Identification of reactive oxygen species in iridium-based OER catalysts by *in situ* photoemission and absorption spectroscopy

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"One never notices what has been done; one can only see what remains to be done."

(Marie Curie)

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Abstract

A change in our energy supply from fossil fuels to intermittent renewables requires energy storage capacity. Part of this capacity may be delivered from chemical energy conversion relying on H_2 as basic fuel. Renewable H_2 can be generated using proton exchange membrane (PEM) electrolyzers able to adapt to the varying voltage inputs of intermittent sources. Such PEM electrolyzers operate in acidic environments requiring corrosion-resistant catalysts for the H_2 and O_2 evolution reactions (HER & OER). Especially the OER is challenging and typical catalysts use rare and precious iridium oxides. Minimizing costs by reducing the iridium usage requires knowledge-based catalyst design: Favorable iridium oxide surface configurations need to be identified.

X-ray photoemission and Near-edge X-ray absorption fine structure spectroscopy (XPS & NEXAFS) are powerful techniques to characterize surfaces. Therefore, having observed the increased catalytic OER activity of X-ray amorphous IrO_x when compared to rutile-type IrO_2 , these techniques were combined with theory to identify respectively present iridium and oxygen species based on their signatures in the electronic structure. While rutile-type IrO_2 was confirmed to consist only of Ir^{IV} and O^{II-} , the more active amorphous IrO_x was observed to contain Ir^{III} and O^{I-} in addition.

The electron deficiency of the O^{I-} species led to the suspicion that they may be good electrophiles and enhance the OER activity. Therefore, their character and reactivity were tested with the prototypical probe molecule CO. By monitoring both the gas phase composition and the spectroscopic fingerprint of O^{I-} in the NEXAFS of the OK-edge, the spontaneous reaction between O^{I-} and CO to form CO_2 at room temperature was observed, confirming the electrophilic character and exceptional reactivity of O^{I-} .

To test the involvement of O^{I-} species in OER catalysis, an electrochemical *in situ* cell was employed to monitor the electronic structure of an oxygen-evolving iridium surface by XPS and NEXAFS. These experiments confirmed the formation of a mixed-valent Ir^{III/IV} matrix hosting both O^{II-} and electrophilic O^{I-} species during the OER. Measurements near the onset of iridium's OER activity yielded a linear correlation between O^{I-} concentration and OER activity. Further, major parts of the O^{I-} contribution could be reversibly switched on and off when turning on and off the applied potential. These observations further indicated the intimate relationship between the presence of electrophilic O^{I-} species and the OER activity of iridium-based catalysts. This connection may be understood by analogy with photosystem II: Electrophilic oxygen species can facilitate the nucleophilic attack of water during the O-O bond formation.

This thesis demonstrates that the integration of electrophilic O^{I-} species is a crucial design criterion for OER catalysts and explains why iridium is a good choice: It has the propensity to form electrophilic O^{I-} species enhancing the O-O bond formation.

Zusammenfassung

Die Umstellung der Energieversorgung von fossilen Brennstoffen auf erneuerbare Energien verlangt Speicherkapazitäten. Teile dieser Kapazitäten können durch chemische Energiekonversion basierend auf H₂ als Brennstoff, produziert von Protonen-Austausch-Membran (PEM)-Elektrolyseuren, generiert werden. PEM-Elektrolyseure arbeiten in sauren Elektrolyten, weshalb korrosionsresistente Katalysatoren für die H₂und O₂-Evolutionsreaktionen (HER & OER) benötigt werden. Die OER stellt eine besondere Herausforderung dar. Typische OER-Katalysatoren verwenden seltene und edle Iridiumoxide. Bei der Kostenminimierung durch einen verringerten Iridiumverbrauch spielt das wissensbasierte Katalysatordesign, welches ein grundlegendes Verständnis vorteilhafter Oberflächenspezies voraussetzt, eine wichtige Rolle.

Mit Röntgenphotoemissions- und -Nahkanten-Absorptions-Feinstruktur-Spektroskopie (XPS & NEXAFS) können Oberflächen charakterisiert werden. Daher wurden diese Methoden nach der Feststellung der erhöhten OER-Aktivität von röntgenamorphem IrO_x im Vergleich zu kristallinem Rutil-Typ IrO₂ mit theoretischen Rechnungen kombiniert, um die jeweils anwesenden Ir- und O-Spezies auf Basis ihrer Signaturen in der elektronischen Struktur zu identifizieren. Es wurde bestätigt, dass Rutil-Typ IrO₂ nur aus Ir^{IV} und O^{II–} besteht, während amorphes IrO_x zusätzlich Ir^{III} und O^{I–} enthält.

