Supplementary Information to

The Electronic Structure of Iridium Oxide Electrodes Active in Water Splitting

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1 X-ray diffraction (XRD)

The two powders were investigated by powder X-Ray diffraction (XRD). A Bruker AXS D8 Advance θ/θ diffractometer was employed in Bragg-Brentano geometry using Ni-filtered Cu K α radiation and a position sensitive LynxEye silicon strip detector. To achieve rutile phase purity in the crystalline powder, the powder was calcined at 1073 K in 10⁵ Pa O₂ for 50 h prior to the measurement. In Figure S1, the crystalline IrO₂ shows all expected rutile-type IrO₂ reflections, whereas the amorphous IrO_x only counts with a broad peak around 35° and sharp metallic reflections. Quantitative Rietveld analysis of the IrO₂/Ir mixture obtained from the amorphous IrO_x sample by thermal dehydration (not shown) yields an estimate of 2.4 wt.-% Ir metal for the original sample, assuming that the metallic amount did not change during dehydration.



Figure S1: Powder diffractogram of the amorphous and the crystalline iridium oxide powders. The crystalline powder (above, orange) shows all reflections of the rutile-type structure while there are only broad peaks in the amorphous powder (blue, below) accompanied by minor reflections of Ir metal.

2 Thermogravimetry (TG)

Thermal analysis of the samples was done *via* thermogravimetry (TG) using a Netzsch STA 449C Jupiter instrument. At a constant rate of 10 K min⁻¹, the samples were heated to 1073 K in 21 vol.-% O_2 in Ar (100 mL min⁻¹) at 10⁵ Pa. A connected Pfeiffer QMS200 Omnistar quadrupole mass spectrometer was employed for gas analysis. The upper part of Figure S2 shows the TG curves of the two powders. The rutile-type IrO₂ does not lose any weight upon heating while the amorphous IrO_x loses approximately 6 wt.-% water according to the QMS trace of mass 18 in the lower part of Figure S2. Two distinct peaks and a broad should toward higher temperature are identified in the H₂O trace. The first peak around 400 K is assigned to physisorbed water. The second peak at 500 K and the long shoulder toward higher temperature are most likely due to chemisorbed water in form of hydroxyl and oxohydroxyl groups. An approximation of the

amount of physisorbed water yields 1.5 - 2 wt.-%. The amorphous IrO_x sample crystallizes at 673 K, where there is an exothermic peak in the simultaneously recorded differential scanning calorimetry (not shown).



Figure S2: (a) TG curves of the two powders are shown. No mass loss is observed in the crystalline sample, while a mass loss of ~6 wt.-% is registered in the amorphous powder. (b) H_2O (m=18 a. u.) QMS-trace of the two powders corresponding to the TG curves is shown. The amorphous sample releases H_2O up to approx. 550 K.

3 Brunauer-Emmett-Teller (BET)-surface area determination

Prior to the surface area determination, the samples were degassed for 3 h at 353 K. Subsequently, the BET-surface area of the powders was determined in N₂ at 77 K using an Autosorb 6-MP from Quantachrome. Considerable differences were obtained for the Brunauer-Emmett-Teller (BET)-surface areas of the samples amounting to 2.1 m² g⁻¹ for rutile IrO₂ and 33.3 m² g⁻¹ for the amorphous IrO_x.

4 Energy-dispersive X-ray spectroscopy (EDX)

The atomic compositions of the samples were determined by EDX (Bruker XFlash detector and Quantax system mounted on a SEM Hitachi S-4800) with an acceleration voltage of 25 kV. The results are listed in Table S1. The stated values were each averaged over five measured positions.

Table S1. EDX results of the elemental composition of the rutile-type and the amorphous indiam oxide powders							
	rutile-ty	pe IrO ₂	amorphous IrO _x				
Element	norm. wt%	norm. at%	norm. wt%	norm. at%			
0	14.3	66.2	22.5	76.5			
Fe	0.8	1.0	0.9	0.9			
lr	84.9	32.8	76.6	22.6			

Table S1: EDX results of the elemental composition of the rutile-type and the amorphous iridium oxide powders

