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Degradation Mechanisms of Oxygen Evolution Reaction Electrocatalysts: A Combined Identical-Location Transmission Electron Microscopy and X-ray Photoelectron Spectroscopy Study

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7 Degradation Mechanisms of Oxygen Evolution
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11 Reaction Electrocatalysts: A Combined Identical-
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15 Location Transmission Electron Microscopy and X-
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19 Ray Photoelectron Spectroscopy Study
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16 **ABSTRACT**
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21 Determining the degradation mechanism of oxygen evolution reaction (OER) catalysts
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24 is fundamental to design improved polymer electrolyte membrane water electrolyser
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27 (PEMWE) devices but remains challenging under the demanding conditions of PEMWE
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31 anodes. To address this issue, we introduce a methodology combining identical-location
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34 transmission electron microscopy, X-ray photoelectron spectroscopy and electrochemical
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37 measurements, and apply it to iridium nanoparticles (NPs) covered by a thin oxide layer
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39
40
41 (IrO_x) in OER conditions. The results show that, whatever the initial OER activity of the
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45 IrO_x nanocatalysts, it gradually declines and reaches similar values after 30,000 potential
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48 cycles between 1.20 and 1.60 V vs. RHE. This drop in OER activity was bridged to the
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52 progressive increase of the Ir oxidation state (fast change during electrochemical
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55 conditioning, milder changes during accelerated stress testing) along with increased
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3 concentration of hydroxyl groups and water molecules. In contrast, no change in the mean
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7 oxidation state, no change in the hydroxyl/water coverage and constant OER activity were
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10 noticed on the benchmark micrometre-sized IrO₂ particles. Besides chemical changes, Ir
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13 dissolution/redeposition and IrO_x nanoparticle migration/agglomeration/detachment were
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17 evidenced in OER conditions. By combining the information derived from identical-
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19
20 location transmission electron microscopy (IL-TEM) images and X-ray photoelectron
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23 spectroscopy (XPS) measurements, we show that Ir(III) and Ir(V) are the best performing
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27 Ir valencies for the OER. These findings provide insights into the long-term OER activity
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31 of IrO_x nanocatalysts, as well as practical guidelines for the development of more active
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35 and more stable PEMWE anodes.
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42 **KEYWORDS:** Proton-exchange membrane water electrolyzers; oxygen evolution
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45 reaction; iridium oxide; antimony-doped tin oxide; identical-location transmission electron
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49 microscopy.
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INTRODUCTION

During the 21st Conference of the Parties held in Paris in 2015, 195 states have agreed to limit global warming to an average of no more than 2 °C relative to pre-industrial level. However, this ambitious objective will not be reached without integrating non-hydro renewables in the energy mix¹. Additionally, the intermittency of alternative energies calls for a joint development of energy storage systems such as water electrolyzers²⁻³. Of the three main water electrolysis technologies (alkaline, proton exchange membrane (PEM) and solid oxide), PEM water electrolyzers (PEMWEs) feature several advantages: they are compact, withstand dynamic operating conditions, and can operate under pressure and at high current densities. However, the massive production of PEMWEs requires (i) enhancing the rate of the oxygen evolution reaction (OER), (ii) improving the durability of the anodic catalytic material, and (iii) decreasing the cost of the catalytic layers *e.g.* by reducing the noble metal content.

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4 Experimental work performed more than 40 years ago has established that ruthenium
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7 oxide (RuO_2) is the most efficient catalyst towards the OER in alkaline media but this
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10 oxide is unstable in acidic media⁴⁻⁹. Iridium oxide (IrO_2) is also highly active for the OER,
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13 chemically stable, a good electronic conductor but suffers of its high cost and scarcity
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16 especially when used in the form of micrometer-sized particles as it is in state-of-the-art
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19 PEMWE anodes^{5-8, 10-16}. Solutions to diminish the iridium (Ir) content have been
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22 intensively investigated, for example partial substitution of Ir by a transition metal^{11-12, 17-}
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28 ²² and/or decrease of the size of the Ir crystallites to the nanometer scale²³⁻²⁴. However,
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31 the very oxidizing environment of PEMWE anodes (electrochemical potential $E > 2.0$ V
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34 vs. the reversible hydrogen electrode - RHE, presence of oxygen, highly acidic
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37 environment) renders classical high surface area carbon supports unstable²⁵ and requires
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40 the development of alternatives such as metal oxides ²⁶⁻²⁹. In addition, it is well-
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43 established that the chemical nature and the crystallographic structure of the IrO_x are
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46 keys to high and sustainable OER activity; in particular thermal oxides are known to be
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49 less active but more stable than electrochemically formed oxides³⁰⁻³⁵. However, because
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56 the energy of the metal-oxygen bonds is stronger than that of the oxygen-oxygen bonds,⁶
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3 metal-oxygen bonds are permanently formed and broken in OER conditions. Thus, the
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7 chemical composition and the intrinsic activity of OER catalysts continuously change in
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10 PEMWE anode operating conditions more specifically at the nanometre-scale^{33, 36-37}.

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17 Surprisingly, despite its great fundamental and technological interest, the fate of
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20 supported-IrO_x nanocatalysts in OER conditions has never been studied hitherto. To
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24 address this issue, we introduce for the first time a methodology combining identical-
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27 location transmission electron microscopy (IL-TEM), X-ray photoelectron spectroscopy
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30 (XPS) and electrochemical measurements, and apply it to iridium nanoparticles (NPs)
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34 covered by a thin oxide layer.
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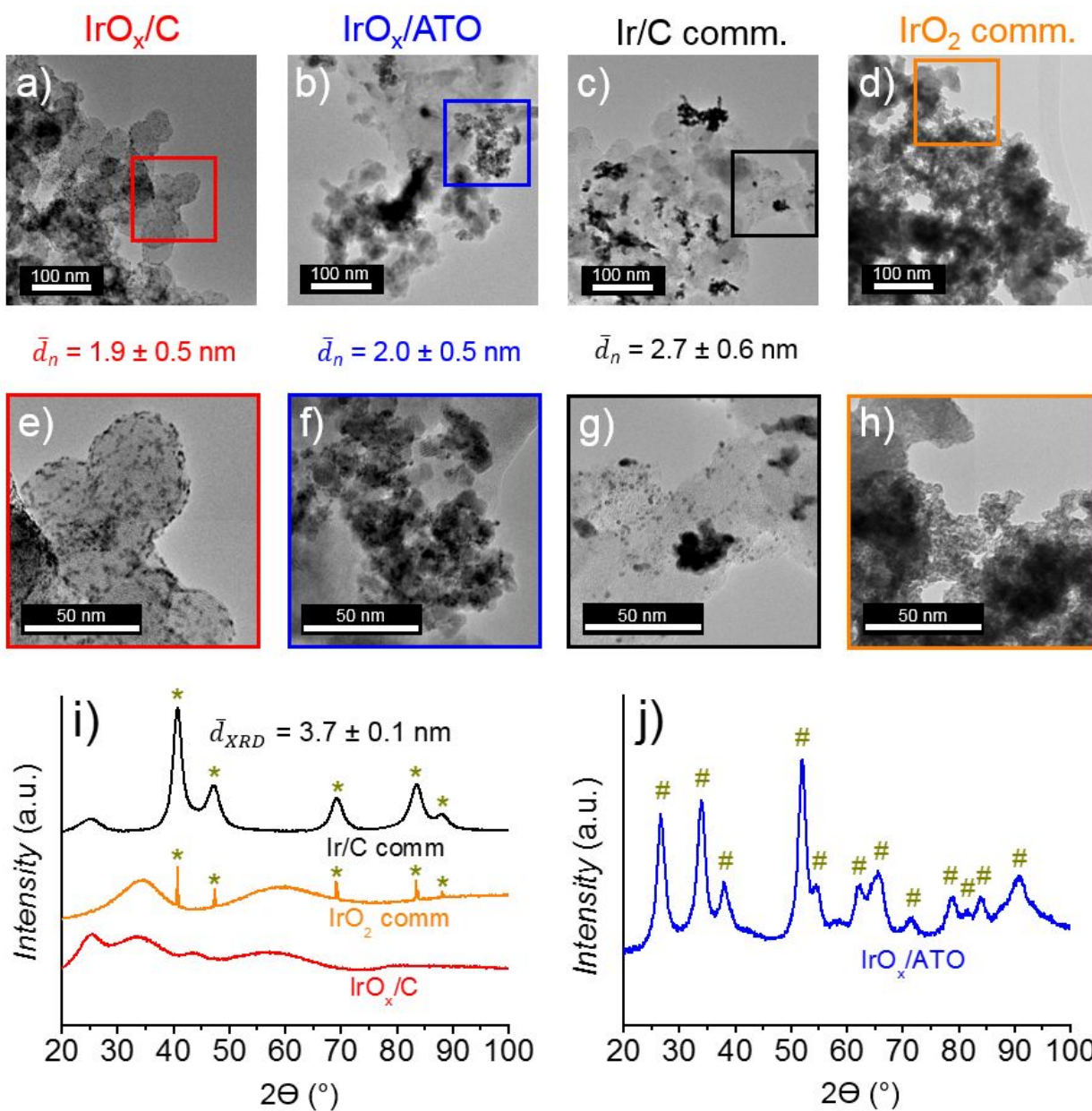
41 RESULTS AND DISCUSSION

