Supplementary Information (SI) for EES Catalysis.

Supporting Information

On the Growth and Water Oxidation Stability of Hydrous Iridium Oxide

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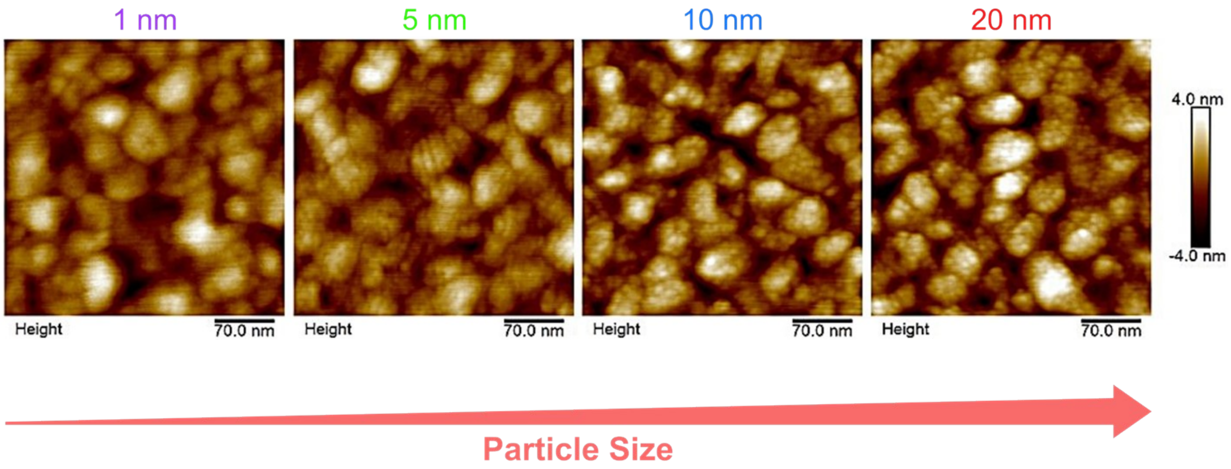


Figure S1. AFM images of Ir thin films with varying thicknesses.

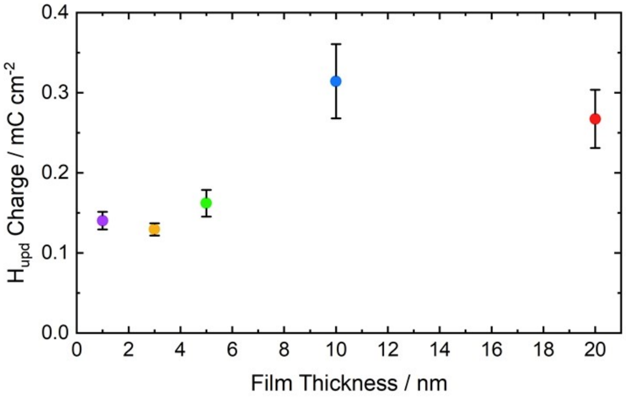


Figure S2. H_{upd} charge (0.04 – 0.4 V_{RHE}) estimated at the 3rd cycle depending on the nominal film thickness.