5 Temperature-programmed reduction (TPR)

Using a home-built fixed-bed reactor, the overall Ir oxidation state of the two powders was determined by TPR in 4.92 vol.-% H₂ in Ar at a heating rate of 6 K min⁻¹ (80 mL min⁻¹, end temperature 600 K). The H₂ consumption was registered via a thermal conductivity detector (TCD). A calibration of the TCD was done by the reduction of a known amount of CuO. 9.8 mg IrO_2 and 8.3 mg IrO_x were used. Both in reduction temperature and peak profile considerable differences are observed for the two powders as shown in Figure S3. The amorphous IrO_x partly already adsorbs hydrogen at room temperature (not shown) and upon heating is reduced in a very narrow temperature window of 15 K around 350 K. The H₂ consumed at room temperature is taken into account for the overall H₂ consumption. The crystalline IrO₂ is reduced at a significantly higher temperature of 510 K in a window of 75 K. When considering the H_2 consumption of the rutile-type IrO_2 sample, an oxidation state of 4.1±0.1 is calculated, which is in good agreement with the expectation of a formal oxidation state of 4+ in rutile IrO₂. In contrast, when taking into account the physisorbed water content (~2 wt.-%) and the Ir metal content (2.4 wt.-%), an oxidation state of the remaining oxidized species of only 3.6±0.1 is obtained for the amorphous IrO_x. This finding suggests the presence of mixed valences of Ir^{III} and Ir^{IV} in the IrO_x powder. A standard deviation of 2 % is assumed based on standardized repeated TPR-experiments on CuO.1



Figure S3: TPR-profiles of the rutile and the amorphous powder. H_2 consumption is plotted against the sample temperature. The amorphous sample is reduced at much lower temperature than the crystalline sample in a narrower temperature window.

6 Electrochemistry

The OER-performance of the powders was assessed by loading defined amounts of catalyst onto a GC-ring disk electrode (RDE, Pine Instruments). To this effect, we prepared catalyst inks from ground Ir powder, 60 % water, 39.6 % isopropanol and 0.4 % Nafion (5 % perfluorinated

resin solution, Sigma Aldrich). The electrode was loaded with defined ink volumes using a micropipette and dried at 333 K in air for 30 min to achieve a constant loading of $20 \ \mu g_{lr} \ cm^2$. Measurements were conducted at a rotational speed of 1600 rpm in N₂-saturated 0.5 M H₂SO₄. Linear sweep voltammetry (LSV) was performed at 5 mV s⁻¹. The OER-onset of the amorphous powder is much steeper than that of the rutile sample, which confirms the expected higher OER activity of the amorphous powder. This difference in activity cannot solely be explained by the larger surface area of the amorphous powder.



Figure S4: LSV of the two powders at 5 mV s⁻¹ in 0.5 M H₂SO₄. The current density of the rutile sample was multiplied by 16 to cancel the difference in BET surface area of the two samples.

7 X-ray photoemission & absorption spectroscopies (XPS & NEXAFS)

Photoemission measurements were performed in а Near-Ambient-Pressure X-ray Photoemission Spectroscopy (NAP-XPS) system at the ISISS (Innovative Station for In-Situ Spectroscopy) beamline at the synchrotron facility BESSYII/HZB (Berlin, Germany).² Prior to the measurement, the crystalline IrO2 powder was washed in Milli-Q water, centrifuged and calcined at 1073 K in 10⁵ Pa O₂ for 50 h. The amorphous IrO_x was measured as received from the supplier. The powders were pressed into self-supporting wafers (40 mg, 3 t, \emptyset = 8 mm) and subsequently measured in UHV (~10⁻⁶ Pa). A pass energy (PE) of 10 eV was used in XPS, which had an approximate resolution of 0.6 eV at 900 eV kinetic energy of the photoelectrons (KE) of the Ir 4f core line. With the model of Tanuma et al.,3 an inelastic mean free path (IMPF) of the photoelectrons of ~ 1.1 nm is calculated. The binding energy calibration was carried out after an evaluation of each corresponding Fermi edge. In NEXAFS, the photon energy was continuously varied between 525 eV and 560 eV by moving the monochromator. The Auger electron yield (AEY) of the O K-edge was collected with the electron spectrometer at a fixed KE of 385 eV (PE 50 eV). The probing depth of this measurement is ~1 nm. The XPS spectra were fit after subtraction of a Shirley background with the commercially available CasaXPS software (www.casaxps.com). In all fits, the peak separation and the peak area ratios between the Ir $4f_{7/2}$ and the Ir 4f_{5/2} components were constrained to 3 eV and 4:3, respectively. Deviations in the peak area ratios of 5 % were allowed to account for the inaccuracies in background subtraction and peak area determination of asymmetric peaks. The employed fit parameters are listed in Table S2 for the rutile IrO₂ and in Table S3 for the amorphous IrO_x. Details on the fit functions can be found in ref. 4. In short, $DS(\alpha,n)$ is a Doniach-Šunjic profile with an asymmetry parameter α that is convoluted with a Gaussian with a width that is characterized by an integer between $0 \le n \le 499$. This DS function is blended toward lower binding energy with a Gaussian-Lorentzian Sum form (SGL(m)) whose ratio is given by the parameter m (0 pure Gaussian, 100 pure Lorentzian). Adding this SGL term accounts for the spectra to be less Lorentzian in nature than the DS function would suggest.

