Supporting Information

Atomically-dispersed Iridium on Indium Tin Oxide Efficiently Catalyzes Water Oxidation

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Materials and methods

Grafting of dimeric [(COD)Ir(OMe)]2 (COD - cyclooctadiene)1-2 on porous ITO electrodes was performed under inert conditions according to the following procedure: 2 mM solution of [(COD)Ir(OMe)]2 in heptane (air and water free) was added to porous ITO electrodes (1.5 cm² of ITO each) in the petri dish in the glovebox. The petri dish was sealed with parafilm to avoid heptane evaporation and left overnight. The electrodes were washed three times with heptane and subsequently calcined at 400 °C for 1 hour (with the ramp of 60 °C / hour).

Electrochemical measurements were performed in a standard single-compartment 3-electrode cell using PGSTAT128N Autolab potentiostat. The porous ITO electrodes were electrically contacted using the uncoated FTO layer and masked to a geometrical surface area of 0.8 – 1.2 cm² using non-conductive epoxy (see Figure S13b). A piece of a platinum mesh served as the counter electrode and saturated Ag/AgCl electrode served as the reference electrode. 0.1 M HClO4 or 0.1 M acetate buffer (the latter with total ionic strength adjusted to 0.5 M with NaClO4) were used as electrolytes and were saturated with Ar prior to the measurements. Cyclic voltammograms (CVs) were recorded in the potential range of 0.46 – 1.56 V at 10-50 mV s⁻¹. Electrochemical impedance spectroscopy measurements were recorded at 1.46 V vs RHE with an amplitude of 10 mV in the range of 10 kHz to 10 mHz. Electrochemical impedance spectroscopy data (Nyquist plot) were fitted using the equivalent circuit consisting of resistor (solution ohmic drop) in series with parallel resistor (charge transfer) and constant phase element:

To measure OER activity of Ir SAC–ITO we performed linear sweep voltammetry (10 mV s⁻¹) as well as chronoamperometric measurements in 0.1 M HClO4. Polarization curves were obtained from the steady-state chronoamperometric measurements: the potential was gradually stepped from 1.41 to 1.53 V vs RHE (with 25 mV steps) while holding for 1 min at each potential. Average of the last 10 s of the current for each potential step and solution ohmic drop corrected potentials were used for Tafel plot construction (Figure S16b). Stability measurements were performed in 0.1 M HClO4 by switching the potentiostat into the galvanostatic mode and maintaining of 0.5 mA cm⁻² or 10 mA cm⁻² current (chronopotentiometry) for three or two hours respectively. Both vigorous stirring and argon bubbling of electrolyte were used for chronoamperometric and chronopotentiometric measurements. Turnover number (TON) was calculated as:

$$\text{TON} = \frac{I t}{4 F N_{Ir}}$$

where I is current in [A], t is time in [s], F is Faraday constant in [C mol⁻¹], N_{Ir} is Ir loading in [mol], and 4 accounts for 4 electrons required to make one O₂ molecule.

Faraday efficiency measurements (Figure S15) were performed in 0.1 M HClO4 with the oxygen detected via Clark electrode sensor in the gas phase. The air-tight electrolysis cell was equipped with a gas inlet (bubbling through electrolyte) and the outlet (from the head space). A constant flow of N₂ at a rate of 5 mL min⁻¹ was passed through the cell over the whole period of the experiment (approx. 7 hours) and the gas at the outlet was constantly analyzed using the O₂ sensor. After approx. 3 h of cell degassing, the current of
7.5 mA cm\(^{-2}\) was applied for 2 h (chronopotentiometry), corresponding to the \(O_2\) flow of 0.04 mL min\(^{-1}\) (which is set to the Faraday efficiency 1 on Figure S15). Solubility of oxygen in the electrolyte as well as diffusion limitations result in the delay of the detection, however integration of the total \(O_2\) produced results in 99% Faraday efficiency. The electrolyte was subsequently titrated using iodometric titration following well-established protocol\(^3\) producing < 1% of \(H_2O_2\) yield based on the total charge passed.

All reported measurements were repeated several times to ensure the reproducibility of the results. Unless specified otherwise, all the potential values are reported vs reversible hydrogen electrode (RHE) scale. The current expressed as [mA cm\(^{-2}\)] refers to the geometrical surface area of the electrode and [A g Ir\(^{-1}\)] refers to the total mass of Ir on the electrode, determined using the elemental analysis.

