Supporting Information

Direct Detection of Surface Species Formed on Iridium Electrocatalysts during the Oxygen Evolution Reaction

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1. Experimental Procedures

The APT specimens were prepared by electropolishing of Ir in the form of as-drawn wires (0.15 mm in diameter, purchased from Goodfellow) in a chemical solution of one part of saturated CaCl$_2$ and two parts of deionized water. The surfaces of the APT specimens were subsequently cleaned of residual oxides by field evaporation in APT and HCl before being exposed to electrochemical treatments.

The size and morphology of Ir APT specimens were first recorded in a JEOL JSM-7200F scanning electron microscope (SEM). Next the surface area of the iridium APT tips were measured by chronoamperometric measurements which were in solutions of 5 mM K$_4$Fe(CN)$_6$ (with a purity of $\geq$99 % from Sigma-Aldrich) and 100 mM KCl (purity of $>99 \%$, Sigma-Aldrich) at a potential of 0.4 V versus a Ag/AgCl 3 M KCl reference electrode. The immersion depth was approximately 500 $\mu$m into the electrolyte solution. A micrometer-screw (Helios) was used for vertical movement of electrodes. The wires were approached to the electrolyte surface until a sudden shift of the open circuit potential was observed. This electrical contact served as a reference point, from which the electrode was immersed by 500 $\mu$m. Afterward, the electrochemical oxides were grown on the iridium APT tips by chronoamperometric measurements at 1.55 V (1.28 V$_{Ag/AgCl}$) for 60, 180 and 300 seconds in a solution of 0.1 M DCIO$_4$ prepared by dilution of a concentrated acid (68 wt% in D$_2$O, Sigma-Aldrich) in D$_2$O. Pt wires (Forschungsbedarf GmbH) with a thickness of 500 $\mu$m and a purity of 99.9 % were used as counter electrodes (CE) and a Ag/AgCl (3 M KCl, equipped with a double junction to prevent electrolyte contamination) was used as a reference electrode (RE). Conversion to the reversible hydrogen electrode scale can be done via: $E_{RHE} = E_{Ag/AgCl} + 0.197 + 0.0592 \, pH$.

All electrochemical measurements were performed using a PalmSens 3 (PalmSens BV) potentiostat. All potentials reported are referred to the reversible hydrogen electrode (RHE) potential, which was separately measured on each day of an experiment.

After the electrochemical treatments, the electronic state of the top $\sim$100 $\mu$m of Ir APT tips after anodic oxidation for 60 s and 300 s at 1.55 V was analyzed in X-ray photoelectron spectroscopy. XPS measurements were performed on VersaProbe II by Ulvac-Phi by applying a monochromatic Al X-ray source (1486.6 eV) operating at 15 kV and 13.2 W. The binding energy scale was referenced to the metallic Ir4f signal at 60.9 eV. Analysis of the spectra was carried out with the software CasaXPS.

The Ir APT specimens after anodic polarization at 1.1 V for 300 s and 1.55 V vs RHE (OER conditions) for 60 s, 180 s and 300 s were characterized by a Cameca LEAP 5000XR instrument under voltage pulsing mode at a specimen temperature of 60 K with a pulse energy of 30 pJ, target evaporation rate of 3 ions per 1000 pulses, and pulse rate of 125 kHz. The APT data was reconstructed and analyzed using the commercial IVAS 3.8.4 software.
2. Simulation of nanoelectrodes

The model for simulation of electrode dimensions was built in the commercial finite element software COMSOL Multiphysics®, where the transport of diluted species module was employed. The program was run on a personal computer with an AMD Ryzen Threadripper 1920X (Advanced Micro Devices) CPU, a GeForce GTX 1080 Windforce OC 8GB GDDR5 (Nvidia Corporation) graphic card, 64 GB DDR4 RAM and was installed on a Samsung SSD PRO Series 256 GB (Samsung Electronics Co., Ltd.).

The model was built in two dimensions, taking advantage of the symmetry axis of conical electrodes. Typical model geometries and mesh structures are shown in Figure S1. Custom mesh refinement was used to grant sufficient mesh densities at regions of high gradients.

![Figure S1](image)

Figure S1 a). The blue line denotes the electrode surface of a tip immersed into solution. b) The blue line marks the outer boundary, where the solution has bulk concentrations.

The simulation conditions are summarized in Table S1, where electrode corresponds to the boundary highlighted in Figure S1a and bulk corresponds to the one highlighted in Figure S1b.
Table S1. Conditions for simulations are shown. The concentration of ferrocyanide is denoted by \( c \), bulk concentration by \( c_0 \) and the net flux through a boundary by \( j \).

| Time parameters | Space parameters | Condition |
|-----------------|-----------------|-----------|
| \( t > 0 \)     | \( r = 0 \)     | \( j = 0 \) |
| \( z = 500 \mu m \) | electrode       | \( c = 0 \) |
| bulk            | \( c = c_0 \)   |
| \( t = 0 \)     | All \( r, z \)  | \( c = c_0 \) |

The individual error of the immersion procedure was determined with one iridium tip electrode, which was immersed and retracted five times, while two chronoamperograms were recorded at each immersion. One representative curve of each immersion is presented in Figure S2a. The exemplary fit of the first chronoamperogram is shown in Figure S2b, which corresponds to an immersion depth of 475 \( \mu m \) and an exposed surface area of 2.49E-8 m\(^2\).