Das Elektronendefizit der O^{I–}-Spezies legt einen für die OER-Aktivität möglicherweise vorteilhaften elektrophilen Charakter der Spezies nahe. Daher wurde deren Reaktivität und Charakter mit dem prototypischen Testmolekül CO untersucht. Durch Überwachung der Gasphasenzusammensetzung und des spektroskopischen Fingerabdrucks der O^{I–}-Spezies in der OK-Kante der NEXAFS wurde bei Raumtemperatur die spontane Reaktion von O^{I–}-Spezies mit CO zu CO₂ beobachtet, wodurch deren elektrophiler Charakter und besondere Reaktivität bestätigt wurden.

Die Beteiligung der O^{I–}-Spezies an der OER-Katalyse wurde mit einer *in situ*-XPS/NEXAFS-Zelle zur Beobachtung der elektronischen Struktur einer sauerstoffentwickelnden Ir-Oberfläche überprüft. Die Bildung einer gemischt-valenten Ir^{III/IV–} Matrix, die sowohl O^{II–} als auch elektrophile O^{I–}-Spezies beherbergt, wurde bestätigt. Experimente am Ansatz der OER-Aktivität ergaben eine lineare Korrelation zwischen der O^{I–}-Konzentration und der OER-Aktivität. Großteile des O^{I–}-Beitrages konnten durch ein Ein- und Ausschalten der angelegten Spannung ein- und ausgeschaltet werden. Diese Experimente sind ein weiteres Indiz für die intime Beziehung zwischen der Präsenz der O^{I–}-Spezies und der OER-Aktivität von Ir-basierten Katalysatoren. Dies kann in Analogie zum Photosystem II verstanden werden: Elektrophile O^{I–} können den nukleophilen Angriff von Wasser während der O-O-Bindungsbildung erleichtern.

Diese Arbeit demonstriert, dass die Integration von elektrophilem O^{I–} ein wichtiges Designmerkmal für OER-Katalysatoren ist und erklärt die Eignung von Iridium: Es beherbergt elektrophile O^{I–}-Spezies, die die O-O-Bindungsbildung erleichtern.

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Abbreviations

AEY	Auger electron yield
BE	Binding energy
BESSY	Berliner Elektronenspeicherring für Synchrotronstrahlung
BET	Brunauer-Emmett-Teller
BSE	Bethe-Salpeter Equation
CE	Counter electrode
CUS	Coordinatively unsaturated site
CV	Cyclic voltammetry
DEMS	Differential electrochemical mass spectrometry
DFT	Density functional theory
DOS	Density of states
DS	Doniach-Šunjić
DSC	Differential scanning calorimetry
EDX	Energy-dispersive X-ray spectroscopy
$E_{\mathbf{F}}$	Fermi energy
EXAFS	Extended X-ray absorption fine structure
FWHM	Full width at half maximum
GIPAW	Gauge-including augmented wave projector
GL	Gaussian-Lorentzian
HER	Hydrogen evolution reaction

HZB	Helmholtz-Zentrum Berlin
IMFP	Inelastic mean free path
ISISS	Innovative station for <i>in situ</i> spectroscopy
KE	Kinetic energy
LDA	Local density approximation
LSV	Linear sweep voltammetry
NAP-XPS	Near-ambient-pressure X-ray photoemission spectroscopy
NEXAFS	Near-edge X-ray absorption fine structure
OER	Oxygen evolution reaction
PBE	Perdew, Burke, Ernzerhof
PDOS	Projected density of states
PE	Pass energy
PEEK	Polyether ether ketone
PEM	Proton exchange membrane
PS II	Photosystem II
QE	Quantum ESPRESSO
QMS	Quadrupole mass spectrometry
RE	Reference electrode
SEM	Scanning electron microscopy
SCE	Saturated calomel electrode
SCF	Self-consistent field
SCLS	Surface core level shift
SGL	Gaussian-Lorentzian sum form
SHE	Standard hydrogen electrode
TEM	Transmission electron microscopy

TEY	Total electron yield
TG	Thermogravimetry
TPR	Temperature-programmed reduction
UHV	Ultra-high vacuum
USPP	Ultra-soft pseudopotential
WE	Working electrode
WOC	Water oxidation complex
XAS	X-ray absorption spectroscopy
XRD	X-ray diffraction
XPS	X-ray photoemission spectroscopy

1 Introduction

This first chapter serves as general introduction to highlight the interest in the identification of iridium and oxygen species contained in iridium-based oxygen evolution reaction (OER) catalysts.