Table S2: Fit parameters for Ir 4f of rutile IrO ₂ , 900 eV KE, 10 eV PE									
Rutile IrO ₂	Ir 4f _{7/2}	Ir 4f _{5/2}	Ir 4f _{7/2}	Ir 4f _{5/2}	Ir 4f _{5/2}				
	lr ^{iv}	lr ^{i∨}	lr [⊮] sat 1	Ir [⊮] sat 1	Ir [⊮] sat 2				
line shape	DS(0.2,230)SGL(55)	DS(0.2,230)SGL(55)	GL(0)	GL(0)	GL(0)				
area	1247	1010	293	220	60				
FWHM / eV	0.9	0.9	2.6	2.6	2.5				
binding	61.8	64.8	62.9	65.9	67.9				
energy / eV									

 Table S3: Fit parameters for Ir 4f of amorphous IrO_x, 900 eV KE, 10 eV PE

Amorphous IrO _x	Ir 4f _{7/2} Ir ^{i∨}	lr 4f _{5/2} Ir [™]	Ir 4f _{7/2} Ir ^{iv} sat 1	lr 4f _{5/2} Ir ^Ⅳ sat 1	Ir 4f _{5/2} Ir ^{iv} sat 2	Ir 4f _{7/2} Ir ^{III}	Ir 4f _{5/2} Ir ^{III}	Ir 4f _{7/2} Ir [⊪] sat 1	lr 4f _{5/2} Ir [⊪] sat 1
line shape	DS(0.2,230) SGL(45)	DS(0.2,230) SGL(45)	GL(0)	GL(0)	GL(0)	DS(0.2,230) SGL(45)	DS(0.2,230) SGL(45)	GL(0)	GL(0)
area	1700	1377	400	300	99	551	441	94	70
FWHM / eV	1.1	1.1	2.6	2.6	2.5	1	1.1	2.6	2.6
binding energy / eV	61.8	64.8	62.9	65.9	67.9	62.4	65.4	63.4	66.4



binding energy / eV

Figure S5. O 1s spectra of the two powders. The amorphous IrO_x spectrum shows more intensity at lower binding energy, reflecting the O 2p hole states, and at higher binding energy, due to the H-bound oxygen species contained in the sample.

Table S4 gives an overview of previously published XPS studies on iridium oxides and one reference for $IrCl_3$. The intrinsic asymmetric shape of stoichiometric IrO_2 was interpreted by Wertheim *et al.*⁵ as well as Kahk *et al.*⁶ Wertheim *et al.* do a full many body calculation of the line shape expected for rutile-type IrO_2 while Kahk *et al.* reason their proposed screened and unscreened states by the Kotani model. Although Wertheim *et al.* predicted that in such an approach the unscreened state would have a binding energy ~3 eV above the main line, Kahk *et al.*'s fits use significantly lower values (~0.6 eV).

In general, for rutile IrO_2 powders most literature findings agree on an Ir $4f_{7/2}$ binding energy value of 61.7 eV - 61.9 eV for Ir^{IV}. Only Hara *et al.*⁷ claim to have a considerable amount of Ir^{III} in commercially available IrO_2 powder and suggest a binding energy of 62 eV for Ir^{III} and 63.7 for Ir^{IV}. Similarly, Augustynski *et al.*⁸ attribute a binding energy of 61.6 eV to Ir^{III} in a compound of Ir₂O₃, for which no crystallographic data is available, and a binding energy of 62.7 eV to Ir^{IV} in IrO₂.

Several groups deconvoluted the recorded Ir 4f spectra and a wealth of different line shapes and interpretations of additionally present species has been proposed.⁶⁻¹² Especially the spectra of anodized iridium and of iridium oxohydroxides were found to be broader than those of rutiletype IrO₂. Augustynski *et al.*⁸ fit an additional peak at 1.6 eV above the main line of rutile-type IrO2 and attribute this to Ir^{VI} present in commercially available IrO₂ due to surface oxidation. Similarly, Atanasoska *et al.*⁹ fit peaks at 1.4 eV and 6.3 eV above the main line of rutile-type IrO₂, which is similar to the fit proposed in this work. However, in their fits symmetric line shapes are used also for the main line, which is unexpected for metallic conductors. In addition, they ascribe the peak seen at 1.4 eV above the main line to Ir in an oxidation state of higher than IV, whereas we show in this work that the feature ~1 eV above the main line is to be interpreted as a shake-up satellite of Ir^{IV} species. Casalongue *et al.*¹⁰ assign an oxidation state of V to species