42 Initial Morphology, Structure and Chemical Composition of Antimony-doped Tin Oxide- 43 44 45 46 supported and Carbon-supported IrO_x Nanoparticles 47 48 49 50 51 52 53 54 55 56 57 58 59 60

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4 **Figure 1a-h** shows TEM images IrO_x NPs supported on Vulcan XC-72 (IrO_x/C) or on
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7 antimony-doped tin oxide aerogel (IrO_x/ATO) synthesized in house using the same
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10 colloidal solution, and two commercial catalysts: metallic Ir NPs supported on Vulcan XC-
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13 72 (Ir/C comm.) and IrO₂ powder (IrO₂ comm.). In the IrO_x/C catalyst, the metal NPs
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16 feature an average diameter of 1.9 ± 0.5 nm and are homogeneously distributed onto the
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19 carbon support. The IrO_x/ATO NPs exhibit similar size (2.0 ± 0.5 nm) but are more
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22 agglomerated when supported on ATO. Similar observations were made by Cognard *et*
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24
25 *al.*³⁸ on Pt/C and Pt/ATO nanocatalysts, and the differences of agglomeration were
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27
28 ascribed to different specific surface areas of the supports. Finally, a mix of large
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31 aggregates and small NPs co-exist in the commercial Ir/C and IrO₂ catalysts, thus
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34 explaining why the crystallite size of Ir/C exceeds the nanoparticle size.
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43 The X-ray diffraction patterns (**Figure 1i, j**) indicate that Ir/C comm. is essentially
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46 metallic, and that small amorphous or poorly crystallize) IrO₂ nanocrystallites and large
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49 metallic Ir crystallites co-exist in the IrO₂ comm. sample. The presence of broad diffraction
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52 peaks for IrO_x/C and IrO_x/ATO suggests small and/or amorphous NPs in these samples.
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No reflection typical of tetragonal IrO₂ (PDF card n° 04-009-8479) was detected in the as-synthesized and benchmark materials.



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3 **Figure 1.** TEM images of IrO_x/C (a, e), IrO_x/ATO (b, f), Ir/C comm. (c, g) and IrO₂ comm.
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7 (d, h). X-ray diffractograms of Ir/C comm., IrO₂ comm. and IrO_x/C (i), and IrO_x/ATO (j).

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10 The star and the hash symbols correspond to cubic Ir (PDF card n° 00-006-0598) and
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13 tetragonal SnO₂ (PDF card n° 00-041-1445), respectively. No reflection typical of
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17 tetragonal IrO₂ (PDF card n° 04-009-8479) was detected in the as-synthesized and
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21 benchmark materials.

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30 Insights into the chemical nature of the IrO_x surface atoms were obtained by XPS
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33 measurements. The Ir4f spectra displayed in **Figure 2** were fitted using the parameters
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36 and the line shapes recently provided by Freakley *et al.*³⁹ (see **Table S1** and Materials
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39 and Methods for more details). Four contributions were considered: metallic Ir, Ir(III), Ir(IV)
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42 and Ir(V) species. **Figure 2** and **Table S2** indicate that: (i) Ir/C comm. is essentially metallic
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47 (**Figure 2c**), (ii) Ir(IV) species predominate in the IrO_x/C (**Figure 2a**) and IrO₂ comm.
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51 (**Figure 2d**) catalysts and that (iii) despite the same colloidal solution was used for the

synthesis of IrO_x/C and IrO_x/ATO catalysts, metallic Ir, Ir(III), Ir(IV), and Ir(V) species co-exist in the fresh IrO_x/ATO (Figure 2b).

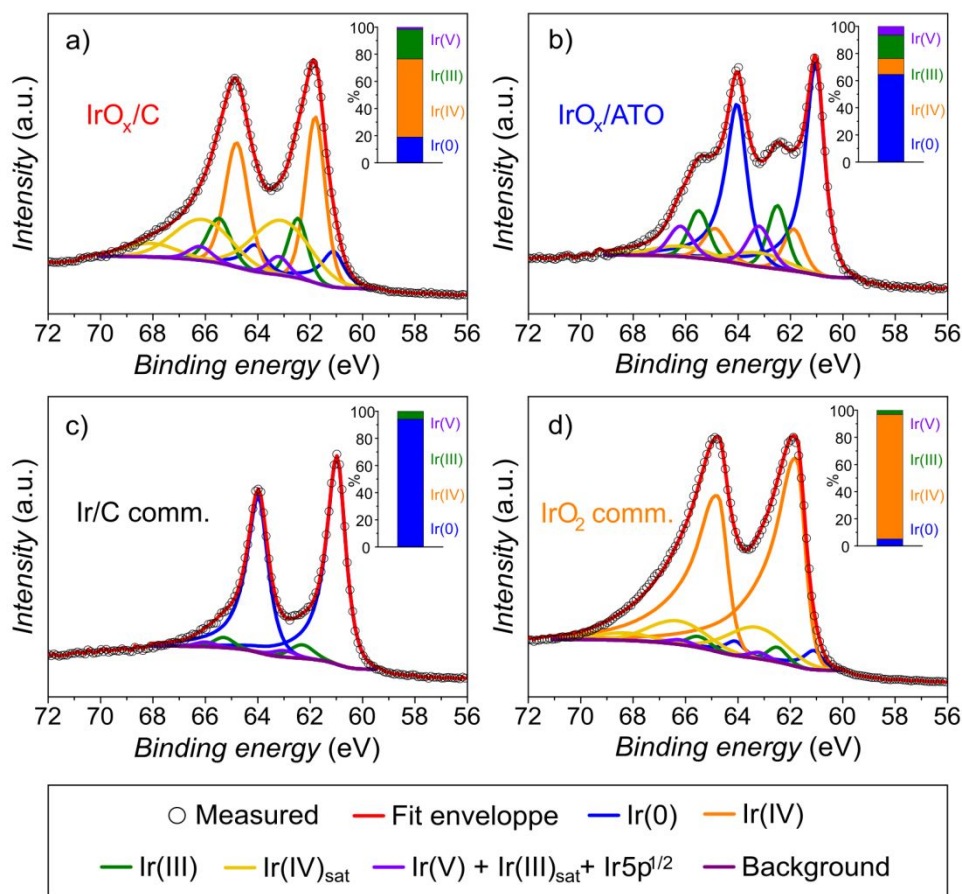


Figure 2. X-ray photoelectron spectra (Ir4f level) for IrO_x/C (a), IrO_x/ATO (b), Ir/C comm. (c) and IrO_2 comm. (d). The Ir(V) content was calculated by subtracting 15% of the area of the peak attributed to Ir(III) and 2.67% of the total area of the Ir4f band (to account for