Initially, Section 1.1 addresses the possibly crucial role of hydrogen production from water splitting in the energy challenge with respect to energy storage. Accordingly, Section 1.2 outlines the fundamentals of H₂ production from water by electrolysis, points out the OER as limiting factor of this process, and describes how iridium oxides have been identified as most suitable OER catalyst materials in acidic media. Subsequently, Section 1.3 focuses on iridium oxide as OER catalyst by describing suggested OER mechanisms and efforts to elucidate the active surface sites of this material. In this respect, Section 1.3 furthermore alludes to the remaining open questions related to OER-active iridium oxide surface species. Section 1.4 gives a short introduction to the measurement techniques employed throughout this work aiming to address these remaining questions, X-ray photoemission spectroscopy (XPS) and Near-edge X-ray absorption fine structure (NEXAFS). Furthermore, density functional theory (DFT) is outlined since it was used to help in the identification of fingerprint features observed by XPS and NEXAFS. Section 1.4 concludes with the presentation of an *in situ* XPS and NEXAFS cell suitable to monitor surface species present on oxygen-evolving iridium surfaces. Finally, Section 1.5 derives the objectives of this work from the previous Sections 1.1 to 1.4 and presents an outline of the thesis.

1.1 The role of hydrogen in the energy challenge

In 2015, the world's total primary energy supply amounted to 160 000 TWh, 81.4% of which was delivered by coal, oil, and natural gas resulting in CO_2 emissions of 32.2 Gt.¹ However, in order to meet the goal of the 2015 United Nations Climate Change Conference to limit global warming to 1.5 K above pre-industrial levels,² the global energy demand of 240 000 TWh projected for 2040³ has to be provided close to carbon-neutral, hence a reduction to less than 10 Gt CO_2 equivalents (i. e. one tonne per capita including all carbon-containing green house gases) is needed.⁴ Therefore, rapid integration of low emission renewable energy technologies is required. Wind and solar power are obvious alternatives to fossil energy carriers given the vast abundance of wind and solar radiation. Indeed, Germany has integrated wind power and photovoltaics into the electricity grid at an enormous pace: While in 2000 their share in the total electricity generation amounted to only 1.6%,⁵ in 2015 it accounted for 19.3%.⁶ Nevertheless, as highlighted in Figure 1.1, which shows energy production over a typical summer week in Germany,⁷ these renewable alternatives have a major drawback from an energy politics point of view: The are intermittent.



Figure 1.1: Net electricity production from wind and solar power for public electricity generation in Germany. Datasoures: 50 Hertz, Amprion, Tennet, TransnetBW, EEX.⁷

Such intermittency is neither tolerated by electricity grids, which require stable feeding conditions, nor by consumers, who demand a reliable electricity supply. Currently, these highs and lows in renewable electricity generation are buffered by conventional sources like coal or gas power plants. When aiming to limit and finally abolish the dependence on such high-emission technologies, the need for flexible and fast-responding storage options for renewable energies becomes obvious.⁸

An attractive solution to this requirement is chemical energy conversion.⁹ Therein, excess energy of intermittent sources is stored in chemical bonds and released when demanded. The major pillar of such a storage scenario is to generate hydrogen by splitting water into its principal components, H_2 and O_2 , via electrolysis.^{9,10} The H₂ molecule itself has the highest gravimetric storage capacity of all chemical compounds.^{10,11} The energy stored in H_2 can be recovered through a reaction with O_2 in combustion engines or fuel cells producing only water. Furthermore, H₂ is a valuable reactant for chemical industry and can be used to synthesize fuels like hydrocarbons, ammonia, or methanol.^{9,11} Despite its benefits, the technology for renewable hydrogen produced from water requires major improvements before it can become a viable solution. To see this clearly, consider the staggering statistic that hydrogen generation by water electrolysis accounts for only 4% of the hydrogen currently produced, with the remaining 96% obtained from fossil fuels.¹⁰ Thus, the successful implementation of cost-effective water electrolyzers capable of storing excess energy of intermittent renewable sources by producing hydrogen would have the potential to make industry less dependent on fossil fuels and to provide it with the basic fuel for a sustainable cycle based on renewable energies and chemical energy conversion.

When aiming to combine intermittent renewable sources with electrolyzers, the latter need to be capable of coping with the varying power inputs of wind and solar energy. While current electrolyzer setups based on alkaline water electrolysis lack this compatibility, a more recent technological approach based on proton exchange membranes (PEM) is able to adapt to varying input voltages.^{12,13} The challenge associated with this PEM-based technology is its highly demanding acidic operation environment. Corrosion-resistant catalysts are needed in such an acidic environment. Unfortunately, these catalysts are usually based on expensive and rare noble metals.^{12,13} And together with the large electrolyzer stack costs, the lack of suitable and cost-effective catalyst materials hinders the maturation of PEM-based electrolyzer systems.¹² While reducing the stack costs will require intelligent engineering solutions, the development of new catalysts requires chemists and material scientists to tailor highly efficient and stable materials. A prerequisite for such a design is a fundamental understanding of favorable electrode surface configurations.