	sample type	BE / eV	type / fit shape	BE / eV	type / fit shape	BE / eV	type / fit shape
Atanasoska <i>et al.</i> 9	IrO ₂ (thermal de- composition IrCl ₃)	61.2	lr ^{i∨} / GL	62.6	lr ^{>ı∨} / GL	67.5	unknown/ GL
Augustynski ⁸	IrO ₂	62.7	lr ^{i∨} / GL	64.3	lr ^{∨ı} / GL		
	Ir_2O_3	61.6	Ir ^{III} / GL				
	anodic IrO _x	62.9	lr ^{ı∨} / GL	64.3	lr ^{∨ı} / GL		
Casalongue et al. ¹⁰	Ir (IV) oxide nanoparticles	61.5	Ir ^{ı∨} / G-DS	62.2	Ir [∨] (only present during OER) / G-DS		
Hall <i>et al.</i> ¹²	anodic IrO _x	61.2	lr ^{ı∨} / GL	63.1	oxide-hydroxide / GL		
Hara <i>et al.</i> 7	IrO ₂ powder	62	Ir ^{III} / not specified	63.7	Ir ^{IV} / not specified		
Kahk <i>et al.</i> 6	IrO ₂ powder	61.7	Ir ^Ⅳ screened / GL	62.4	Ir ^{i∨} unscreened / GL	74.5	satellite/ GL
Kim <i>et al.</i> ¹³	IrO ₂ powder/anodized Ir electrode	61.9	Ir ^{ı∨} / no fit	63.4	Ir ^{∨ı} / no fit		
Kötz <i>et al.</i> ¹⁴	IrO ₂ (reactively sputtered)	61.8	lr ^Ⅳ / no fit				
	anodic IrO _x	62.4	not specified / no fit				
Peuckert et al. ¹⁵	IrO ₂ (thermally oxidized Ir)	61.9	lr [™] / no fit				
	anodic IrO _x	61.2	not specified / no fit				
Wertheim <i>et</i> <i>al.</i> ⁵	IrO ₂ single crystal	61.6	Ir ^Ⅳ / calculated asym.				
Folkesson ¹⁶	IrCl ₃	62.6	Ir ^{III}				

Table S4: Literature values of $Ir4f_{7/2}$ binding energies of IrO_x and $IrCl_3$. Fit shape abbreviations: GL:Gaussian-Lorentzian, G-DS:Gaussian convoluted Doniach-Šunjic.

appearing at 0.7 eV above their asymmetric main line during OER which encouraged Nong et al.¹¹ to also mention that the species they observe at higher binding energy after OER might be Ir with an oxidation state higher than IV. Furthermore, Kim *et al.*¹³ discuss about the presence of Ir^{VI} on anodized Ir electrodes as they observe intensity at binding energies 2.5 above the main line. It needs to be noted that all assignments of higher oxidation states than IV for iridium were based simply on the shifts of the components to higher binding energy, although Kötz *et al.*¹⁴

and Hall *et al.*¹² had pointed out that there might not be a correlation between higher oxidation state and higher binding energy of iridium species. In line with this advice, the Ir 4f binding energy of IrCl₃, with Ir in oxidation state III, was found to be at higher values than those of rutile IrO₂ with Ir in oxidation state IV (62.6 eV vs. 61.8 eV). A well-defined reference material with Ir in oxidation state V has not yet been characterized *via* XPS to the best of our knowledge. In the present study of the OER-active X-ray amorphous IrO_x, neither from our TPR measurements nor from the charge balance in the employed defect model we see evidence for the presence of Ir^V but only for Ir^{III}, which is why we attribute the additional peak located 0.6 eV above the main line of Ir^{IV} to Ir^{III} species.

An alternative technique to monitor the oxidation state of Ir is X-ray absorption spectroscopy, which several groups have used *in situ* to relate changes in the white line of the Ir L-edge with the present Ir oxidation state.¹⁷⁻¹⁹ For electrodeposited, hydrated Ir oxohydroxide films, it was observed that the white line is broadened and shifted to higher excitation energies with increased potential. In comparison with reference compounds (IrO₂ and IrCl₃), these results were interpreted as to initially have Ir in oxidation states III and IV and to later have in addition Ir in an oxidation state of up to V present during OER. All these studies restricted their investigations to monitoring changes in the metal states, whereas possible changes in their environment, hence the oxygen states, were not considered.