**X-ray absorption (XAS)** spectra were collected at the Advanced Photon Source (APS) at Argonne National Laboratory on bending magnet beamline 9. The radiation was monochromatized by a Si (110) crystal. The intensity of the X-rays was monitored by three ion chambers (I\(_0\), I\(_1\) and I\(_2\)) filled with 100% nitrogen. Pt metal foil was placed between the I\(_2\) and I\(_3\), and its absorption was recorded with each scan for energy calibration. The X-ray energy was calibrated by setting the first maximum in the derivative of the Pt metal L\(_3\) -edge XANES spectrum to 11564 eV.

The XAS data were recorded as fluorescence excitation spectra using a 4-element Si drift detector and defocused beam with size 1 x 1 mm. No more than 1 scan was taken at each sample position. The ion-chambers was shielded with lead tape. IrO\(_2\) pellet was used a reference compound and its XAS data were recorded in transmission mode. \textit{Ex situ} XAS was taken for pristine IrSAC–ITO and IrSAC–ITO after 2 hours of electrolysis at 10 mA cm\(^{-2}\) in 0.1 M \(HClO_4\) (Figure S19 – S20). Electrochemical cell (10 mL) with custom design was used for the \textit{in situ} measurements. Ag/AgCl reference electrode and Pt counter electrodes were used in the 3-electrode configuration. Before potential was applied to the electrodes for \textit{in situ} experiments each electrode has been kept in 0.1 M \(HClO_4\) water solution for an about 1 h. In total, about 20 scans were taken at 1.46 vs RHE and averaged to obtain \textit{in situ} EXAFS (Figure S21 - S22). All measurements were performed at room temperature.

EXAFS data were analyzed using the Athena software package.\(^4\) All data were background-corrected, normalized, and deglitched (if necessary), then converted to wave vector space (k-space) and weighted by \(k^3\). k-space data were truncated near zero crossings before Fourier transformation. The Artemis software package was used for curve fitting (Figure S20 - S21). Curve fitting was done using \textit{ab initio} calculated phases and amplitudes from the FEFF8 code\(^5\). These amplitudes and phases were used in the EXAFS equation:

\[
\chi(k) = S^2_0 \sum_j \frac{N_j}{kR_j} f_{\text{eff}}(\pi, k, R_j)e^{-2\sigma_j^2k^2} e^{-2R_j/k} e^{\pi \sigma_j R_j} \sin(2kR_j + \phi_j(k)),
\]

where \(N_j\) is number of atoms in \(j\)\(^{th}\) shell, \(R_j\) is mean distance between absorbing atom and atoms in \(j\)\(^{th}\) shell, \(f_{\text{eff}}\) is calculated amplitude function. The Debye-Waller term \(e^{-2\sigma_j^2k^2}\) accounts for damping due to thermal disorder. The \(e^{-2R_j/k}\) term reflects losses caused by inelastic scattering. \(\lambda_j (k)\) is the electron mean free path, \(\phi_j\) is the calculated phase function, and \(S_0^2\) is the amplitude reduction factor.

This equation was used to fit the experimental Fourier isolated data (q-space) using \(N, R, E_0\) and \(\sigma^2\) as variable parameters. \(S_0^2\) was set to 1. The quality of fit was evaluated by \(R\)-factor (less than 2% denotes a
good fit\(^6\) and the reduced \(\chi^2\) value was used to compare fits as more backscatters are included. A smaller \(\chi^2\) value implies a better fit. See Figure S22 for raw data in \(k\) space and fitting results and Table 1 for parameters of the fits.