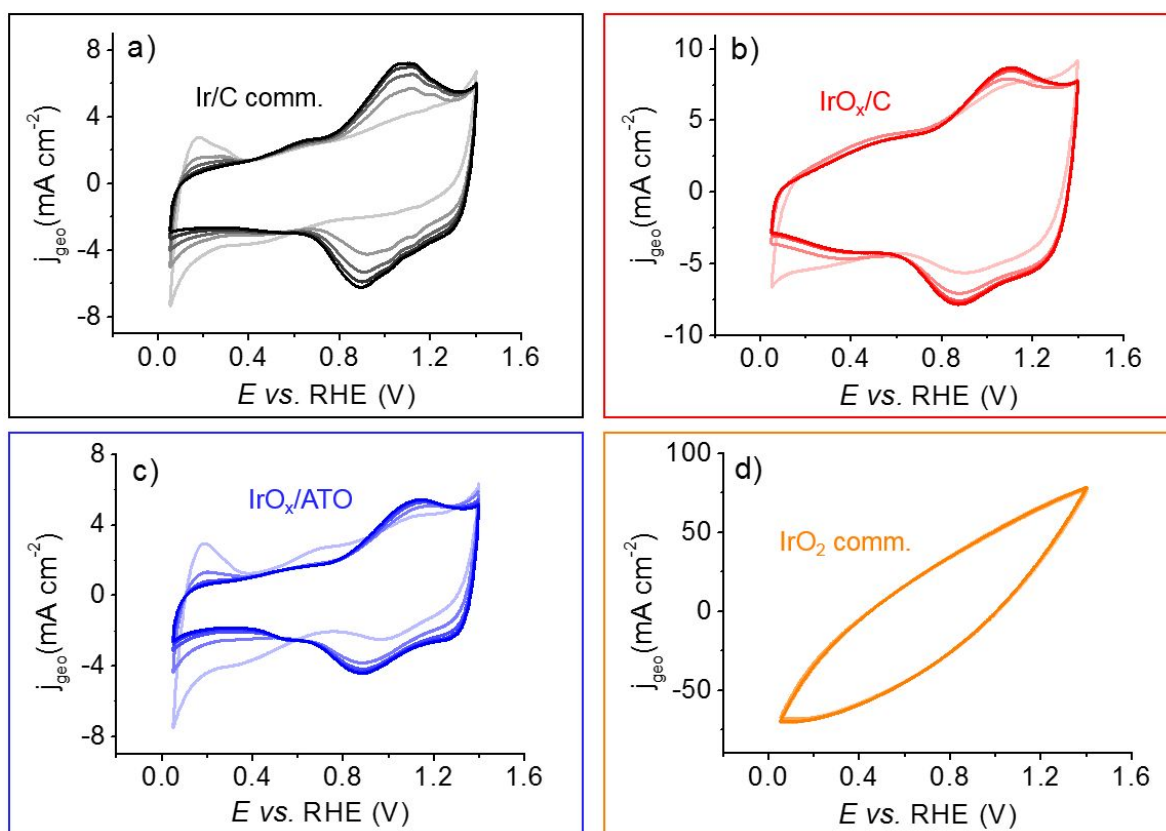
1
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3 the theoretical contribution of Ir(III) satellites and Ir5p_{1/2}, respectively) to the areas of the
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7 peaks located at 63.1 and 66.1 eV.
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15 **Electrocatalytic Activity for the Oxygen Evolution Reaction in Acidic Electrolyte**

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18 Changes of the cyclic voltammograms (CVs) during ‘electrochemical conditioning’ (100
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21 potential cycles between 0.05 and 1.40 V *vs.* RHE at 500 mV s⁻¹) confirmed the XPS
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24 results. Indeed, the electrical charge associated with the adsorption/desorption of
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27 underpotentially-deposited hydrogen (H_{upd}) gradually decreased during the conditioning
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31 cycles on Ir/C comm. (**Figure 3a**). In contrast, the CVs stabilized after *ca.* 25 potential
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33
34 cycles for the IrO_x/C catalyst (**Figure 3b**), thus confirming that the IrO_x/C NPs were partly
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37 oxidized in the fresh state. An intermediate behaviour was observed for the IrO_x/ATO
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40 catalyst (**Figure 3c**): H_{upd} features were observed during the first conditioning cycles but
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43 rapidly disappeared highlighting that the NPs were in average more metallic in IrO_x/ATO
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49 than in IrO_x/C. Last, the CVs measured on IrO₂ comm. featured no change (**Figure 3d**),
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53 in agreement with the predominance of Ir(IV) species in this catalyst.
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Ohmic-drop corrected polarization curves in 0.05 M H₂SO₄ (Figure 4a-c) were used to determine the OER activities of the different nanocatalysts. We are aware that a fraction of the measured current arises from the electrochemical dissolution of the IrO_x NPs. However, based on dissolution rates of 10 and 0.1 ng cm⁻² established for metallic Ir and IrO₂ electrodes, respectively⁴⁰ we estimated that the Ir dissolution current contributed to less than 0.05 % to the total electrical charge of the OER polarization curve.



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3 **Figure 3.** Conditioning cycles between 0.05 and 1.40 V *vs.* RHE in Ar-saturated 0.05 M
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7 H₂SO₄ electrolyte on (a) Ir/C comm., (b) IrO_x/C, (c) IrO_x/ATO and (d) IrO₂ comm. The
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10 potential sweep rate was 500 mV s⁻¹. The shades of colours (lightest to darkest) represent
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13 the 2nd, 25th, 50th, 75th and 100th potential cycles.

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21 The Ohmic-drop corrected OER current measured at 1.51 V *vs.* RHE ($\eta = 280$ mV)
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23 normalized by the initial mass of Ir on the electrode (j_{mass}) or by the anodic charge
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25 obtained after integration of the current between 0.40 and 1.40 V *vs.* RHE (j_{spec}) and the
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27 background corrected OER specific activities using IrO_x NPs-free supports ($j_{\text{spec-support}}$) is
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29 displayed in **Figure 4d**, **Figure 4e** and **Figure 4f**, respectively. The mass activity towards
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31 the OER of all catalysts approached the recent record value of 100 A g_{Ir}⁻¹ reported in Ref.
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41 and reached an optimal value for IrO_x/C (221 ± 14 A g_{Ir}⁻¹). Using the conclusions derived
from XPS spectra (**Table S2**), we can thus confidently confirm that amorphous
nanometer-sized Ir oxides containing a mixture of Ir(0), Ir(III) and Ir(IV) species better

perform than crystalline nanometer-sized Ir oxides containing predominantly Ir(IV) species³⁶.