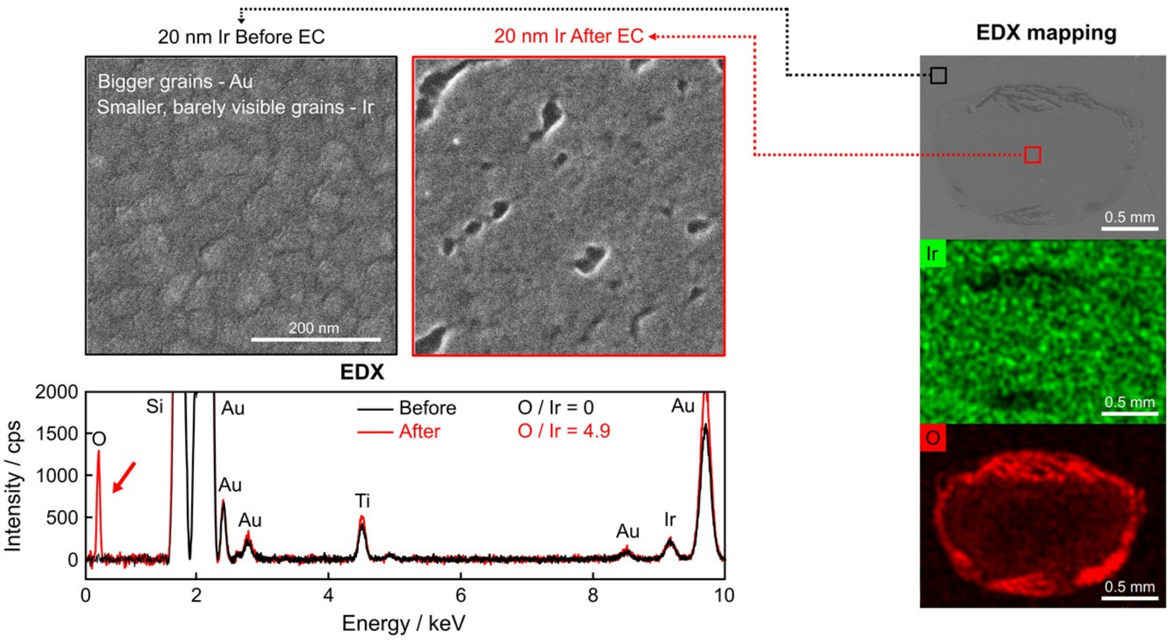


Figure S3. SEM and EDX characterization of 20 nm thick metallic Ir film, before and after applying electrochemical protocol.