**Density Functional Theory (DFT)** calculations were carried out using periodic boundary conditions as implemented in the *Vienna Ab Initio Simulation Package* (VASP) code.\(^7\)\(^-\)\(^8\) All calculations were performed considering the projector augmented wave (PAW) pseudopotentials. Valence electrons were expanded in plane waves with kinetic energy cutoff equal to 500 eV. The chosen functional was the PBE exchange correlation GGA functional.\(^9\) This functional have been largely used for the study of oxygen evolution reaction by a variety of heterogeneous catalysts\(^10\)\(^-\)\(^13\) but it does not properly describe dispersion forces. This has been corrected by adding the Grimme’s (D2) empirical correction.\(^14\) This correction has been recently reported to better reproduce lattice parameters for a larger variety of systems when compared with the D3 one.\(^15\)\(^-\)\(^16\) The energy threshold for the self-consistency of the electron density was set to 10\(^{-5}\) eV and the optimization of the structure was conducted through a conjugate gradient technique, which stops when Hellmann-Feynman forces on all atoms are less than 0.01 eV Å\(^{-1}\). Bulk calculations were performed considering a K-point mesh for the Brillouin Zone (BZ) of (6,6,6) employing the Monkhorst-Pack grid (MP), while slab calculations were performed considering a Monkhorst-Pack K-point mesh of (6,6,1). The cutoff and K-point mesh were calibrated by ensuring the convergence of both cell parameters and cell energies. All calculations involving the monodisperse single-site Ir species onto the surface were performed as spin-polarized. Iridium electron configuration is 6s\(^2\) 5d\(^7\), thus Ir\(^{III}\), Ir\(^{IV}\), Ir\(^{V}\) and Ir\(^{VI}\) pseudo-octahedral complexes present 6, 5, 4 and 3 electrons respectively on the t\(_{2g}\) d orbitals. Therefore, the ground states of Ir\(^{III}\), Ir\(^{IV}\), Ir\(^{V}\) and Ir\(^{VI}\) should be singlet, doublet, triplet and quartet respectively, and this can only be properly described with a spin-polarized formalism.

In these periodic calculations, the isolated Ir centers on ITO have been represented with a slab periodic model of the (111) surface (Figure S23) containing the Ir center coordinated to indium oxide support via three In-\(\mu^2\)-OH-Ir bonds. Tin atoms were omitted in the calculation for simplification as we do not expect that the presence of very few Sn in the model would influence the electronic structure of Ir. The slab models were constructed from the fully optimized unit cell. The slabs were constructed using a 4-layer thickness model, the minimum slab thickness for achieving the convergence of surface energy. The \(c\) value was set to 35 Å ensuring an interlayer distance of at least 21 Å to minimize the interaction between replicas at the (hkl) perpendicular direction. The size of the models was large enough to represent the main properties and atoms positions were fully relaxed. Due to the induced dipolar moment by the addition of the iridium catalyst and high local water coverage onto a non-polar surface, dipolar correction in the z axis has been added.\(^17\)

Addition of the Ir center on the (111) surface was made in two steps. First, we constructed a solvated model of the (111) indium oxide surface without the presence of iridium with a high local water coverage in the area in which the Ir center was subsequently placed. The local water coverage was large enough to represent the solvent around without increasing excessively the number of potential conformations due to the presence of a large number of water molecules. In a second step, Ir center in the form of Ir(OH)\(_3\)(H\(_2\)O)\(_3\) cluster was added on the locally solvated surface, which was followed by three proton transfers from surface In-OH to the OH ligands of iridium. This releases three water molecules and
establishes the new In-µ²-OH-Ir bonds, thus leading to a tris-bound species (Figure 4). Note that additional proton transfer occurs during the optimization between the Ir ligands and the surface as well as between adsorbed water molecules and the In-µ²-OH-Ir bonds. As a consequence, several species for each oxidation state are plausible and they have been explored (Figure S24) at this PBE-D2 level of theory. In total, the initial IrIII complex supported on indium oxide model presents 48 indium, 83 oxygen, one iridium and 19 hydrogen atoms. The IrIV, IrV and IrVI species are thus modeled subtracting one hydrogen atom in a stepwise manner.