1.2 Hydrogen production by water electrolysis

The overall water splitting reaction into hydrogen and oxygen in acidic environments, Equation (1.1), can be divided into two half reactions as described by Equations (1.2) and (1.3).¹³ After water has been oxidized at the anode during the oxygen evolution reaction (OER), protons are transported through the electrolyte and finally reduced at the cathode during the hydrogen evolution reaction (HER).¹²

Total :	$2\mathrm{H_2O} \longrightarrow 2\mathrm{H_2+O_2}$	$E = 1.23 \mathrm{V} \mathrm{vs.} \mathrm{SHE}$	(1.1)
Anode :	$2\mathrm{H_2O} \longrightarrow 4\mathrm{H^+} + \mathrm{O_2} + 4\mathrm{e^-}$	$E = 1.23 \mathrm{V} \mathrm{vs.} \mathrm{SHE}$	(1.2)
Cathode :	$4 \mathrm{H^+} + 4 \mathrm{e^-} \longrightarrow 2 \mathrm{H_2}$	E = 0 V vs. SHE	(1.3)

Considering thermodynamics at standard conditions, electrochemical water splitting has a molar enthalpy change of $\Delta H = +286$ kJ and a Gibbs Free Energy change of $\Delta G = +237$ kJ per mole of water. Hence, water electrolysis is an endothermic and non-spontaneous process. That is, energy input is needed to drive the reaction.¹³ At equilibrium, the Gibbs Free Energy is directly linked to the minimum electrical energy $2FV_{rev}$ required for splitting one mole of water via the following equation:

$$\Delta G = 2FV_{rev} \tag{1.4}$$

Here F is the Faraday constant and 2 is the number of transferred electrons. A reversible cell potential V_{rev} of 1.23 V results for an ideal process.¹³ In real systems, however, voltages considerably higher than these 1.23 V are required to successfully drive the reaction. The reasons for this need are so-called overpotentials that arise on real electrodes due to sluggish reactions, diffusion limitation, slow charge transfer kinetics, or ohmic losses.¹⁴ To minimize the connected energy losses, suitable electrocatalysts with overpotentials as small as possible are employed. In water electrolysis with state-of-the-art electrocatalysts, the overpotentials due to the sluggish OER far outnumber the overpotentials due to the HER.¹³ Owing to the necessary transfer of four electrons and four protons to release one oxygen molecule, a complex reaction mechanism forms the basis of the OER (see Section 1.3.1). Therefore, water electrolysis research is centered on understanding the OER to markedly improve electrolyzer cell performances.

Since the 1940s, many research groups have aimed to find and improve suitable catalysts for the OER.¹⁵ Especially in the acidic environment of proton exchange membrane (PEM) electrolyzers the primer requirement for the electrocatalyst is stability against corrosion. Typical candidates for electrode materials are noble metals like Pt, Ir, or Ru due to their stability in corrosive environments. Early on, it was found that oxide lay-

ers form on these noble metal surfaces prior to oxygen evolution.¹⁶ This finding led researchers to consider conductive metal oxides as electrocatalysts for the OER.

For being able to predict well-suited materials, researchers tried to correlate inherent material properties with catalytic activity. Rüetschi and Delahay¹⁷ proposed the energy of the metal-hydroxide bond to be a crucial parameter needing optimization for a good catalyst while Trasatti^{18,19} correlated the enthalpy of redox transitions from lower to higher oxides with catalytic activity. As a result, the volcano curve in Figure 1.2 evolved, revealing an optimum enthalpy for this redox transition: Neither too strong nor too weak enthalpies of the transition are desired.



Figure 1.2: Electrocatalytic activity for the OER at oxide electrodes over the enthalpy of lower to higher oxide transition. Circles indicate alkaline, dots acidic solutions. Reprinted from Trasatti, S., Electrocatalysis in the anodic evolution of oxygen and chlorine, *Electrochim. Acta*, **1984**, 29, 1503-1512 with permission from Elsevier.

In the past decade, theoretical calculations have become more prominent tools in the search for a suitable descriptor for catalytic activity. Based on scaling relationships, Rossmeisl *et al.*^{20,21} proposed the binding energy of oxygen species as a suitable indicator: On the one hand, the binding energy between oxygen and the surface needs to be high enough for oxygen species to readily adsorb. On the other hand, they should not be bound too tightly as later oxygen needs to desorb from the surface and form molecular oxygen. In agreement with prior experimental findings and activity measurements, ^{18,19,22,23} the noble metal oxides most closely approaching this criterion are RuO₂ and IrO₂. Although RuO₂ shows a lower overpotential than IrO₂, it is not stable under oxidizing conditions due to the formation of higher-valent volatile oxides.¹³ Owing to its higher stability, IrO₂ is the better alternative and considered the state-of-the-art OER catalyst.^{24,25}

While theoretical calculations mainly focused on the investigation of rutile-type IrO₂,²¹ experiments yielded that amorphous forms of iridium oxides are considerably more active than crystalline ones.²⁶ The reasons for the superiority of amorphous over crystalline iridium oxides in catalyzing the OER have not yet been resolved.