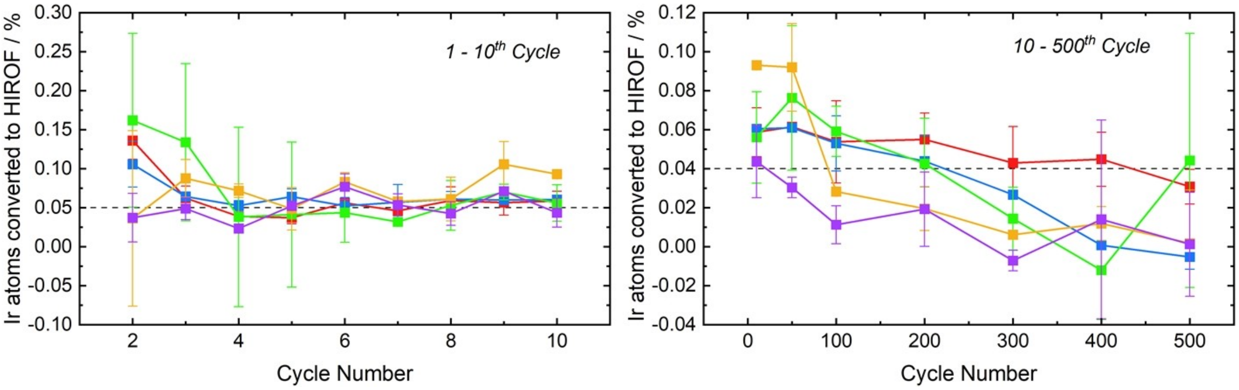
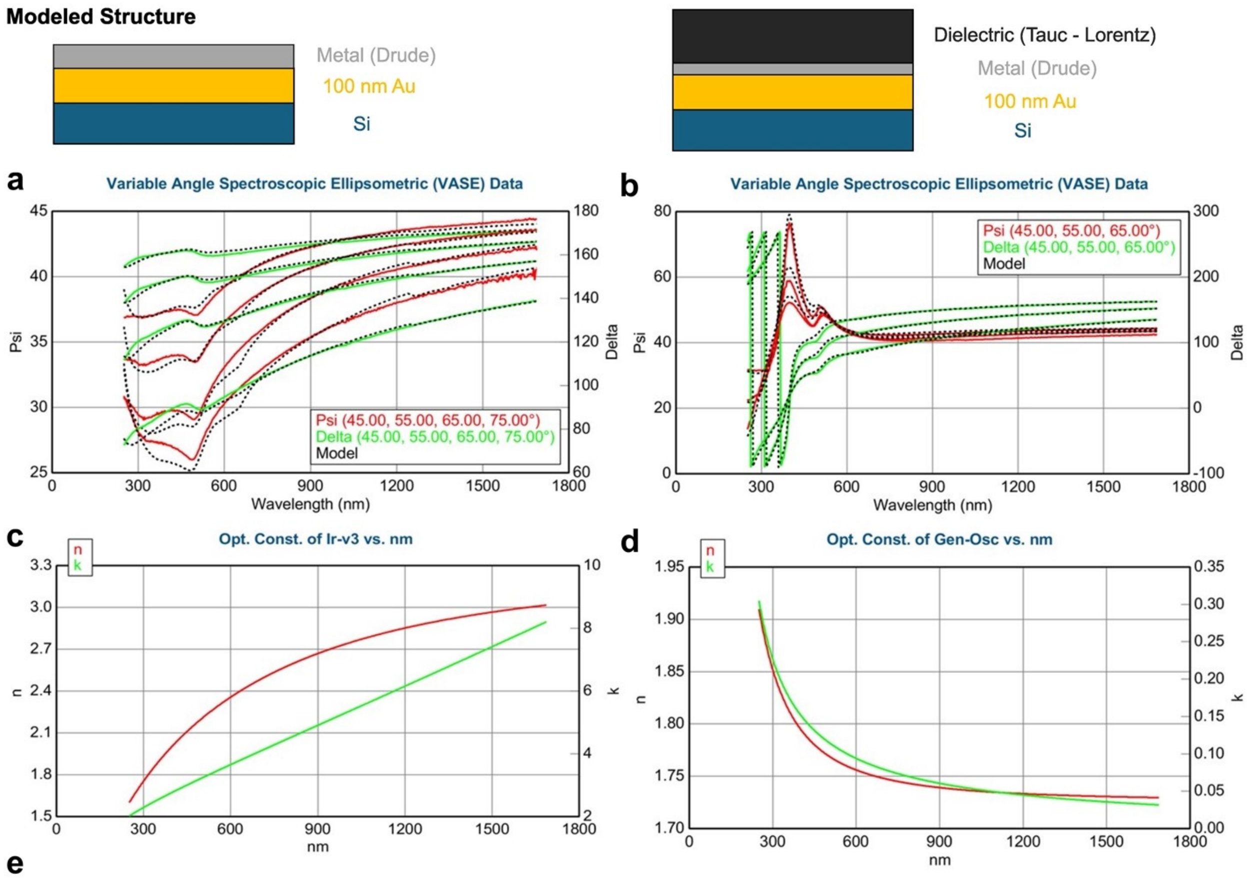


Figure S4. Percentage of Ir surface atoms converted to HIROF per cycle. The conversion was estimated by subtracting the total anodic charge of each cycle from the previous cycle, and dividing by the charge corresponding to 1 electron per Ir atom at the metal surface, as described in ref. [1]



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Aimed Sputtering Thickness	Thickness of Metallic Iridium	Thickness of HIROF
Before EC		
20 nm	19.79 nm	0.00 nm
10 nm	9.29 nm	0.00 nm
5 nm	6.61 nm	0.00 nm
3 nm	3.86 nm	0.00 nm
1 nm	1.69 nm	0.00 nm
After EC		
20 nm	6.83 nm	45.31 nm
10 nm	3.73 nm	45.15 nm
5 nm	1.05 nm	14.43 nm
3 nm	2.25 nm	1.48 nm
1 nm	0.13 nm	2.41 nm

Figure S5. Example of ellipsometry measurements for a 20 nm metallic iridium thin film sample: a) before and b) after the electrochemical protocol. c) Refractive index (n) and extinction coefficient (k) based on the Drude model for the reference iridium samples. d) n and k values obtained using the Tauc-Lorentz model for the hydrous iridium oxide. e) Thickness of the metallic Ir film and hydrous oxide before and after the electrochemical protocol, as measured by ellipsometry.