The electronic energies for the iridium single site system along the OER were corrected with single point calculations applying an ONIOM like scheme18 with two layers: i) the low level corresponds to the PBE-D2 periodic model computed with VASP and ii) the inner layer corresponds to the (H₂O)(OH)Ir(OH)₂(H₂O) cluster (for the initial Ir(III) species) computed with the highly accurate double-hybrid functional B2GP-PLYP19 as implemented in ORCA.20 The B2GP-PLYP method includes a 36 and 65 percentage of MP2 and HF, respectively. In the molecular calculation, atoms were represented with the split-valence triple-z basis set with polarization def2-TZVP.21 The equation for the electronic energy correction is:

\[
E_{\text{intermediate}} = E_{\text{PBE-D2(full)}} + (E_{\text{PBE-D2(SAC)}} - E_{\text{B2GP-PLYP(SAC)}}),
\]

where the term \(E_{\text{PBE-D2(full)}}\) consists in the electronic energy of the full system using VASP, \(E_{\text{PBE-D2(SAC)}}\) is the electronic energy of the above-mentioned cluster with the same theoretical level as the full VASP intermediate, and finally \(E_{\text{B2GP-PLYP(SAC)}}\) is the electronic energy of the molecular cluster computed using a double-hybrid functional with ORCA DFT code.

The Pourbaix diagram is constructed assuming that the electrochemical reactions are described by a set of supported Ir intermediates without the active participation of the support. For the supported Ir system we chose the species with the highest content of H atoms as reference (GIr(ref)). From these species we proceeded by removing hydrogen atoms to obtain the different species (GIr(i)). This methodology has been used widely in literature.22-23 The change of Gibbs energy results in:

\[
\Delta G_{\text{Ir(i)}}(U, pH) = G_{\text{Ir(i)}} - G_{\text{Ir(ref)}} - n_H\left(\frac{1}{2}G_{H_2} + U + k \cdot pH\right)
\]

Here \(n_H\) is the number of (H⁺ e⁻) transferred to the media as a full electrochemical proton coupled electron transfer (PCET) process. The effect of the bias on all steps involving an electron is included by shifting the energy of these states by (-eU), where \(U\) is the electrode potential. The dependence on the pH is accounted in the \(k\cdot pH\) term, which comes from:

\[
\Delta G(pH) = -k_B T \cdot \ln[H^+] = k \cdot pH
\]

Therefore, we can derive a relation between potential and pH for a wide variety of adsorbates on a supported catalyst in reference to standard condition when \(\Delta G_{\text{Ir(0)}}(U, pH)=0\). The Pourbaix diagram is shown on Figure S25.
The equilibrium potential to produce oxygen by water oxidation is 1.23 eV. Then, the overpotential at (pH=0) is calculated through Gibbs free energy of the potential determinant step (PDS) including the energy barriers associated with the chemical steps.

\[ \eta \text{OER} = \frac{\Delta G_{\text{PDS}}}{e} - 1.23 \text{ (Volts)} \]

Cluster calculations on dimeric species have also been performed to analyze if their formation is consistent with the available experimental data. Similarly to the model used for the high-level calculations in the monomeric species, the cluster includes the first Ir coordination sphere, the models for the Ir(III)-Ir(III) dimer being (H\textsubscript{2}O)\textsubscript{2}(OH)\textsubscript{2}Ir(\mu-OH)Ir(H\textsubscript{2}O)\textsubscript{2}(OH)\textsubscript{2}. Geometry optimizations were performed with B3LYP-D2/def2-TZVP level of theory and the final energies were computed with single point calculations at the B3LYP-D2 geometry with the double-hybrid B2GP-PLYP functional and the same basis sets. Figure S26 summarizes the obtained results.

Oxidation of the Ir(III)-Ir(III) dimer to an Ir(V)-Ir(V) species takes place through four proton coupled electron transfer steps, leading to the formation of the (H\textsubscript{2}O)(OH)\textsubscript{2}(O)Ir(\mu-OH)Ir(H\textsubscript{2}O)(OH)\textsubscript{2}(O) bisoxo species. The first oxidation step requires a potential of 0.49 V and subsequent steps occur at 1.13-1.25 V, which contradicts experimental electrochemical and in situ XAS data. In this context, calculations suggest that it is highly unlikely that iridium dimers are present in the initial catalyst.