1.3 Iridium-based electrocatalysts for the oxygen evolution reaction (OER)

This section provides an overview of the research done in terms of understanding the OER on Ir-based catalysts for water electrolysis. First, Section 1.3.1 pays attention to mechanisms proposed for describing the reaction steps of the OER on iridium. Second, Section 1.3.2 discusses approaches toward unveiling the active species on Ir surfaces.

1.3.1 Mechanism

The mechanism of the OER consists of various reaction steps. Especially those steps kinetically limiting the OER need to be understood in order to design novel catalysts. The mechanisms proposed for the OER typically consist of several intermediate steps including water adsorption, proton abstraction, oxygen-oxygen bond formation, and the release of molecular oxygen.²⁷ Plenty of models have been derived based on classical current-potential-time measurements.^{28–30} Of these, an often cited mechanism is the "Electrochemical oxide path" of water oxidation, Equations (1.5) to (1.7), introduced by Bockris in 1956.²⁸ Damjanovic *et al.*^{29,31} suggested it to be valid on Ir a decade later:

$$^{*} + H_{2}O \longrightarrow ^{*} - OH + H^{+} + e^{-}$$
(1.5)

$$^* - OH \longrightarrow ^* - O + H^+ + e^-$$
 (1.6)

$$2^* - O \longrightarrow O_2 + 2^*$$
 (1.7)

* represents the active site for the OER. In this reaction scheme, water is first adsorbed dissociatively at an active surface site while separating one proton, Equation (1.5). Sub-sequently, another proton is split off, Equation (1.6), which Damjanovic *et al.* considered to be rate determining. In the last step, two oxygen atoms bound to the surface form molecular oxygen, which desorbs form the surface.

With regard to metal oxides (MO_x), Fierro *et al*.³² adapted this model. They described two parallel reaction paths, both in which dissociation of water is the first step:

$$MO_x + H_2O \longrightarrow MO_x(^{\cdot}OH) + H^+ + e^-$$
 (1.8)

Fierro *et al.* considered the subsequent step to be determined by the interplay between the oxide and the hydroxyl radical. For the case of physisorption, in their model oxygen evolves over a hydrogen peroxide intermediate electrochemically:

$$MO_x(OH) \longrightarrow MO_x + H^+ + \frac{1}{2}O_2 + e^-$$
 (1.9)

For the case of chemisorption, in their model a higher oxide forms before a decomposition of this oxide takes place during oxygen evolution:

$$MO_{x}(^{\cdot}OH) \longrightarrow MO_{x+1} + H^{+} + e^{-}$$
 (1.10a)

$$MO_{x+1} \longrightarrow MO_x + \frac{1}{2}O_2$$
 (1.10b)

To find out whether the oxide layer on IrO_2 is actively participating in the mechanism of the OER as described in Equations (1.10a) and (1.10b), Fierro *et al.* used differential electrochemical mass spectrometry (DEMS) with isotope-labeled water (H₂¹⁸O, 66 %-70 %). During cyclic potential sweeps of an originally $Ir^{16}O_2$ surface, the amount of detected ${}^{16}O_2$ decreased while simultaneously the amount of ${}^{16}O^{18}O$ increased until reaching steady concentrations. This observation implies that oxygen from the lattice is released during oxygen evolution and is replaced by oxygen from water. Furthermore, Fierro *et al.* reported that $Ir^{18}O_2$ is formed on the surface owing to the exchange of oxygen atoms. Nevertheless, they found only 1 % of the lattice oxygen was involved in the OER. Therefore, Fierro *et al.* concluded that only the outer surface of the IrO_2 layer is actively involved in the OER.

Nørskov and coworkers^{20,21,33} performed density functional theory (DFT) calculations to contribute to the understanding of the OER mechanism. They concluded that a direct recombination of oxygen atoms (as in Equation (1.7)) should have a fairly high activation barrier and is therefore unlikely to take place.^{20,33} Instead, they suggested an associative mechanism via a peroxide HOO* species:

$$2 \operatorname{H}_2 O \longrightarrow \operatorname{HO}^* + \operatorname{H}_2 O + \operatorname{H}^+ + e^-$$
(1.11)

$$\longrightarrow O^* + H_2O + 2H^+ + 2e^-$$
 (1.12)

$$\longrightarrow \text{HOO}^* + 3 \text{ H}^+ + 3 \text{ e}^- \tag{1.13}$$

$$\longrightarrow O_2 + 4 H^+ + 4 e^- \tag{1.14}$$

in which * denotes an active surface site. By DFT calculations of Gibbs Free Energies, they concluded that on IrO_2 the potential-determining step of the OER is the O-O bond formation of the HOO* intermediate. What remains unresolved is which type of surface species of the iridium oxide catalyst, which according to Fierro *et al.*'s³² measurements is actively involved in the OER, enhances the formation of this intermediate.