8 Theoretical calculations

Density functional theory (DFT) calculations were performed with the Quantum ESPRESSO package version 5.1.2²⁰ using the Perdew, Burke, and Ernzerhof (PBE) exchange and correlation potential²¹ with spin polarization and scalar relativistic corrections. Ultrasoft pseudopotentials were taken from the PS library²² and two Gauge-Including Augmented Wave (GIPAW) projectors were included for the I=1 channel of the oxygen pseudopotential to allow us to compute the O K-edge spectra. A plane wave basis set was employed with a kinetic energy cutoff of 50 Ry and a charge density cutoff of 500 Ry. A **k**-point mesh equivalent to (8x8x8) for the 24 atom cell shown in Figure S6 was used in all calculations along with Marzari-Vanderbilt cold smearing²³ with a smearing parameter of 0.005 Ry.



Figure S6: (left) 24 atom supercell of rutile IrO₂ used in this work. (right) Supercell with Ir vacancy in the middle.



Figure S7: (left) Ir-O internuclear distances and angles around an iridium atom in rutile IrO₂. (right) Internuclear distances in second and third coordination spheres around an iridium atom in rutile IrO₂.



Figure S8: (left) Ir-O internuclear distances and angles around an iridium vacancy in rutile IrO₂. (right) Internuclear distances in second and third coordination spheres around an iridium vacancy in rutile IrO₂. Both results are shown after cell relaxation.

The rutile cell volume was optimized, resulting in a=b=4.56 Å and c=3.19 Å for the crystallographic unit cell, in good agreement with the a=b=4.51 Å and c=3.16 Å measured experimentally.²⁴ lonic relaxations were performed until all components of the forces were less than 10^{-3} a. u. while the total change in energy was simultaneously less than 10^{-4} a. u. The vacancy was computed with ionic relaxation alone and with both ionic and cell relaxation, the latter of which led to a compression of c to c=3.17 Å with no noticeable change in the calculated spectroscopic properties.

Core level binding energies (BE) were computed using the Δ SCF method to accurately recover initial and final state effects.²⁵ The relative O 1s BEs were shifted to absolute BEs using a reference calculation on a (4x4x4) supercell of IrO₂, for which we took the measured O 1s BE to be 530.0 eV. The relative Ir 4f BEs were shifted relative to a reference calculation on a (4x4x4) supercell of Ir metal, which we took to have an Ir 4f_{7/2} BE of 60.8 eV. We verified that the relative BEs in IrO₂ were converged to better than 0.1 eV with our computational setup, including super cell size.

Oxygen K-edge spectra were computed from Fermi's golden rule using the XSpectra package.^{26, 27} Because powders were used in the experiments, we report the trace of the computed absorption cross section tensors. These computed spectra were convoluted using a Lorentzian with an energy dependent linewidth, $\Gamma(E)=\Gamma_0+\Gamma(E)$, to account for lifetime broadening. The natural linewidth of oxygen, 0.14 eV,²⁸ was used for Γ_0 . The energy dependence was assumed to scale linearly, $\Gamma(E)=0.1(E-E_f)$. Gaussian broadening (FWHM=0.6 eV) was also introduced to account for instrument resolution and phonon broadening. Because we expect the oxygen species in the local distortions in the amorphous structure to further broaden the spectra we used a slight larger FWHM, 0.8 eV, for the linear combination of O^L and O^{IL} spectra shown in Figure 3 of the manuscript. The Fermi energy of each computed spectrum was set to the computed O 1s BE of the absorbing atom. With this method the O K-edge spectrum of the bulk oxide, IrO₂, was well reproduced without a core hole on the absorbing atom.





Figure S10: Calculated DOS of rutile-type IrO₂ without (left) and with (right) spin-orbit coupling.



Figure S11: Calculated PDOS(d) of Ir^{IV} (left) and Ir^{III} (right) in presence of Ir 4f core holes. Strong features at ~1 eV (left) and ~1.5 eV (right) cause shake-up satellites in Ir 4f spectra.

We also computed the O1s and Ir4f binding energies using constrained DFT²⁹ to access the properties of IrO_x with formally O^{II-} and Ir^V . To do so we employed the IrO_2 supercell with an iridium vacancy (Figure S8) while constraining the occupation of the O2p states to be within 0.1 electrons of their occupations in defect-free rutile-type IrO_2 , where the localized occupation matrices were defined by projecting on atomic pseudo-wave-functions.³⁰ We found that, while iridium with a computed Ir 4f binding energy of 62.5 eV was present, the under-coordinated oxygen atoms have a computed O1s binding energy of ~527 eV, significantly lower than anything observed experimentally.

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