We decided to explore the reaction mechanism of this bisoxo species, since Ir clustering is observed experimentally during the stability tests. We considered both the water nucleophilic attack and the oxo-coupling mechanisms. The water nucleophilic attack to the bisoxo Ir(V)-Ir(V) species is thermodynamically accessible with a reaction energy of 0.42 eV (40.5 kJ mol\textsuperscript{-1}). Moreover, the subsequent PCET processes leading to O\textsubscript{2} release and catalyst regeneration show accessible reaction energies at the applied potential. The oxo-coupling reaction mechanism is even more likely thermodynamically and again the computed energy cost for the PCET is consistent with reaction conditions. Thus, the water nucleophilic attack and the oxo-coupling mechanism are competitive pathways at the present level of modeling, the latter being slightly preferred. Overall, calculations suggest that in case of being formed during reaction, dimeric species can be at least as reactive as the monomeric centers without reaching a Ir(VI) species due to the presence of a second oxo group nearby.
**STEM characterization**

**Figure S1.** HAADF-STEM images of blank ITO prior to grafting of [Ir(COD)(IMes)(OH)]. Panels a. – d. show different regions of the sample, all scale bars are 5 nm. Note presence of thin areas of approx. 5 nm diameter, which are intrinsic of ITO and most probably were formed during the flame spray synthesis.
Figure S2. HAADF-STEM images of [Ir(COD)(IMes)(OH)] grafted on ITO. Panels a. – d. show different regions of the sample, all scale bars are 5 nm.
Figure S3. More HAADF-STEM images of Ir\textsubscript{SAC}–ITO. Panels a. – d. show different regions of the sample, all scale bars are 2 nm.
Figure S4. Fourier filtered (periodic component was masked on FT image prior to inverse FT) HAADF-STEM images of pristine ITO (a, c, e) and IrSAC−ITO (b, d, f). All scale bars are 2 nm.
Figure S5. HAADF-STEM images of [[(COD)Ir(OMe)]_2 grafted on ITO and calcined at 400 °C. Panels a. – d. show different regions of the sample, all scale bars are 2 nm.
Figure S6. HAADF-STEM images of IrSAC-ITO after contacting with the 0.1 M HClO₄ for 5 min with the subsequent water washing. Panels a. – d. show different regions of the sample, all scale bars are 2 nm.
Figure S7. HAADF-STEM images of IrSAC–ITO after 10 CV cycles from 0.46 to 1.56 V vs RHE (0.1 M HClO₄), 25 mV s⁻¹. Panels a. – d. show different regions of the sample, all scale bars are 5 nm.
Figure S8. HAADF-STEM images of IrSAC−ITO after activity evaluation test (chronoamperometry from 1.41 to 1.53 V vs RHE with 25 mV steps in 0.1 M HClO₄). Panels a. – d. show different regions of the sample, all scale bars are 2 nm.
Figure S9. HAADF-STEM images of IrSAC-ITO after 3 hours at 0.5 mA cm$^{-2}$. Panels a. – d. show different regions of the sample, all scale bars are 5 nm.
**Figure S10.** HAADF-STEM images of Ir$_{SAC}$–ITO after 2 hours at 10 mA cm$^{-2}$. Panels a. – d. show different regions of the sample, all scale bars are 5 nm.
**Electrochemical characterization**

**Figure S11.** CV studies of IrSAC−ITO in 0.1 M HClO₄ at 25 mV s⁻¹ (a) and 50 mV s⁻¹ (b).

**Figure S12.** CV studies of IrSAC−ITO at pH 1 (0.1 M HClO₄) and pH 4 (0.1 M acetate buffer with total ionic strength adjusted to 0.5 M with NaClO₄) at 10 mV s⁻¹ (a) and corresponding acidic part of Pourbaix diagram of IrSAC−ITO (b). Circles represent the experimental points whereas dotted lines represent theoretical 59 mV (pH unit)⁻¹ slope.
**Figure S13.** Photos of pristine ITO and IrSAC–ITO prior to electrochemical measurements (a) and photo of the IrSAC–ITO electrode prepared for the measurements (b); The copper wire is glued via conducting epoxy (silver) and the electrode is covered with the transparent non-conductive epoxy (scale is in cm). The peak current of the forward IrIV/III redox event as a function of the sweep rate (c). Linear dependence confirms the surface bound nature of the Ir species.

