taking the average between the forward (positive) and the backward (negative) scans<sup>10</sup> (fig S4).



**Figure S4.** Ohmic and capacitance corrected cyclic voltammetry of 2.9  $10^6$  u thermally oxidized RuO<sub>2</sub> nanoparticles on Glassy carbon. The data were first compensated for the Ohmic resistance and then for the capacitance, by taking the average between the anodic and cathodic sweeps.

The rotating ring disk electrode (Pine) with a Platinum ring was calibrated using the same configuration with a ferricyanide redox couple in a 0.1M KOH solution (Merck)<sup>11</sup>. The collection efficiency was estimated to be  $0.20 \pm 0.01$ , evaluated from three different measurements. The ring was held either at 1.1 V vs. RHE to reduce the RuO<sub>4</sub> produced during OER<sup>12</sup> or at 0.4 V vs. RHE to collect the generated oxygen<sup>11</sup>.



**Figure S5.** RRDE voltammogram of as deposited 2.9  $10^6$  u Ru nanoparticles at 1600 rpm in N<sub>2</sub> saturated electrolyte with the disk current (black), the ring current (red) and the current corresponding to Oxygen Evolution (blue). While cycling the potential on the disk, the generated RuO<sub>4</sub> is collected and reduced at the ring, which is held at 1.1 V (vs. RHE).

By integrating the charge due to the reduction of  $RuO_4$ , it is possible to evaluate the mass loss of Ru during Oxygen Evolution, as follows:<sup>12</sup>

Initial mass from deposition current =  $0.18 \ \mu g$ 

Integration of the ring peak,  $Q_{ring} = 0.063 \text{ mC}$ 

Number of electrons per RuO<sub>4</sub> reduced,  $n_{e^-} = 1$ 

Number of Ru atoms, natoms:

$$\frac{Q_{ring}}{n_{e^-}e^- \times 1000} = 3.93 \text{ x } 1014$$

Mass of dissolved Ru, m:

$$\frac{n_{atoms} \times Molecular \ weight_{Ru}}{N_A} = 6.6 \ x \ 10-8 \ g$$

Mass loss:

$$\frac{m_{dissolved,Ru}}{m_{initial}} = \frac{6.6 \times 10^{-8} \times 10^{6}}{0.18} \times 100 = 37 \%$$



**Figure S6.** RRDE voltammogram of thermally annealed 2.9  $10^6$  u RuO<sub>2</sub> nanoparticles at 1600 rpm in N<sub>2</sub> saturated electrolyte with the disk current (black) and the ring current (red).

In the case of thermally annealed 2.9  $10^6$  u nanoparticles, shown in Figure S6, the ring current can be neglected, since it does not significantly exceed the noise level. This suggests that the oxygen evolution can account for the entire disk current. This is confirmed by direct measurement of  $O_2$  with a Gas Chromatograph.

#### **Mass Activity**

The mass activity was evaluated by taking the value of the current, after Ohmic drop compensation and capacitance correction (as shown in Figure S4) at 1.48 V vs. RHE ( $\eta = 0.25$  V) and then normalizing the value with the mass of ruthenium. The mass was estimated from the neutralization current during the cluster deposition.



**Figure S7.** OER mass activities at 1.48 V (vs. RHE) of different single particle mass (0.035, 0.1, 0.5, 1.4, 2.9  $10^6$  u) of thermally oxidized RuO<sub>2</sub>, from cyclic voltammogram in N<sub>2</sub> saturated 0.05M H<sub>2</sub>SO<sub>4</sub> at 1600 rpm with a sweep rate of 20 mV/s. All the data points are shown. Activity on Au polycrystalline disk for 2.9  $10^6$  u nanoparticles is also shown.

Figure S7 shows that similar activities can be obtained both on glassy carbon disk and on gold polycrystalline disk.