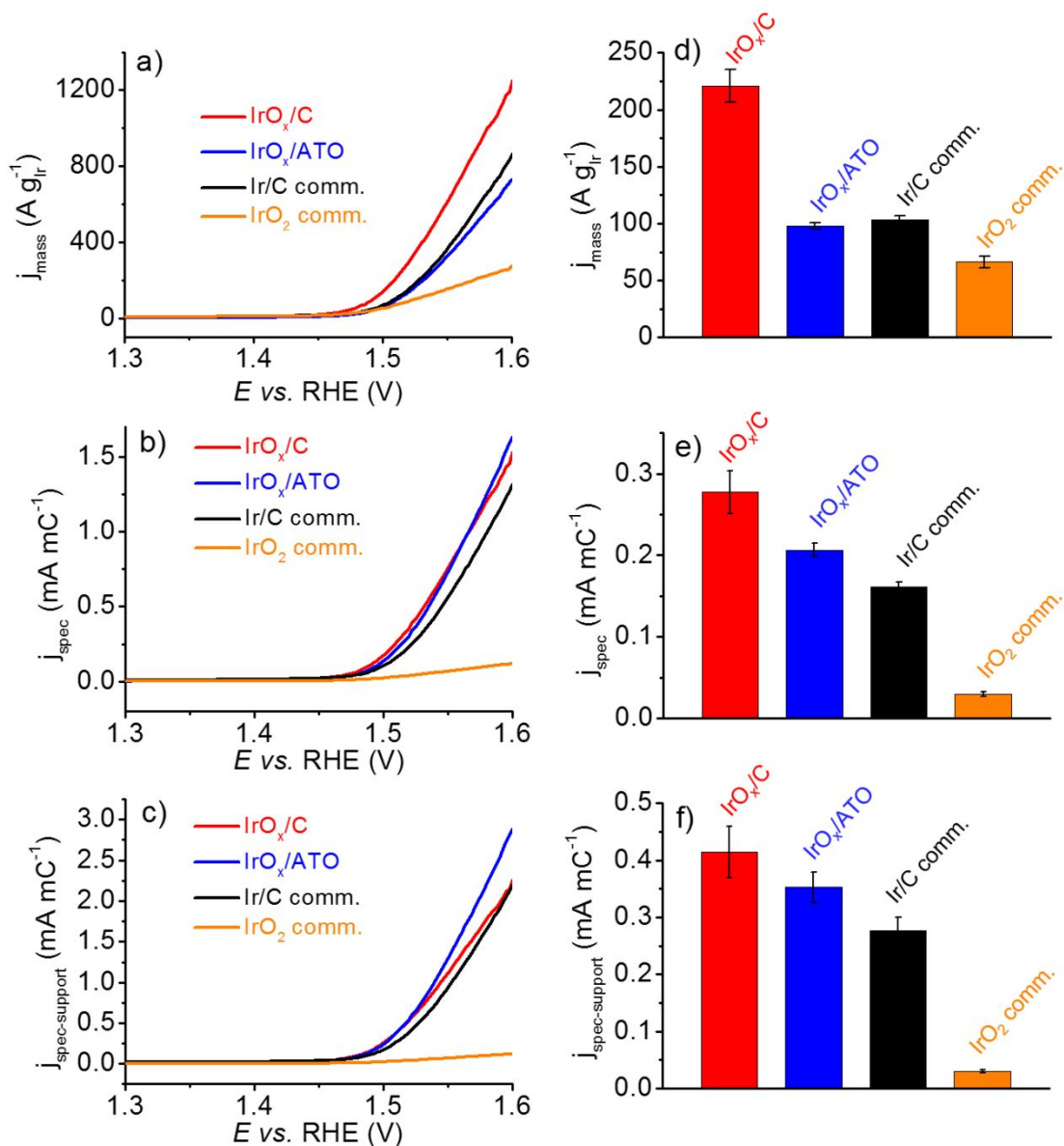


Figure 4. Ohmic-drop corrected polarization curves measured between 1.20 and 1.60 V vs. RHE at 5 mV s⁻¹ and 293 K in Ar-saturated 0.05 M H₂SO₄. The OER current was

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3 determined at $E = 1.51$ V vs. RHE, and normalized by (a) the mass of Ir initially loaded
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6 onto the electrode (j_{mass}), (b) the anodic charge obtained by integrating the current
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9 between 0.40 and 1.40 V vs. RHE (j_{spec}), and (c) the anodic charge obtained by integrating
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12 the current between 0.40 and 1.40 V vs. RHE after background subtraction ($j_{\text{spec-support}}$).
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17 The experiments were repeated three times and the error bars correspond to the standard
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20 deviation of the measurements.
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24 25 26 27 28 Changes of the Oxygen Evolution Reaction Activity in OER Conditions

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31 The catalytic powders were then electrochemically aged using an accelerated stress
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34 test (AST) comprising 30,000 potential steps between 1.20 and 1.60 V vs. RHE with
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37 square-wave potential ramp (3 s at each potential). **Figure 5a-d** show the CVs measured
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39
40 on the fresh and aged Ir/C comm., IrO_x/C, IrO_x/ATO and IrO₂ comm. catalysts. For all
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43 materials, except IrO₂ comm., the anodic charge between 0.40 and 1.40 V vs. RHE
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46 increased during the first 1,000 (1 k) potential cycles, more remarkably on IrO_x/C,
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49 suggesting continuous growth of an electrochemical oxide layer^{17, 42}. Also, a peak
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3 commonly associated to the Ir(III)/Ir(IV) transition^{33, 43-44} was noticed at *ca.* 0.97/0.93 V
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7 *vs.* RHE (positive-and negative-going potential sweep, respectively) on the three
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10 supported catalysts. This peak was broad for the fresh IrO_x/C and IrO_x/ATO but it
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13 sharpened and shifted towards negative potentials during the first AST cycles, thus
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16 suggesting a change in the nature of the surface species (**Figure 5b** and **Figure 5c**). It
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19 was already sharp and negatively shifted for the fresh Ir/C comm. catalyst (**Figure 5a**).
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22 Remarkably, another redox peak emerged at 1.20 V *vs.* RHE (positive-going potential
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25 sweep) after 10,000 (10 k) potential cycles on IrO_x/C or after 4,000 (4 k) potential cycles
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28 on IrO_x/ATO and Ir/C comm. It was formerly documented by Saveleva *et al.*³⁶ and by Oh
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31 *et al.*²⁴ for Ir@IrO_x catalysts and Ir nanodendrites, respectively. Oh *et al.*²⁴ ascribed this
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34 peak to the transition of Ir(IV) to Ir(V) although this change in Ir oxidation state may occur
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37 at *ca.* 1.40-1.45 V *vs.* RHE, as suggested by the redox peaks observed on the CVs in
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40 other works^{30, 33, 43-44}. An alternative explanation was provided by Pfeifer *et al.*⁴⁵: using
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43 density functional theory, these authors proposed that this peak should be rather ascribed
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46 to the oxidation of O(-II) in O(-I). They predicted a standard potential approaching 1.20 -
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49 1.30 V *vs.* RHE for this reaction, in excellent agreement with our results.
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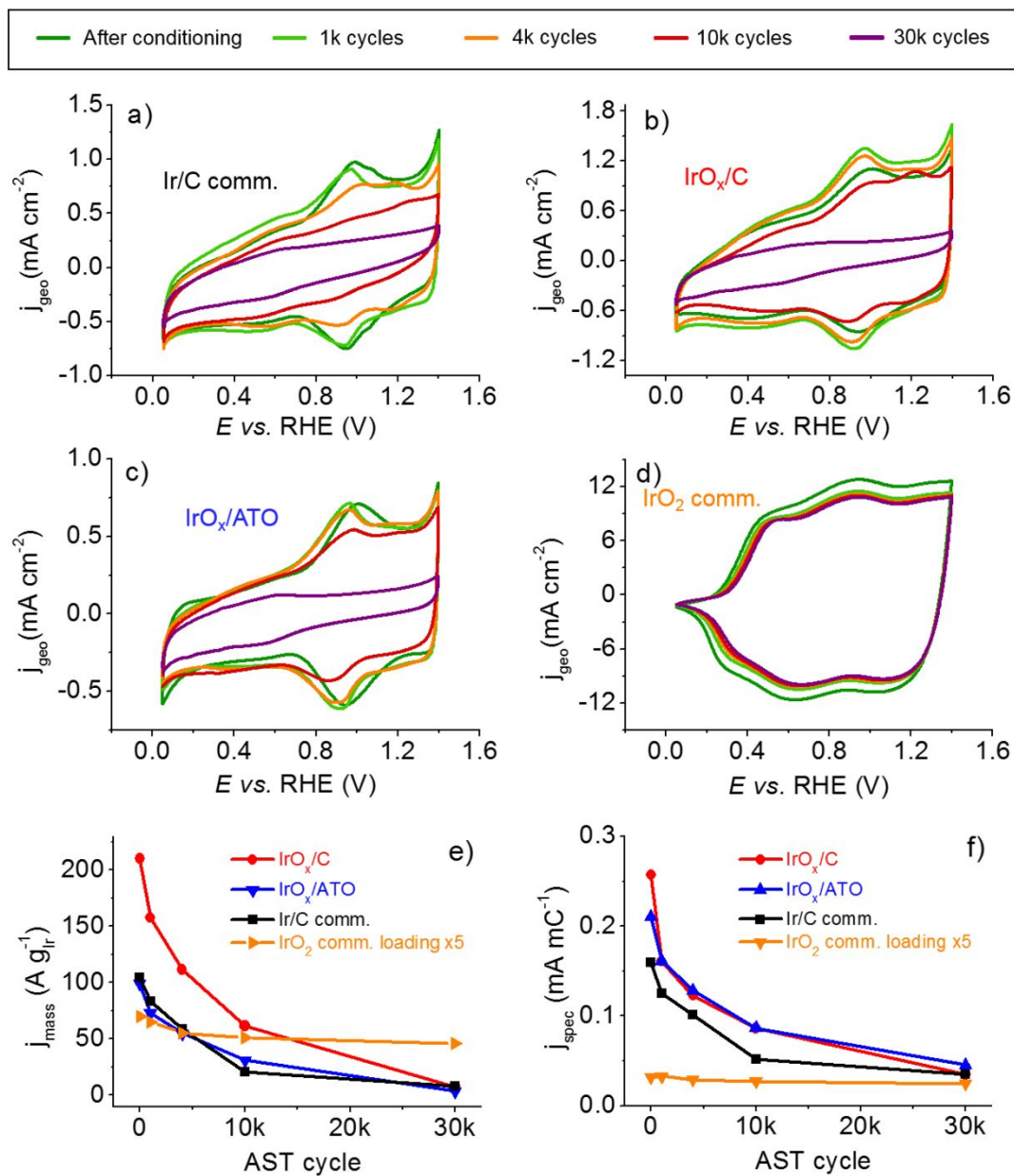