Figure S2 a): One chronoamperogram for each retraction immersion cycle is presented, and b) the fit to the chronoamperogram of the first immersion cycle.

Analytical solutions were not possible since convection induced the establishment of quasi-steady-state currents and prohibited the development of purely diffusional steady-state currents during experiments (Figure 1c). Since the experimental setup was prone to convection effects, only the first ten seconds of each chronoamperograms were used for fits. The standard deviation of the mean surface area was 7.4 % within five immersion cycles. The effective surface area was decreasing with an average of 4.8 % each cycle, which indicates a deactivation of the tips with each retraction and immersion cycle. Since the total number of those cycles was highest in the control experiment, a standard deviation of below eight percent can be safely used as a representative error.
3. XPS on APT tip

Figure S3. (a-b) Secondary x-ray induced electron images of two Ir tips recorded in XPS, and XPS of (c-d) Ir 4f level from the top 20 µm region and their fitting curves (marked by the blue circles in (a-b)) of APT samples treated for 60 s and 300 s at 1.55 V (the quantification error can be ~10% [1].
4. APT

Table S2. Image compression factor (ICF), field factor (Kf) and tip radius of the APT reconstruction shown in Figure 3a (60s), Figure 3d (180s), and Figure 3g (300s) calibrated by the procedure mentioned in Ref [2].

| APT reconstruction at various conditions | ICF  | Kf  | Radius (nm) |
|----------------------------------------|------|-----|-------------|
| 60 s (Figure 3a)                       | 1.65 | 3.75| 33          |
| 180 s (Figure 3d)                      | 1.43 | 3.9 | 45          |
| 300 s (Figure 3g)                      | 1.35 | 3.1 | 33          |
Figure S4. a) field ion microscopy image of Pt (taken from Ref. [3] with permission) overlapped with circular rings that delineate the terraces of high-indexed planes (open planes marked by green circles and closed planes marked by blue circles) and terrace edges of (002) planes (in yellow-shaded ring pattern), b) atom map (top-down view) in Figure 2g overlayed with the circular-ring pattern, (c-d) atom maps in Figure 3d, e, g overlayed with circular-ring patterns in a) demonstrating the regions of high-indexed terraces and terrace edges of (002) plane. Figures S4c-e suggests that OER occurs dominantly on the high-indexed planes and partly on the terrace edges of the high-indexed planes.
Figure S5. Cross-sectional atom maps selected from the regions shown in the top-down views in (a-c) for the samples treated after anodic oxidation for (d-f) 60 s, (g-k) 180 s and (l-n) 300 s at 1.55 V. The regions with the white arrows in (d-n) are cropped and shown in Figure 3j-z, and 1D concentration profiles in Figure 4 and Figure S6 are plotted along these white arrows.
Figure S6. 1D concentration profiles along the (002), (026), (115) and (220) and (111) planes in Figure 3j-k, n-p, s-w, z) respectively (plotted along the white arrows marked in Figure S5d-e, g-k, l-m.

Table S3. Coverage of IrO-OH on the topmost surface layer Ir after anodic oxidation at 1.55 V vs RHE for 60 s (estimated by the ratio of IrO:Ir on the topmost atomic layer), and Gibbsian surface excess $\Gamma$ of oxygen, in atoms per nm$^2$ in the oxide layers [4] (for the (024) plane both surface and near-surface regions are included).

|               | (002) | (026) | (024) | (113) | (115) |
|---------------|-------|-------|-------|-------|-------|
| IrO-OH coverage on the topmost surface layer (%) | ~0.4% | ~12.0% | ~3.6% | ~18.2% | ~7.4% |
| $\Gamma$ (atoms/nm$^2$) | ~0.21 | ~3.7  | ~5.4  | ~4.8  | ~2.7  |
Figure S7. Mass spectra of the oxides grew on the (024) and (113) planes after anodic polarisation at 1.55 V for (a-c) 60 s, (d-f) 180 s and (g-i) 300 s. The mass spectra was selected locally from the topmost 1-2 nm surface and sub-surface oxide along (024) and the surface oxide on (113), as illustrated by the black circles shown in Figure S5f, d, g, n.

References

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[2] B. Gault, D. Haley, F. de Geuser, M. P. Moody, E. A. Marquis, D. J. Larson, B. P. Geiser, Ultramicroscopy 111 (2011) 448-457.
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[4] P. Felfer, A. Ceguerra, S. Ringer, J. Cairney, Ultramicroscopy 132 (2013) 100-106.