# Calculation of how many years of precious metal annual production would be required to install 1 TW of hydrogen storage capacity

*Pt-Ir PEM electrolysers*<sup>13</sup>

Pt at the cathode:  $0.05 \text{ mg/cm}^2$ Pt at the anode:  $0.15 \text{ mg/cm}^2$ Ir at the anode:  $0.15 \text{ mg/cm}^2$ Equilbrium potential at 80°C: 1.18 VCalculate at  $1.4 \text{ A/cm}^2$  (65% efficiency) Annual Pt production =  $2 \times 10^8 \text{ g}^{14}$ Annual Ir production =9 x  $10^6 \text{ g}^{14}$ 

Power stored:  $P_{stored} = 1.18 \times 1.4 = 1.65 \text{ Wcm}^{-2}$ 

Total Precious metal:  $Pt_{cathode} + Pt_{anode} + Ir_{anode} = 0.35 \text{ mg cm}^{-2}$ 

Total Precious metal requirement:  $0.35/1.65 = 0.21 \text{ g kW}^{-1}$ 

Total precious metal / TW of hydrogen storage capacity: 2.1  $\times$  10<sup>8</sup> g

Total Pt / TW =  $2.1 \times 10^8 \times \frac{0.2}{0.35} = 1 \times 10^8$  g, which corresponds to 0.5 year of Pt annual production

Total Ir/ TW =  $2.1 \times 10^8 \times \frac{0.15}{0.35} = 9 \times 10^7$  g, which corresponds to 10 years of Ir annual production

The  $RuO_2$  nanoparticles presented in this work shows a 30-fold improvement in mass activity compared to PtIr. If we could reproduce such an improvement in a real electrolyzer, we could decrease the precious metal loading of at least one order of magnitude. By doing a similar calculation as above and considering that the annual Ru production is higher than Ir  $(2.5 \ 10^7 \ g)^{14}$  we find that the amount of Ru required per TW of hydrogen storage capacity would constitute less than half a year of the annual production.

# Specific activity

The specific activity was evaluated for  $0.1 \ 10^6$  u RuO<sub>2</sub> nanoparticles, which shows spherical shape, by normalizing the current with the surface area of ruthenium. The surface area was calculated form the deposition cluster current as follows:

$$A_{dep} = A_p I_{dep} t_{dep} n_p$$

Where  $A_p$  is the projected area of the single particle,  $I_{dep}$  is the the deposition current,  $t_{dep}$ , is the deposition time and  $n_p$  is the number of particles per Coulomb. In Figure S8 the specific activity of 0.1 10<sup>6</sup> u RuO<sub>2</sub> is compared with the work by Shao-Horn and co-workers. In their investigations, they evaluated the specific activity of RuO<sub>2</sub> nanoparticles and RuO<sub>2</sub> thin films, estimating the surface area of the catalysts.



**Figure S8.** Comparison of the specific activity of  $0.1 \ 10^6$  u RuO<sub>2</sub> NPs from this work with RuO<sub>2</sub> (100) film from ref <sup>15</sup> and RuO<sub>2</sub> NPs from ref <sup>16</sup>.

### **Turnover Frequency (TOF)**

Turnover frequency (TOF) was calculated in two ways:

 TOF<sub>min</sub> represents the lower bound and it was estimated from the mass activity, using the following formula:

$$TOF_{min} = \frac{J M W_{RuO_2}}{n_{e-} N_A e^-}$$

Where J is the mass activity in A/g,  $MW_{RuO_2}$  is the molecular weight,  $n_{e-}$  is the numbers of electrons involved in the reaction (4 electrons),  $N_A$  is the Avogadro's number and  $e^-$  is the charge of the electron.

 TOF<sub>max</sub> represents the upper bound and it was estimated from the specific activity, using the following formula:

$$TOF_{max} = \frac{J MW_{RuO_2}}{h_{ML} d n_{e-} N_A e^{-1}}$$

Where J is the specific activity in A/cm<sup>2</sup>,  $MW_{RuO_2}$  is the molecular weight,  $h_{ML}$  is the height of a monolayer, d is the density,  $n_{e-}$  is the numbers of electrons involved in the reaction (4 electrons),  $N_A$  is the Avogadro's number and  $e^-$  is the charge of the electron.