Figure 5. Cyclic voltammograms recorded in Ar-saturated 0.05 M H₂SO₄ at 50 mV s⁻¹ at 293 K after the conditioning step (100 cycles between 0.05 and 1.40 V vs. RHE) and after 1,000, 4,000, 10,000 and 30,000 potential cycles between 1.20 and 1.60 V vs. RHE

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3 for a) Ir/C comm., b) IrO_x/C, c) IrO_x/ATO and d) IrO₂ comm. Changes of the OER catalytic
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7 activity measured at 1.51 V *vs.* RHE as a function of the number of cycles for the four
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10 catalysts investigated in this study. The OER activity was normalized by e) the mass of Ir
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13 initially loaded onto the electrode (j_{mass}) and f) the anodic charge obtained by integrating
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17 the current between 0.40 and 1.40 V *vs.* RHE (j_{spec}).
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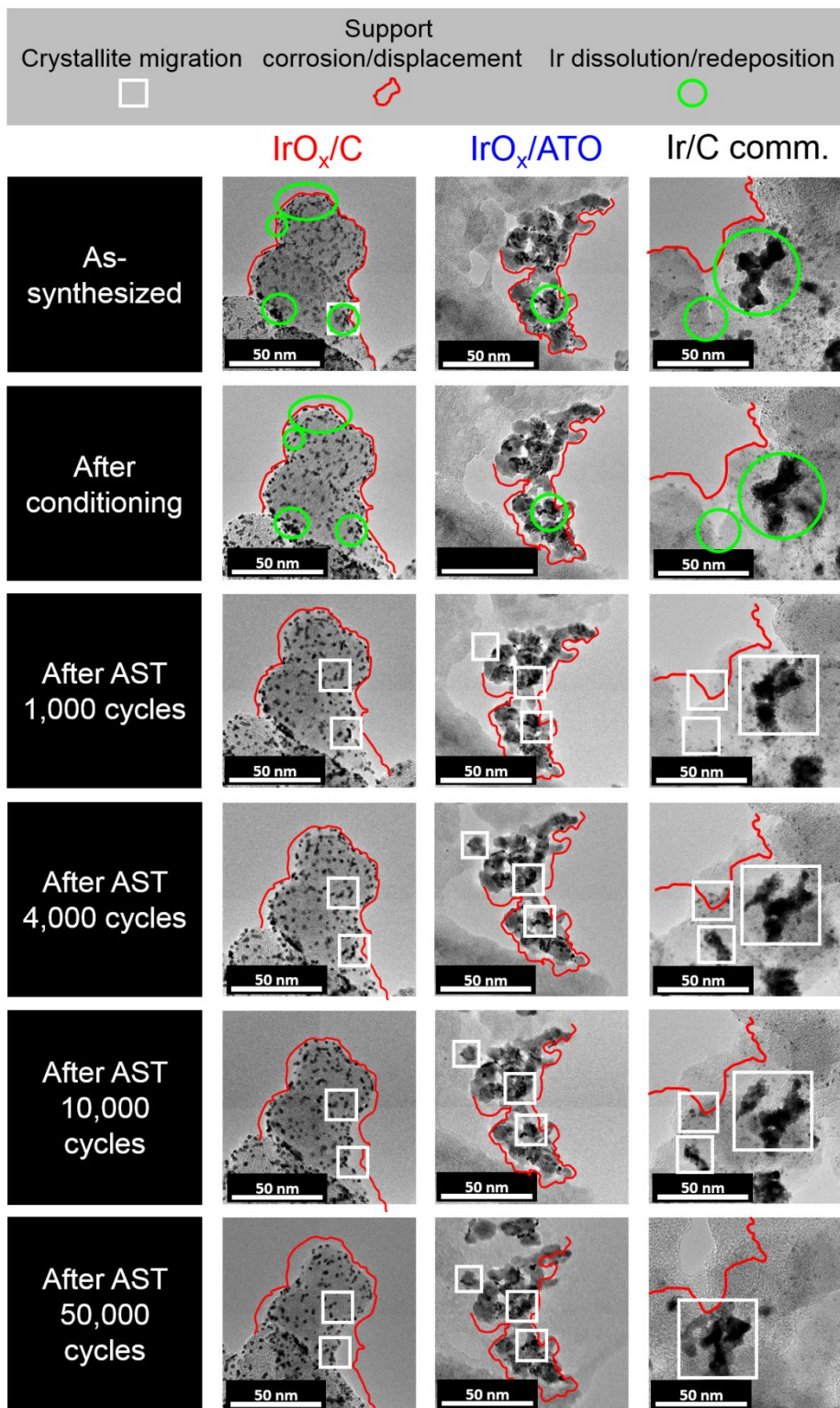
24 As shown by **Figure 5e** and **Figure 5f**, the OER performance dropped for all supported
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27 catalysts during the AST. IrO_x/C remained the most active electrocatalyst both from mass
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30 and specific activity perspectives during the first 10 k potential cycles but IrO₂ comm.
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33 revealed the most robust catalyst in terms of mass activity towards the OER (**Figure 5e**),
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36 the most important metrics in terms of PEMWE device. Fitting the Tafel plots in the linear
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39 region of the $\eta = f(\log(j_{\text{mass}}))$ plots (**Figure S2**) confirmed the drop in performance during
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42 the AST. In the fresh state, Tafel slopes of 52 and 50 mV dec⁻¹ were obtained for IrO_x/C
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45 and IrO_x/ATO, respectively and higher values were obtained for Ir/C comm. and IrO₂
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48 comm. (58 and 78 mV dec⁻¹, respectively). These values increased on all supported-
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51 electrocatalysts after 10 k potential cycles.
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Morphological Evolution of the Nanocatalysts during AST Monitored by IL-TEM

To disclose chemical composition-morphology-OER activity relationships, the morphological changes occurring on IrO_x/C, IrO_x/ATO and Ir/C comm. during the AST were assessed using IL-TEM. The IL-TEM images were recorded in the fresh state (as-synthesized), after conditioning, and after 1 k, 4 k, 10 k and 50 k potential cycles. Key to these measurements was to use a TEM grid made of titanium (indeed, gold TEM grids dissolve at potential > 1.40 V *vs.* RHE⁴⁶). To the best of our knowledge, this is the first time that IL-TEM measurements are performed in OER conditions.