**Figure S14.** CV studies of IrSAC–ITO before and after chronopotentiometric measurement at 10 mA cm⁻² (0.1 M HClO₄, 10 mV s⁻¹); note slight broadening of both redox waves (a). Three-hour chronopotentiometry of IrSAC–ITO at 0.5 mA cm⁻², average overpotential is 255 ± 10 mV (b).
Figure S15. Faraday efficiency measurement of IrSAC−ITO. Prior to the measurement the cell was degassed using the N₂ gas flow of 5 mL min⁻¹, which was kept constant throughout the whole experiment. The current of 7.5 mA cm⁻² was applied for 2 h (vertical dashed lines), which in case of 100% O₂ faraday efficiency corresponds to the O₂ flow of 0.04 mL min⁻¹ (horizontal dashed line). Integration of the curve results in 99% Faraday efficiency. Delays in the oxygen detection are due to O₂ solubility in the electrolyte. Detection of H₂O₂ using iodometric titration gives < 1% H₂O₂ yield based on the total charge passed.

Figure S16. Linear sweep voltammetry (10 mV s⁻¹) (a) and Tafel plot measurements of three different IrSAC−ITO electrodes (b). Average Tafel slope is 46 ± 4 mV dec⁻¹
Table S1. Comparison of OER activity of IrSAC−ITO with literature reports of Ir-based catalysts

| Ref. | Catalyst                                      | Conditions                        | j @ 250 mV overpotential (A gIr⁻¹) | j @ 280 mV overpotential (A gIr⁻¹) | overpotential @ 10 mA cm²geo (mV) |
|------|----------------------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|
| This work | IrSAC−ITO                                    | 0.1 M HClO₄                      | 49 ± 5                            | 156 ± 13                          | 350 ± 20                          |
| 24   | Oxidized [Cp*Ir(pyalc)(OH)] on ITO          | 0.1 M KNO₃ adjusted to pH 2.6 with HNO₃ |                                    | 200                               | 250 - 300                         |
| 25   | InNi NCs supported on carbon *Δ              | 0.1 M HClO₄                     | ~ 200                             |                                    | 350                               |
| 26   | Li-IrSe₂*                                    | 0.5 M H₂SO₄                      | ~ 170                             | ~ 400                             | 220                               |
| 27   | IrOₓ*Δ                                       | 0.05 M H₂SO₄                     | ~ 22                              | ~ 125                             |                                    |
| 28   | IrOₓ/GCN *Δ                                   | 0.5 M H₂SO₄                     | ~ 43                              | ~ 136                             | 278                               |
| 29   | high purity Ir nanoparticles Δ               | 0.5 M H₂SO₄                     | 24                                | 100                               |                                    |
| 30   | IrO₂@RuO₂ *Δ                                  | 0.5 M H₂SO₄                     | ~ 24                              |                                    | 260                               |
| 31   | 3D-ordered macroporous IrO₂ *Δ               | 0.5 M H₂SO₄                     | ~ 20                              |                                    | ~ 330                             |
| 32   | IrNiO/x/Meso-ATO *Δ                         | 0.05 M H₂SO₄                     | ~ 90                              |                                    | ~ 320                             |
| 33   | Ir nanodendrides Δ                           | 0.05 M H₂SO₄                     | 71                                |                                    | ~ 270                             |
| 34   | La₂LiIrO₆                                     | pH 1 (H₂SO₄)                    | ~ 11                              |                                    | ~ 50                               |
| 35   | Ir nanoparticles on ITO (IrNP−ITO)           | 0.1 M HClO₄                     | 16 ± 3                            | 35 ± 3                            | 340 ± 20                          |
| 36   | Rutile IrO₂ NPs (6 nm)                       | 0.1 M HClO₄                     | ~ 3.5                             | ~ 14.5                            |                                    |
| 37   | IrO₂ nanoneedles *Δ                          | 1 M H₂SO₄                       | ~ 11                              |                                    | 313                               |
| 38   | Ir-Cu nanocrystals *                         | 0.1 M HClO₄                     | ~ 52                              |                                    | 310                               |
| 39   | IrW nanodendrites *Δ                         | 0.05 M H₂SO₄                     | ~ 310                             |                                    | 310                               |
| 40   | Ultrathin Ir nanowires *Δ                    | 0.1 M HClO₄                     | ~ 67                              |                                    | 270                               |
| 41   | Mesoporous Ir sheets *Δ                      | 0.5 M H₂SO₄                     | ~ 110                             |                                    | 240                               |
| 42   | Ir-SrTiO₃ *                                   | 0.1 M HClO₄                     | ~ 170                             | ~ 410                             | 247                               |

*activity was determined based on the linear sweep voltammetry, which can result in higher current (as compared to steady-state chronoamperometry) if capacitive contribution was not corrected

Δ No oxygen detection was performed
Spectroscopical characterization

Figure S17. Visible-Near IR spectrum of Ir$_{\text{SAC}}$−ITO in transmission mode. The spectrum of blank ITO was used as a background. The detector changeover occurs at 800 nm.