1.3.2 The active surface

Identifying active surface species that catalyze the investigated reaction is a common aim in basic heterogeneous catalysis research. In electrocatalysis in general, and for investigating the OER on iridium oxides in particular, it is therefore important to be aware of surface modifications induced by voltage alterations. In the following, attempts to describe the species present on iridium oxide surfaces at different applied potentials will be presented.

A technique commonly used to characterize electron transfer processes at electrodes is cyclic voltammetry.³⁴ For Ir, a peculiar behavior in cyclic voltammetry is observed.^{35–42} After the immersion of an Ir sample into acidic solution and subsequent potential sweeps between the hydrogen (0 V vs. the standard hydrogen electrode (SHE)) and the oxygen (\approx 1.5 V vs. SHE) evolution potentials, the course of the cyclic voltammogram significantly changes with increasing number of cycles (see Figure 1.3): Initially, the anodic and cathodic peaks are small whereas they can be clearly identified at high cycle numbers. Furthermore, at high cycle numbers the rate of the OER is enhanced.



Figure 1.3: Effect of continuous cycling on the cyclic voltammogram of Ir in 1M H_2SO_4 . a-h were recorded in 5 min intervals, a being the first, h being the last measurement. Reprinted from Capon, A., and Parsons, R., The effect of strong acid on the reactions of hydrogen and oxygen on the noble metals. A study using cyclic voltammetry and a new teflon electrode holder, *J. Electroanal. Chem.*, **1972**, 39, 275-286 with permission from Elsevier.

Nowadays, it is generally accepted that an amorphous hydrous oxide layer with an increased surface area forms on Ir, having a higher charge storage capacity and being a better electrocatalyst than the pure metal.⁴³ The main oxidation and reduction processes at 1 V vs. SHE (see Figure 1.3) are accompanied by a color change from bleached to black and show little hysteresis. Buckley et al.³⁸ related the lack of hysteresis and the color change directly to the formation of the hydrous oxide layer and explained it by a mere stoichiometry and valence change within this iridium oxide layer at 1 V vs. SHE. Numerous authors agreed that the interconversion takes place via a proton transfer rather than via an oxygen exchange as the ionic radius of oxygen is considered too large for a reversible mechanism.^{38–42} For activated surfaces, the overall measured cathodic current is smaller than the anodic from which Buckley et al.³⁸ concluded that during the cyclic oxidation of Ir, two processes take place: First, Ir metal is irreversibly oxidized forming a hydrous Ir oxide layer. Second, the already present oxidized Ir is changing to a higher oxidation state. An example for a lower to higher oxide transition was given from Buckley et al. by the oxidation from a hydroxide to an oxide. With respect to a phase identification of the hydrous layer presenting a better catalyst than the pristine metal, Buckley et al. indicated that the film probably consists of a mixture of non-stoichiometric oxides, hydrated oxides, and hydroxides. Nevertheless, they also stressed that cyclic voltammograms are no reliable tools for an exact identification. Instead, they proposed XPS investigations to clarify the nature of the activated anodic film by the electronic structure fingerprints of contained species.

Indeed, a considerable number of ex situ investigations on Ir electrode surfaces combining electrochemical methods with surface science techniques like XPS exist.^{43–46} In a common procedure, the material is first stressed electrochemically in an electrolyte and, after emersion at a certain potential, the sample is transferred into UHV to perform surface-sensitive measurements. The virtue of this approach is that the nature of species constituting the surface of an electrochemically stressed Ir electrode can be explored. Depending on the selected emersion potential, different compositions of the Ir surface can be identified. With respect to the oxidation state changes in Ir, several groups suggested a change from the oxidation states II or III to IV in the main anodic peak at 1 V vs. SHE.^{39,47} In line with these suggestions and based on their XPS studies, Kötz et al.⁴⁵ stated that a tetravalent surface oxide or hydroxide was the starting point for oxygen evolution and corrosion on Ir. Furthermore, they found that upon polarization the total amount of oxygen species remained constant. At 0 V vs. the saturated calomel electrode (SCE), their O1s spectrum was dominated by hydroxy species whereas during the anodic potential scan, deprotonation caused an increase in the oxide contribution to the O1s signal. Thus they concluded that with increasing potential, oxide species grew at the expense of hydroxide species as it had already been predicted

by Buckley *et al.*³⁸ Kötz *et al.*^{44,45} suggested $IrO(OH)_2$ as starting point for the OER cycle and, based on shifts towards higher binding energies in the Ir 4f spectra of electrodes emersed at 1.5 V vs. SHE, IrO_3 as active site for the OER as well as a corrosion process.