The changes in morphology for the three supported nanocatalysts are displayed in **Figure 6**. Quantitative information was derived from the IL-TEM images: the average Feret diameter was measured for the exact same NPs in the fresh state, and after conditioning, 1 k, 4 k, 10 k and 50 k potential cycles. The NP size distributions of the fresh and aged IrO_x/C, IrO_x/ATO and Ir/C comm. catalysts determined by eye-counting using the ImageJ software (automated determination revealed less precise, see **Figure S5**) are

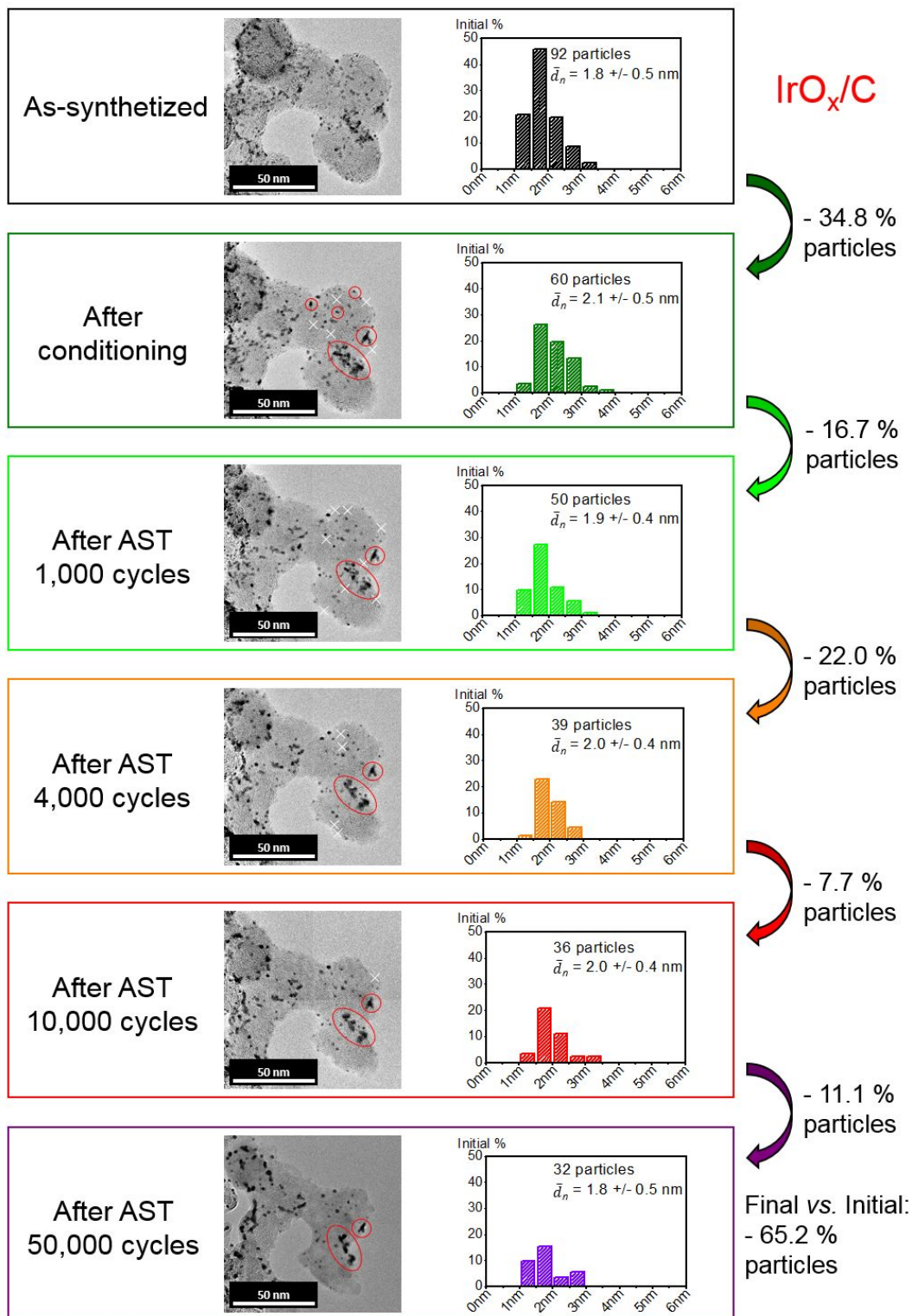
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3 displayed in **Figure 7**, **Figure S3** and **Figure S4**, respectively. They show that the smallest
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7 IrO_x/C and IrO_x/ATO NPs preferentially disappeared during the conditioning step along
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10 with a small increase in NP size, thus suggesting that Ostwald ripening occurred during
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13 this stage. In contrast, during the AST, crystallite migration/agglomeration/coalescence
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16 and detachment of the largest IrO_x NPs were the predominant degradation mechanisms.
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21 These results are in excellent agreement with the inductively-coupled plasma mass
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24 spectrometry results of Cherevko *et al.*^{43-44, 47-48} pointing towards dissolution of bulk Ir
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27 surfaces in similar potential conditions. They also agree with thermodynamics,⁴⁹ as Ir³⁺
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30 ions produced by dissolution can redeposit in the metallic form only onto for potentials
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34 below *ca.* 1.16 V *vs.* RHE that is during the conditioning step.
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3 **Figure 6.** IL-TEM images of IrO_x/C, IrO_x/ATO and Ir/C comm. as-synthesized, after the
4 conditioning step ($0.05 < E < 1.60$ V *vs.* RHE) and after different stages of potential cycling
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7 between $1.20 < E < 1.60$ V *vs.* RHE, highlighting major degradation mechanisms
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10 occurring during OER.
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21 Along with Ir dissolution, a strong corrosion of Vulcan XC72 was noticed, in line with
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23 thermodynamics⁴⁹ and with former results showing massive carbon corrosion at
24 potentials above 1.50 V *vs.* RHE⁵⁰⁻⁵¹. It is noteworthy that the ATO support was also
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27 corroded in OER conditions, indicating mild or no positive metal/metal-oxide support
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30 interaction effect. This statement was supported by X-EDS measurements showing a
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33 gradual loss of Sb atoms from the conditioning stage leading. After 50 k potential cycles,
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36 there was no Sb remaining in the ATO aerogel thus attenuating the ability of the IrO_x NPs
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39 to exchange electrons. These results are in line with former report by Cognard *et al.*⁵²
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42 showing dissolution and concomitant restructuring of ATO in PEMFC cathode operating
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45 conditions. By combining rotating disk and rotating ring disk electrode, X-ray energy
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48 dispersive X-ray spectroscopy and inductively-coupled plasma mass spectrometry, the
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3 authors showed that both Sb and Sn atoms are dissolved from ATO. The concomitant
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7 restructuring of the ATO support was accelerated during potential excursions at low
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10 electrode potential, *e.g.* during electrochemical characterizations or kinetic
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14 measurements.
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4 **Figure 7.** IL-TEM images and associated changes of the particle size distribution for
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7 IrO_x/C during potential cycling between 1.20 < E < 1.60 V vs. RHE at $T = 298$ K. Only
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10 isolated particles were considered to build the histograms. Red ellipses were used to
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13 highlight migration/agglomeration/coalescence of IrO_x NPs and white crosses highlight
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16 their detachment. The number-averaged average Feret diameter (\bar{d}_n) is plotted in the
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21 histograms.
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28 29 **Compositional Evolution of the Nanocatalysts During AST Monitored by XPS**