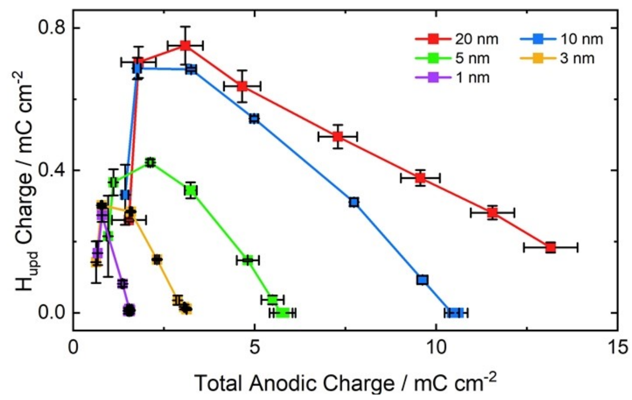

Figure S6. Relation between total anodic charge (0.4 – 1.3 V_{RHE}) and H_{upd} charge (0.04 – 0.4 V_{RHE}) during 500 cycles (0.04 – 1.4 V_{RHE}, 500 mV s^{-1}) across various nominal thicknesses of metallic Ir films.

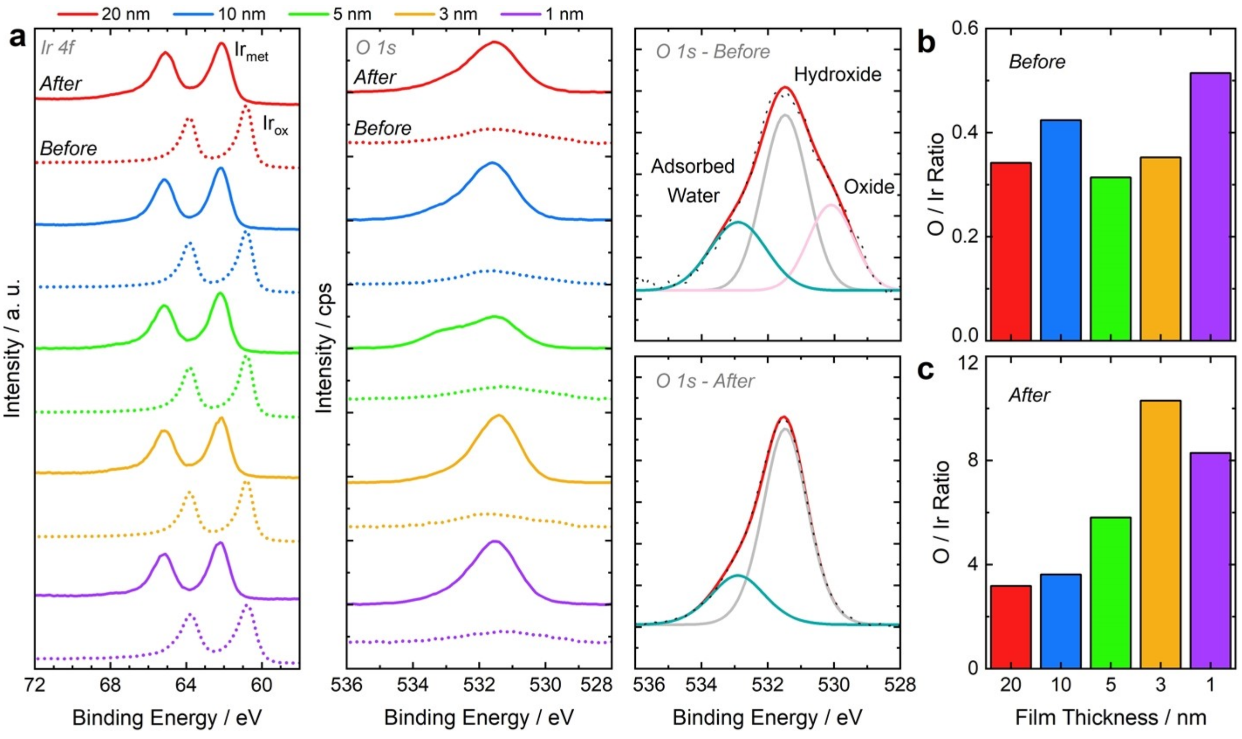

Figure S7. XPS analysis of metallic Ir films before and after the EC protocol. a) Ir 4f spectra (normalized to highest intensity) and O 1s spectra (not normalized), shown before and after the EC protocol, including an example of