However, these *ex situ* studies face several limitations. First, they are unable to monitor the surface during the OER. Thus, species only present during the reaction cannot be characterized. Second, after emersion at a certain potential, the sample needs to be transferred into UHV to perform surface-sensitive measurements. During this transfer, the sample is prone to undergo compositional modifications like oxidation when the transfer involves air exposure or dehydration of the hydrous film when brought into vacuum. Therefore, one cannot be sure that, after the emersion from the electrolyte and the transfer into the vacuum chamber, the surface probed with XPS has retained its original composition.^{43,45,48,49}

Due to these shortcomings, significant effort has been invested in the development of *in situ* methodology to assess the active state of electrode materials under working conditions (see Section 1.4.4). It is now possible to drive electrochemical reactions and simultaneously record XPS^{50–52} and XAS,^{53,54} hence to monitor the electronic structure of oxygen-evolving surfaces *in situ*.

Nevertheless, the interpretation of XPS and XAS measurements and the identification of relevant surface species on iridium and its oxides is challenging. While the literature agrees that hydrated and hydroxylated amorphous forms of iridium oxide with mixed iridium oxidation states have intrinsically higher OER activities than pristine iridium metal and crystalline rutile-type IrO₂,^{26,51,54} dissent remains about which types of iridium surface species form part of the catalytic OER cycle.^{51,54} The difficulties in pinpointing iridium oxidation states partly originate from the lack of well-defined oxidic iridium reference materials other than the tetravalent Ir in rutile-type IrO₂.⁵⁵ In addition, iridium species with different oxidation states present in non-conductive, non-oxidic reference materials show only small⁵⁶ or reverse⁵⁷ shifts in excitation or binding energy and usually overlap to a large extent. Finally, unambiguous speciation based on XPS has proven elusive and controversial because of the not fully understood peculiar Ir 4f line shape of iridium oxides, which cannot be fit with conventional line profiles.^{58–60} Hence, while in situ XPS investigations were interpreted to show the presence of iridium species with oxidation states of IV and V during the OER,⁵¹ in situ XAS measurements were deconvoluted into contributions of Ir^{III} and Ir^{V.54}

Finally, in order to further elucidate both the mechanism of the OER on iridium surfaces and active surface configurations, additional *in situ* studies are needed. Due to the lack of well-defined oxidic reference materials, comprehension of such *in situ* studies will require a combination with theoretical calculations able to identify the observed fingerprints of present species.

1.4 Spectroscopic methods and theory

Before introducing an *in situ* cell enabling the spectroscopic observation of the electronic structure of oxygen-evolving catalyst surfaces in Section 1.4.4, the principles of the techniques used are outlined. While Sections 1.4.1 and 1.4.2 describe X-ray photoemission and Near-edge X-ray absorption fine structure spectroscopy (XPS & NEX-AFS), Section 1.4.3 explains how density functional theory (DFT) calculations can aid in the interpretation of XPS and NEXAFS spectra.

1.4.1 X-ray photoemission spectroscopy (XPS)

X-ray photoemission spectroscopy (XPS) is a surface-sensitive technique that enables the investigation of occupied electronic states. Irradiation of surfaces with electromagnetic radiation of sufficiently high energy leads to the emission of photoelectrons from the sample based on the outer photoelectric effect explained by Einstein in 1905.⁶¹ XPS aims to analyze the respective characteristic kinetic energy of the emitted photoelectrons. The resulting spectrum of the emission lines enables the identification of the elements contained in the surface and their oxidation state.⁶² Classical XPS measurements are performed in ultra-high vacuum (UHV) to ensure high surface cleanliness and to prevent inelastic scattering of photoelectrons leaving the sample with gas molecules. The following description of the technique is based on references 63–65.

An XPS apparatus consists of three main parts: a photon source, the investigated sample, and a spectrometer. The penetration depth of the incident photons depends on their energy and usually amounts from a few to several micrometers. While penetrating the sample surface, the photons can transfer their energy $h\nu$ to bound electrons. These electrons may then leave the sample surface with the specific kinetic energy $E_{\rm kin}$, which depends on their binding energy $E_{\rm B}$ and the work function of the sample $\Phi_{\rm sample}$:

$$E_{\rm kin} = h\nu - E_{\rm B} - \Phi_{\rm sample} \tag{1.15}$$

Since the sample and the spectrometer are in electrical contact, their Fermi levels align. This alignment leads to a contact potential of $\Delta \Phi = \Phi_{\text{sample}} - \Phi_{\text{spectrometer}}$ that may deor accelerate the emitted photoelectrons. Therefore, the modified kinetic energy of the emitted photoelectrons is independent of the work function of the sample:

$$E_{\rm kin}^{\rm spectrometer} = h\nu - E_{\rm B} - \Phi_{\rm sample} + \Delta\Phi = h\nu - E_{\rm B} - \Phi_{\rm spectrometer}$$
(1.16)

The work function of spectrometers is usually between 4 eV and 5 eV. An exact calibration can be achieved by using metal standards. A constant Fermi level is the reference point for the binding energy of XPS.

To achieve an energy dispersive detection, the emitted photoelectrons are decelerated before entering the analyzer. Only electrons with a set pass energy per unit time are admitted. By varying the deceleration voltage, the entire spectrum is reproduced.