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32 Changes in the chemical composition of IrO_x/C, IrO_x/ATO, Ir/C comm. and IrO₂ comm.
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35 during the AST were also monitored. As indicated by **Figure 8**, the Ir4f_{7/2} band typically
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38 shifted to higher binding energy for all supported catalysts indicating an increase in the
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41 oxidation state. This result agrees with the early findings of Kötz *et al.*³³ on anodic Ir oxide
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44 films. Similarly, Li *et al.*⁵³ polarized a 100 nm-thick Ir film at 1 mA cm⁻² for 4, 69 or 120
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47 hours. Based on XPS measurements, the authors claimed that metastable Ir–O species
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50 first form and then transform into IrO₂ in OER conditions. The results displayed in **Figure**
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4 **8** confirm these findings but they also indicate that Ir(III), Ir(IV) and Ir(V) species co-exist
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7 in the aged nanocatalysts, in agreement with the *operando* XPS results of Sanchez-
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10 Casalongue³⁷ and the X-ray absorption near-edge spectroscopy (XANES) measurements
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13 of Minguzzi *et al.*⁵⁴⁻⁵⁵. Therefore, the mixture of Ir valencies observed after the AST can
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16 be rationalized by considering an Ir cation *red – ox* mechanism, such as that recently
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19 proposed by Cherevko *et al.*⁴⁴:
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41 In which IrO₂(OH) species eventually chemically decompose into IrO(OH) and O₂⁴⁴:
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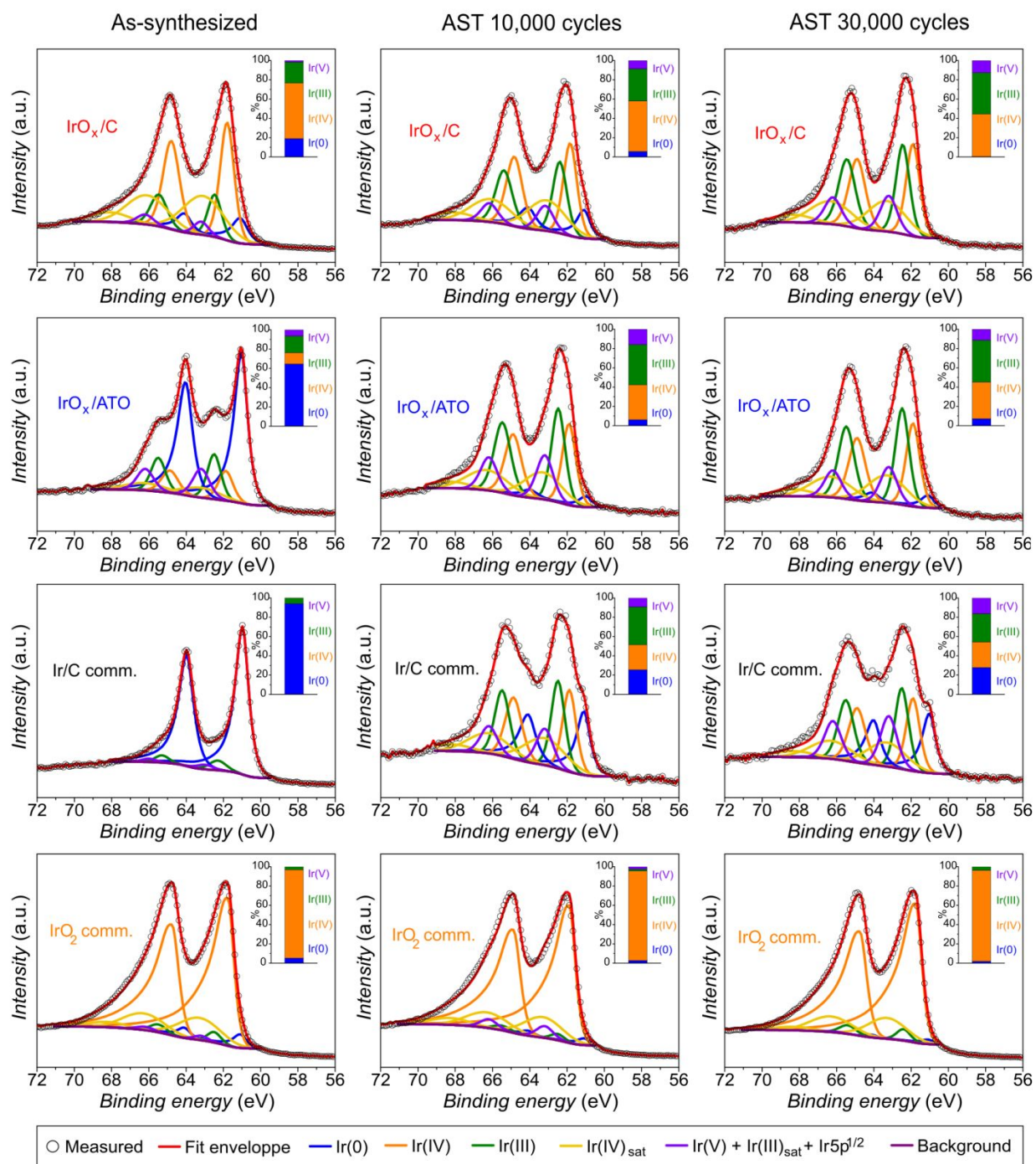
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4 Alternatively, based on *operando* near-ambient pressure X-ray photoelectron and
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7 absorption spectroscopy results, Pfeifer *et al.*^{45, 56-57} and Saveleva *et al.*³⁶ proposed that
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10 the oxygen (O) anions rather than the Ir cations play a key role in the OER mechanism
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13 (O anion *red-ox* mechanism). These authors argue that O(-I) anions are formed via an
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16 electrochemical step. However, because of their electron-deficient nature, O(-I) anions
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19 are prone to nucleophilic attack by water molecules hence favouring the O-O bond
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22 formation through a chemical step⁵⁸⁻⁵⁹. Finally, other mechanisms consider both the
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25 electronic transitions of O and Ir atoms and assume that lattice O atoms participate in the
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28 OER mechanism, leading to the formation of oxygen vacancies and dissolution of Ir atoms
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35 60-63.

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41 In the light of our results, we assigned Reaction (1) to the Ir(III)/Ir(IV) redox couple
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44 observed at *ca.* 0.95 V *vs.* RHE, and Reaction (2) to the Ir(IV)/ Ir(V) redox peak emerging
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47 at *ca.* 1.4 - 1.45 V *vs.* RHE^{30, 33, 43-44}. As shown by Kasian *et al.*⁶⁴ using differential
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50 electrochemical mass spectrometry, the fate of Ir(III) species depends on the value of the
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53 electrochemical potential: at low electrochemical potential ($E < 1.6$ V *vs.* RHE), Ir(III)
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3 species are oxidized to Ir(V) whereas at high electrochemical potential, Ir(V) species are
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7 further oxidized leading ultimately to formation of gaseous IrO₃.
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14 Besides the increase of the mean oxidation state of Ir, the O1s XPS spectra (**Figure S6**)
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17 and the O1s/Ir4f integrated intensities ratios (**Table S3**) evidence that the fraction of OH
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20 species and water molecules adsorbed on IrO_x/C and Ir/C comm. increased during the
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AST. In contrast, no change in the hydroxyl/water coverage was noticed on the
benchmark micrometre-sized IrO₂ particles. Our findings are in line with the experimental
observations of Abbott *et al.*⁶⁵ after an AST composed of 250 potential steps between
1.00 and 1.60 V *vs.* RHE. Combining the XPS results in the O1s region with the changes
observed in the CVs during the AST (**Figure 5**), we thus assign the peak emerging at *ca.*
1.20 V *vs.* RHE during the AST to the oxidation of O(-II) in O(-I) (reaction (4) proposed by
Pfeifer *et al.*⁴⁵):





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4 **Figure 8.** X-ray photoelectron spectra of the Ir4f level on IrO_x/C, IrO_x/ATO, Ir/C comm.
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7 and IrO₂ comm. before and after 10,000 and 30,000 potential cycles. Insets show the
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10 percentage of Ir(0), Ir(IV), Ir(III) and Ir(V). To estimate the intensity of the peak ascribed
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13 to the Ir(V) component, we subtracted 15% of the area of the peak attributed to Ir(III) and
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17 2.67% of the total area of the Ir4f band (to account for the theoretical contribution of Ir(III)
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20 satellites and Ir5p_{1/2}, respectively) to the areas of the peaks located at 63.1 and 66.1 eV.
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29 **Disclosing Chemical Composition – OER Activity - Stability Relationships**

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34 To disclose chemical composition - OER activity- stability relationships, the information
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37 obtained from IL-TEM and XPS were combined. We assumed that the OER activity of the
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41 IrO_x NPs after 10 k potential cycles can be expressed as:
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$$47 \frac{100 \times j_{meas}}{(1 - \%_{lost})} = j(Ir(0)) \times \% (Ir(0)) + j(Ir(IV)) \times \% (Ir(IV)) + j(Ir(III/V)) \times \% (Ir(III) + Ir(V)) \quad (5)$$