O 1s peak fitting (normalized to highest intensity). b) O / Ir ratio prior to the EC protocol. c) O / Ir ratio after the EC protocol. Ratios were calculated by integrating the areas under the Ir 4f and O 1s peaks.

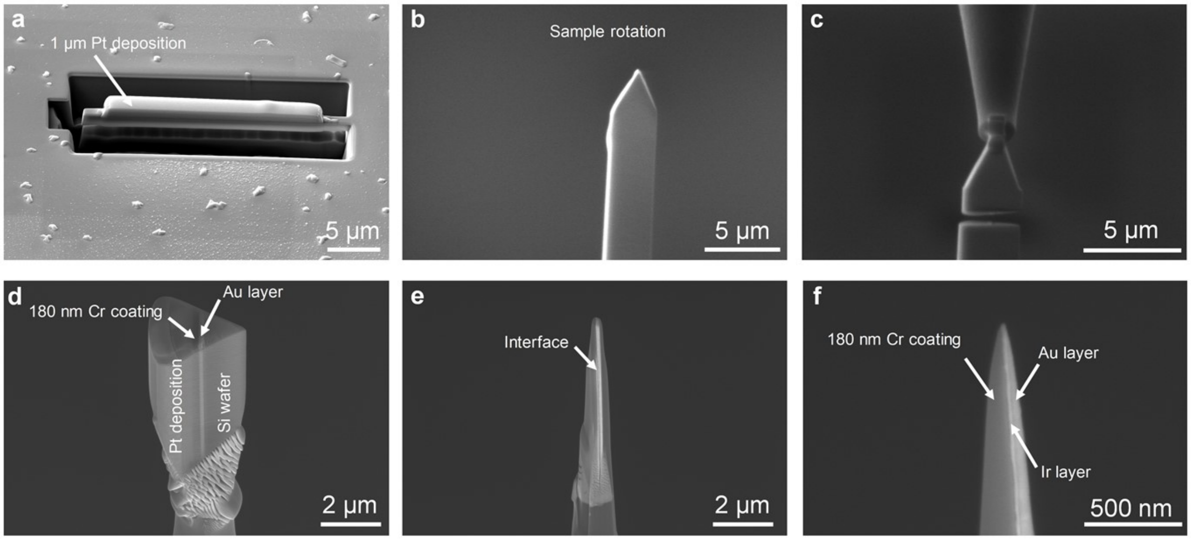

Figure S8. APT Sample preparation. a) Local Pt deposition on liftout region. b) Rotation of the liftout sample to align the interface vertically. c - d) Vertical liftout welded to a Si microtip. e - f) Annular milling of the sample with the Ir layer in the center of the tip.