# Coverage on Au(111) electrode



Figure S9. Comparison of 2.9  $10^6$  u thermally oxidized RuO<sub>2</sub> coverage on Au(111) disk, calculated with the neutralization cluster current and using the capacitance measured with electrochemical impedance spectroscopy.

# **Stability measurements**

# **Chronoamperometry and Inductively Coupled Plasma – Mass Spectrometer**

The ruthenium dissolved into the electrolyte was measured ex-situ by ICP-MS at the end of the chronoamperometrical test. A performance check and calibration were performed prior to each experiment.



**Figure S10.** Chronoamperometry at 1.5 V (vs. RHE) in  $N_2$  saturated electrolyte at 1600 rpm for 2.9  $10^6$  u (a) as-deposited Ru and (b) thermally oxidized RuO<sub>2</sub> nanoparticles.



**Figure S11.** Ruthenium dissolution percentage relative to the initial mass loading, evaluated from the deposition cluster current, after 20 minutes of chronoamperometry for the metallic nanoparticles and 15 hours for the oxide.



**Figure S12.** Comparison of OER mass activities extrapolated from Chronoamperometry at 1.5 V (vs. RHE) after 5 seconds (to avoid the initial charging current) and after 1 hour for 0.1, 0.5, 1.4 and 2.9  $10^6$  u thermally oxidized RuO<sub>2</sub> nanoparticles

### **Electrochemical Scanning Tunneling Microscope characterisation**

The EC-STM images were acquired using a custom-build EC-STM setup, which is described in detail elsewhere<sup>17</sup>. Tunneling tips were prepared by electrochemical etching of a 0.25 mm Pr/Ir (90/10) wire and subsequently coated with commercial hot-glue. All STM images were recorded in constant current mode and under a protective gas atmosphere of argon (scientific quality, 6.0). A Pt wire served as a Pt/PtO pseudo reference electrode, for calibration against RHE the potential of the well-known "butterfly"-peaks of the order/disorder transition of sulfate on Au(111) was used<sup>18</sup>. The potential stability and accuracy of this pseudo reference electrode amounts to  $\pm 25$  mV. A 0.05 M H<sub>2</sub>SO<sub>4</sub> solution was used as electrolyte, which was deaerated prior to measurements with argon (scientific quality, 6.0).

Potentiodynamic STM images were obtained by sweeping the working electrode's potential with a linear ramp of 2 mV s<sup>-1</sup> while acquiring a STM image. Before and after acquisition of each potentiodynamic image, STM images under constant potential conditions were recorded at the same place (Fig. S13), allowing to distinguish between a local inhomogeneity of the particle distribution and the corrosion reaction.

The appearance of the particles in STM images is heavily influenced by the shape of the tunneling tip and does not reflect their actual shape. However, this tip-convolution effect does not affect the qualitatively observed stability of the Ru and RuO<sub>2</sub> particles under certain potential conditions; consequently we choose to neglect it in the discussion.



**Figure S13.** STM images recorded before (a,c) and after (b,d) the potentiodynamic STM images in the manuscript. a), b) 0.001 ML Ru particles (3 nm): (520 nm)2, E = 1277 mV, UB=-299 mV, IT=1 nA; c), d) 0.001 ML RuO<sub>2</sub> particles (3 nm): (516 nm)2, E = 1277 mV, UB=-245 mV, IT=1 nA.

#### Determination of Oxygen concentration and Faradaic efficiency

The Faradaic efficiency of  $RuO_2$  nanoparticles was measured using gas chromatography in an H-type electrochemical cell. The cell was purged using He to remove air from the electrolyte and headspace before the beginning of the experiment. The complete removal of air was verified using the gas chromatograph. The system was subsequently kept under closed circulation loop condition by using a pump. The gas present in the headspace was sampled during the experiment every 10 minutes using an automated injection valve for determination of the gas composition.



**Figure S14.** Oxygen evolution directly measured with a Gas Chromatograph in a He saturated H-cell and compared with the oxygen evaluated from the charge.



Figure S15. Faradaic efficiency as a function of time.

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