Figure S18. Survey XPS spectra of pristine Ir$_{\text{SAC}}$−ITO (black) and Ir$_{\text{SAC}}$−ITO after 2 h @ 10 mA cm$^{-2}$ (blue).
Figure S19. *Ex situ* XANES spectra of Ir\textsubscript{SAC}−ITO, Ir\textsubscript{SAC}−ITO after 2 h at 10 mA cm\textsuperscript{-2}, and reference IrO\textsubscript{2}.

Figure S20. Fitting of the *ex situ* EXAFS data for pristine Ir\textsubscript{SAC}−ITO (Fit 1 in Table 1): \(q\) space (a) and \(R\) space (b); and for spent electrode (after 2 h at 10 mA cm\textsuperscript{-2}, Fit 2 in Table 1): \(q\) space (c) and \(R\) space (d).
Figure S21. Fitting of the *in situ* EXAFS data for IrSAC−ITO at 1.46 V vs RHE: First coordination shell of 6 O neighbours, (Fit 5 in Table 1): q space (a) and R space (b), and split first coordination shell of 5+1 O neighbours, (Fit 6 in Table 1): q space (c) and R space (d).

Figure S22. Raw *k* space EXAFS for pristine IrSAC−ITO and *in situ* for IrSAC−ITO at 1.46 V vs RHE.
**Computational modelling**

![Top view of In$_2$O$_3$ slab models](image)

**Figure S23.** Top view of In$_2$O$_3$ slab models

| Intermediate | Ir(III) | Ir(IV) | Ir(V) | Ir(VI) | Ir-OOH | Ir-OO |
|--------------|---------|--------|-------|--------|--------|--------|
|              | 0.00    | 0.00   | 0.00  | 0.00   | 0.00   | 0.00   |
|              | 0.42    | 0.70   | 0.22  | 0.28   | 4.73   | 4.77   |
|              | 0.50    | 1.55   |       |        |        |        |
|              | 0.53    | 0.44   |       |        |        |        |
|              | 1.44    | 0.55   |       |        |        |        |
|              |         | 0.59   |       |        |        |        |

**Figure S24.** Computationally considered isomers of the different Ir$_\text{SAC}^{-}$ITO intermediates. The relative energies to the most stable isomer for each intermediate correspond to the periodic PBE-D2 values in eV.
Table S2. Computed Ir-O bond distances for selected Ir species.

| Surface species | Potential window, V vs RHE | Ir oxidation State | Distance, Å | Ir-OH₂ | Ir-OH | Ir=O | Ir-OH-In | Average |
|-----------------|----------------------------|-------------------|-------------|--------|-------|------|---------|---------|
| 1 (≡InOH)₃Ir(OH)₂(H₂O) | 0.00–0.60 | +3 | 2.14 | 2.02 | 2.06 | - | 1.98 | 2.05 | 2.10 | 2.06 |
| 2 (≡InOH)₃Ir(OH)₃ | 0.60–1.34 | +4 | - | 1.96 | 1.97 | 2.03 | - | 1.98 | 2.08 | 2.10 | 2.02 |
| 3 (≡InOH)₃Ir(O)(OH)₂ | 1.34–1.55 | +5 | - | 2.00 | 2.05 | 1.80 | - | 2.05 | 2.08 | 2.08 | 2.01 |
| 4 (≡InOH)₃Ir(O)₂(OH) | > 1.55 | +6 | - | 1.98 | 1.76 | 1.82 | - | 2.04 | 2.08 | 2.18 | 1.98 |

Figure S25. Computed Pourbaix diagram.
Figure S26. OER mechanism involving the WNA directly on intermediate (3). Energies are given in eV.
Figure S27. Generation of bisoxo Ir(V) dimeric species from Ir(III) dimers and OER reaction mechanisms (water nucleophilic attack and oxo-coupling) involving dimeric species. Energies are given in eV.
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