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4 Where j_{meas} is the background and Ohmic-drop corrected OER specific activity after
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7 10 k potential cycles extracted from **Figure S7**, $\%_{lost}$ is the percentage of lost
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10 electrochemically active surface area between the conditioning step and the 10 k potential
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13 cycled sample estimated using IL-TEM images, $j(Ir(A))$ is the intrinsic OER specific
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16 activity of Ir in the oxidation state +A, and $\%(Ir(A))$ is the fraction of oxide in the oxidation
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19 state +A estimated from XPS spectra fits. Since the +III and +V oxidation states of Ir are
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22 related by Equation (3), their intrinsic contributions to the intrinsic OER activity were
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25 considered interdependent.
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36 Applying Equation (5) to IrO_x/C , IrO_x/ATO , Ir/C comm. (due to the micrometre-size of
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39 the particles, IL-TEM measurements could not be performed on the IrO_2 comm. catalyst)
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42 led to a system of three equations and three unknowns, which was solved, and the
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45 calculated intrinsic OER specific activity values of Ir(0), Ir(III/V) and Ir(IV) are presented
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48 in **Table 1**. Verification of the results was achieved by comparing the measured (j_{meas}) and
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51 calculated values (j_{calc}) of the OER specific activity after the conditioning step (**Table 2**)
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and the values used for the calculation and for the verification are given in **Table S4** and

Table S5.

Table 1. Calculated intrinsic OER specific activity values of Ir(0), Ir(III/V) and Ir(IV).

	j (mA mC ⁻¹)	OER activity contribution (%)
$j_{\text{calc}}(\text{Ir}(0))$	0.0539	16.3
$j_{\text{calc}}(\text{Ir(III/V)})$	0.2373	71.5
$j_{\text{calc}}(\text{Ir(IV)})$	0.0406	12.2

Table 2. Verification of the model using the measured (j_{meas}) and calculated (j_{calc}) OER activities after the conditioning step.

	IrO _x /C	IrO _x /ATO	Ir/C comm.	IrO ₂ comm.

j_{meas} (mA mC ⁻¹)	0.3793	0.3726	0.2660	0.03152
j_{calc} (mA mC ⁻¹)	0.1118	0.1700	0.1563	0.0491
Error (%)	70.5	54.4	41.2	35.8

In view of the assumptions (areas analysed in IL-TEM and XPS representative of the sample) and the uncertainties (size and shape of nanoparticles, chemical composition) associated with the different physico-chemical measurements, we first stress that the values of OER activities calculated from Equation (5) must be regarded as semi-quantitative. Despite this, some interesting findings emerge from **Table 1**. First, the results indicate that the combined Ir (III) and Ir(V) valencies are far more active for OER than Ir(0) and Ir(IV), thus confirming the better OER activity of Ir oxyhydroxides reported in the literature^{30-31, 33}. This trend is independent on the OER mechanism since the Ir(III) valency plays a key role both in the Ir cation *red-ox* mechanism (Ir(III) – Ir(IV) – Ir(V) transitions^{33, 37, 54-55, 64}) and in the O anion *red-ox* mechanism (the Ir(III) valency is the most likely to accommodate electrophilic O(-I) species⁴⁵). Second, the results of the

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3 combined IL-TEM – XPS – electrocatalytic measurements indicate that the progressive
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7 increase of the Ir(IV) fraction associated with the decrease in the number of isolated
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10 nanoparticles (due to Ir dissolution and
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13 migration/agglomeration/coalescence/detachment of the IrO_x nanoparticles)
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17 concomitantly contribute to the drop of the OER mass activity in the long-term.
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26 CONCLUSION

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29 In conclusion, by combining accelerated stress tests, IL-TEM and XPS measurements,
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32 we rationalized OER activity losses in simulated PEMWE anode operating conditions. IL-
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36 TEM images showed that IrO_x NPs are prone to dissolve during the conditioning stage
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39 and migrate/agglomerate/coalesce/detach in OER conditions, independently on the type
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42 of support (Vulcan XC72 and ATO). XPS analyses revealed that these morphological
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46 changes are accompanied by gradual oxidation of Ir(0) and Ir(III) into Ir(IV) and Ir(V)
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49 species along with increased concentration of hydroxyl groups and water molecules on
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53 IrO_x nanocatalysts. In contrast, no change in the mean oxidation state, no change in the
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3 hydroxyl/water coverage and constant OER activity were noticed on the benchmark
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7 micrometre-sized IrO₂ particles. Our results thus indicate that the progressive increase of
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10 the Ir fraction with +IV valency associated with the decrease in the number of isolated
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14 nanoparticles concomitantly contribute to the drop of the specific activity towards the OER
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17 in practical PEMWE anode operating conditions.
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26 ASSOCIATED CONTENT

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30 Supporting Information.

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35 The Supporting Information is available free of charge via the Internet at
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37
38 <http://pubs.acs.org>. It comprises:
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42

43 - Materials and Methods
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45
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47 - XPS spectra (Ir4f bands) of Ir/C comm. after 10 k potential cycles.
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52 - Changes of the Tafel slopes for all catalysts during the 10 k potential cycling protocol.
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4 - Identical-location transmission electron microscopy of IrO_x/ATO and Ir/C comm. during
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7 the 50 k potential cycling protocol.
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11 - Comparison of IrO_x NP size distribution achieved by automated determination or by eye-
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15 counting.
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19 - XPS spectra (O1s band) of IrO_x/C, Ir/C comm. and IrO₂ comm., before and after 10 k
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23 and 30 k potential cycles.
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27 - Changes of the OER catalytic activity as a function of the number of AST cycles for all
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31 catalysts.
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35 - Parameters used to fit the XPS spectra (Ir4f and O1s band).
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40 - Atomic percentages of the different Ir valencies for the as-synthesized catalysts.
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44 - O1s/Ir4f integrated intensities ratios for the as-synthesized and aged (10 k or 30 k
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48 potential cycles) IrO_x/C, Ir/C comm. and IrO₂ comm. catalysts.
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3 - Values used for the calculation of the intrinsic OER activities of the different Ir valencies
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7 obtained after 10 k potential cycles and values used to check this calculation obtained
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10 after the conditioning step.
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34 Author Contributions

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38 All authors analysed, discussed the results, drew conclusions and approved the final
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41 version of this manuscript.
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48 CONFLICT OF INTEREST

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52 The authors declare no competing financial interest.
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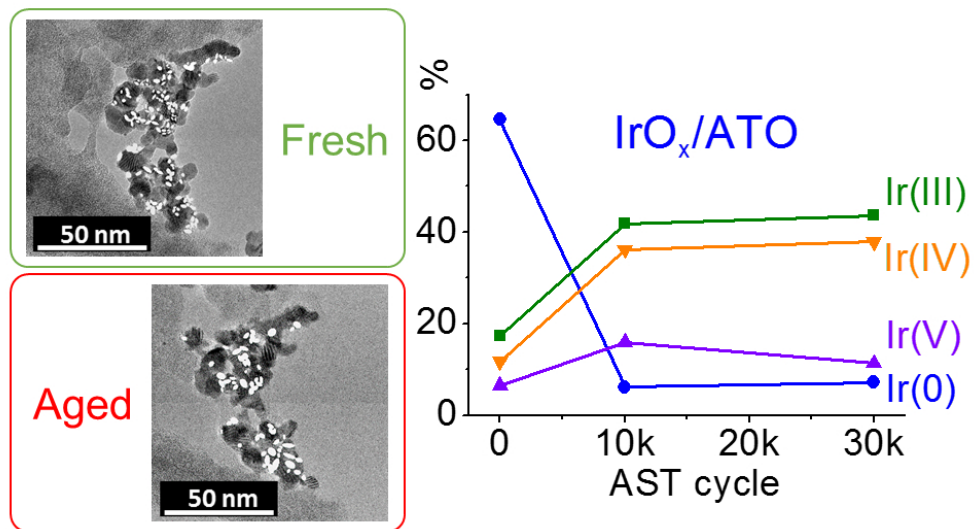
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Identical-location transmission electron microscopy, X-ray photoelectron spectroscopy and electrochemistry were combined to unravel the degradation mechanisms of iridium oxide nanoparticles in oxygen evolution reaction conditions.

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