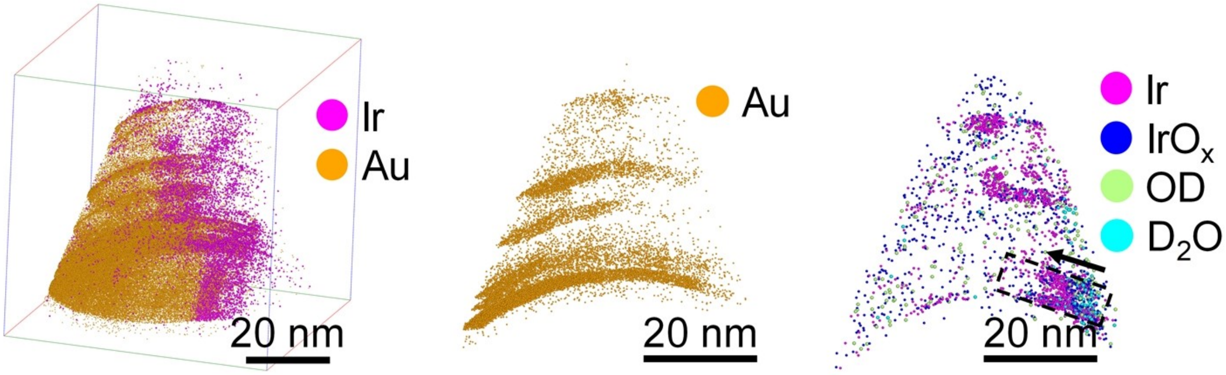

Figure S9. 3D-APT tip reconstruction of a 2 nm thick film after 500 cycles.

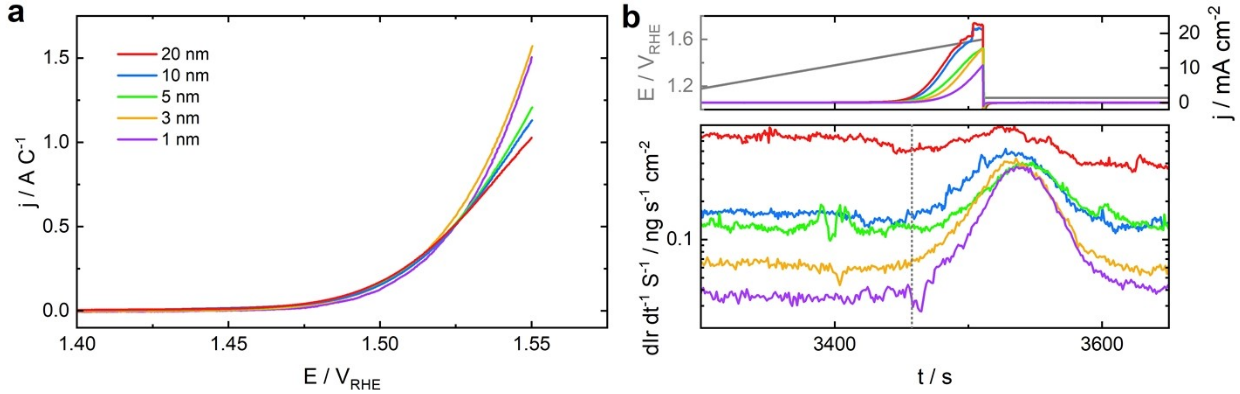

Figure S10. a) Total anodic charge-normalized LSV of HIROF, performed in the potential range of 1.2 – 1.6 V_{RHE} at 2 mV s^{-1}. b) OER onset potentials (top) and dissolution onset potentials (bottom).

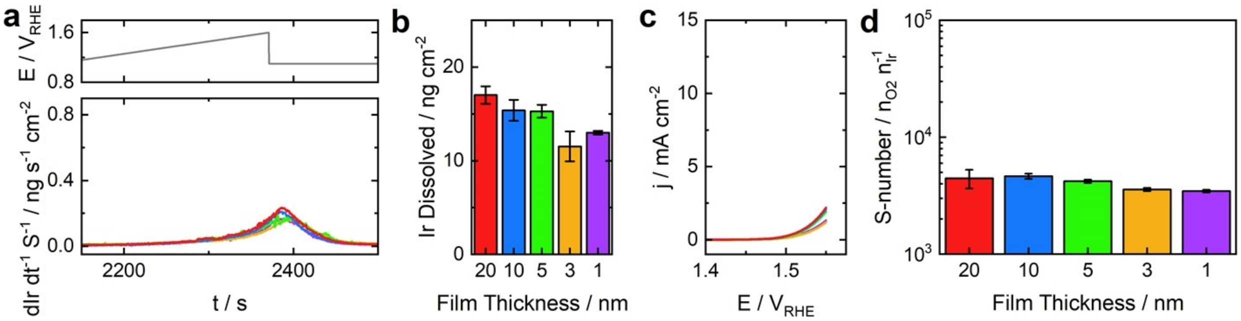

Figure S11. Activity and stability of metallic iridium films during OER: a) Applied potentials (top) and corresponding dissolution profiles (bottom) measured by SFC-ICP-MS. b) Amount of iridium dissolved during LSV, estimated by integrating dissolution profiles from a). c) Surface area-normalized LSV, performed in the potential range of 1.2 – 1.6 V_{RHE} at 2 mV s^{-1}. d) Stability numbers, calculated based on the dissolution data from b) and charge integrated from c).

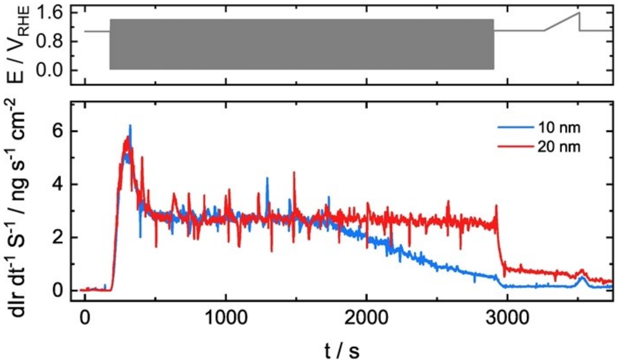

Figure S12. Iridium dissolution during the whole applied electrochemical protocol: (a) Applied potential (top) and corresponding dissolution profiles measured by SFC-ICP-MS (bottom).

1. Calculation of Theoretical Loadings of Thin Films

Total volume of the measured spot is given by:

$$V_{spot} = A \times d$$

where:

- A is the spot area $(r_{spot}^2 \times \pi)$, calculated as 0.01 cm^2
- d represents the film thickness (1, 3, 5, 10, 20 nm)

The theoretical mass of Ir in the measured spot is:

$$m_{Ir} = \rho \times V_{spot}$$

where:

- ρ is the density of metallic Ir $(22.56\ g\ cm^{-3})$

2. Estimation of Charge if All Theoretical Ir Undergoes Ir^{III} ↔ Ir^{IV} Transition

The number of moles of Ir in the spot is given by:

$$n_{Ir} = \frac{m_{Ir}}{M_{Ir}}$$

where:

- M_{Ir} is the molar mass of Ir $(192.22\ g\ mol^{-1})$

The theoretical charge if all Ir undergoes the $Ir^{III} \leftrightarrow Ir^{IV}$ transition:

$$Q_{theor} = n_{Ir} \times z \times F$$

where:

- $z = 1$ (electrons transferred per Ir atom)
- F is the Faraday constant $(96485\ mol\ C^{-1})$

The fraction of Ir oxidized during cycling is:

$$\%_{Ir^{III} \rightarrow Ir^{IV}} = \frac{Q_{exp}}{Q_{theor}}$$

where Q_{exp} is obtained by integrating anodic charge from Figure 2b over 0.4 – 1.3 V_{RHE}

3. Quantification of Ir Surface Atoms Converted to HIROF per Cycle

The roughness factor R_f is calculated using:

$$R_f = \frac{Q\ (H_{UPD})}{(220\ \mu C\ cm^{-2} \times 0.65)}$$

where:

- $Q\ (H_{UPD})$ is obtained from CV integration (Figure 2b) over 0.04 – 0.4 V_{RHE}
- $220\ \mu C\ cm^{-2}$ is the charge corresponding to a monolayer coverage of hydrogen on Pt
- A correction factor 0.65 is applied due to lower hydrogen coverage on Ir compared to Pt

The real surface area of the thin films is given by:

$$A_{real} = R_f \times A_{geometric}$$

The number of Ir atoms converted to HIROF per cycle is calculated as:

$$N = \frac{\Delta Q_{anodic}}{(0.218\ mC\ cm^{-2} \times 1.2\ )}$$

where:

- ΔQ_{anodic} is anodic charge difference per cycle (Figure 2b, 0.4 – 1.3 V_{RHE}), normalized by real surface area
- $0.218\ mC\ cm^{-2}$ corresponds to one-electron transfer per Ir atom on the surface

- 1.2 accounts for the fraction of Ir sites oxidized to Ir^{IV} at 1.3 V_{RHE} (determined by chemical analysis)

4. Determination of Estimating the thickness of formed HIROF

The number of moles of HIROF formed is:

$$n_{HIROF} = \frac{Q_{exp}}{zF}$$

where Q_{exp} is obtained by integrating anodic charge from Figure 2b over 0.4 – 1.3 V_{RHE}

The HIROF thickness is estimated using:

$$d_{HIROF} = \frac{V_{HIROF}}{A_{spot}} = \frac{(n_{HIROF} \times M_{HIROF})}{(\rho_{HIROF} \times A_{spot})}$$

where:

- $A_{spot} = 0.01\ cm^2$
- ρ_{HIROF} is estimated density of HIROF $(2\ g\ cm^{-3})$
- $M_{HIROF} = 208.2\ g\ mol^{-1}$

5. Calculation of Cycles Required for Complete HIROF Conversion

The total number of Ir atoms in a nanoparticle is given by:

$$N_{total} = \frac{V_{particle} \times \rho_{Ir} \times N_A}{M_{Ir}}$$

where:

- $V_{particle}$ is the volume of a nanoparticle
- $N_A = 6.022 \times 10^{23}\ mol^{-1}$

Assuming spherical nanoparticles which size correspond to Ir film thickness:

$$V_{particle} = \frac{4}{3}\pi r^3$$

The number of surface atoms (assuming FCC {111} plane) is:

$$N_{surface} = A_{nanoparticle} \times PD\ (planar\ density) = 4\pi r_{nanoparticle}^{2} \times \frac{4}{\sqrt{3}a^2}$$

Where a is the lattice parameter of Ir

Each conversion cycle converts approximately 5% of the surface Ir atoms into HIROF (see Supporting Calculation 3). Hence, the number of Ir atoms converted per cycle is:

$$N_{HIROF/cycle} = N_{surface} \times 0.05$$

Therefore, the total number of cycles needed for complete conversion to HIROF is:

$$N_{cycles} = \frac{N_{total}}{N_{HIROF/cycle}}$$

5.1. Adjustments for Hemispherical Particles

If the nanoparticles are hemispherical rather than spherical, both the total number of atoms and the surface atoms must be adjusted accordingly

A hemisphere has half the volume of a sphere of the same radius. Therefore:

$$N_{total,\ hemisphere} = \frac{1}{2} N_{total}$$

The total surface area of a hemisphere (including the flat base) is $3\pi r^2$, which is three-quarters the surface area of a full sphere $4\pi r^2$. Consequently:

$$N_{surface,\ hemisphere} = N_{surface} \times \frac{3}{4}$$

These corrections can be substituted into the above equations for N_{total} and $N_{surface}$ when calculating $N_{HIROF/cycle}$ and N_{cycles} for hemispherical nanoparticles.

References:

(1) Pickup, P. G.; Birss, V. I. A model for anodic hydrous oxide growth at iridium. *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry* **1987**, *220* (1), 83-100. DOI: https://doi.org/10.1016/0022-0728(87)88006-3.