The high surface sensitivity of XPS results from the low inelastic mean free path (IMFP) of photoelectrons in solids (e. g. for Ir: $E_{kin}=130 \text{ eV IMFP}\approx 0.4 \text{ nm}$; $E_{kin}=1500 \text{ eV}$ IMFP $\approx 1.6 \text{ nm}$). Depending on the photon excitation energy used, XPS causes valence or core electrons to be excited from the sample. The latter are element and environment specific and are the basis for a chemical surface characterization.

Figure 1.4 shows a survey spectrum of a sputter-deposited iridium film on a proton exchange membrane that consists of the elements carbon, oxygen, fluorine, and sulfur. Besides the characteristic core level emission lines of the contained elements, the spectrum also features the so-called Auger emission lines (e. g. OKLL), which will be further addressed in Section 1.4.2. In addition to the core level and Auger emission lines, the survey spectrum has an unspecific background, which results from inelastic scattering of photoelectrons.



Figure 1.4: XPS survey of Ir-coated Nafion[®] 117 (60 s Ir sputtered) with an identification of the observed core levels.
This background can be subtracted to aid in the quantification of the elemental composition of the surface, for which an integration of the intensity of the core level emission lines as well as setup and element specific information like the photon flux, photoionization cross sections, and asymmetry parameters are required. Proper background subtraction can be a challenge in XPS. The most suitable ways to subtract XPS backgrounds are based on the methods developed by Shirley⁶⁶ and Tougaard.⁶⁷ In the former, the background intensity at a given point is proportional to the total integral peak intensity above the background towards lower binding energies while in the latter, the background intensity at a given point is proportional to the integral of the background intensity towards lower binding energies. Although Tougaard's method presents the most precise background approximation, Shirley's method is more commonly used since it requires smaller measurement ranges and copes more easily with overlapping peaks.

The binding energy shifts observed in XPS core levels can either be due to initial- or final-state effects. Initial-state effects are dominated by the properties of the atom prior to the photoemission process. For example, different oxidation states of a material may cause the electrons to be more or less strongly bound. In contrast, final-state effects are caused by relaxations or interactions occurring after the photoemission process. For example, in a simplified one electron picture, a photoelectron leaving the atom may interact with valence electrons on its way out and thereby lose discrete amounts of its kinetic energy by exciting valence electrons into unoccupied states above the Fermi energy. Such a discrete energy loss causes the appearance of so-called shake-up satellites towards higher energies in the binding energy spectrum. In how far such initial- and final-state effects influence the Ir 4f spectrum of iridium oxides is discussed in detail in Chapter 2.

For a speciation of recorded spectra, XPS peak fitting based on least-squares fits is a valuable tool. Depending on the nature of the core emission line, different line shapes are adopted. For non- or semi-conductors, Voigt line profiles, which are convolutions of Gaussian (instrumental, thermal, X-ray line shape broadening) and Lorentzian (life-time broadening) functions,⁶⁸ are appropriate while for metallic conductors the asymmetric Doniach–Šunjić⁶⁹ line shape, which takes into account electron screening, is most suitable.

1.4.2 Near-edge X-ray absorption fine structure (NEXAFS)

Near-edge X-ray absorption fine structure (NEXAFS) is a surface-sensitive X-ray absorption spectroscopy (XAS) technique that enables the investigation of unoccupied electronic states and is therefore complementary to XPS. NEXAFS is not only element specific but also sensitive to the local coordination environment of the investigated elements. The following description of the technique is based on references 70–72.

In NEXAFS, core electrons are not emitted from the sample as photoelectrons but excited into unoccupied bound states or into the quasicontinuum just above the ionization threshold. Dipole selection rules need to be fulfilled for transitions of electrons from occupied into unoccupied states. In NEXAFS, not the kinetic energy of emitted electrons but the photon excitation energy is scanned. Hence, monochromatized, tunable photon sources like synchrotrons are needed to perform NEXAFS experiments. Besides this requirement, the same setups can be used for XPS and NEXAFS. A schematic representation of the difference between XPS and XAS is given in Figure 1.5.



Figure 1.5: Schematic representation of the processes occurring during XPS and XAS. In XPS, core electrons are ejected above the vacuum level by the excitation of a photon with sufficiently high energy. Their kinetic energy is analyzed and provides information about occupied electronic states of the sample. In XAS, core electrons are lifted into unoccupied bound states above the Fermi level or into the quasicontinuum just above the ionization threshold. Electrons from higher shells fill the created core hole and either emit photons or transfer their energy to other electrons that are ejected as Auger electron from the sample. The amount of Auger electrons is proportional to the X-ray absorption of the sample and therefore delivers information about unoccupied electronic states of the sample. Drawn in the style of reference 71.

To investigate surfaces with the NEXAFS technique, indirect probes like Auger electrons or fluorescent radiation, which result during the annihilation of core holes created during the preceding absorption process, are used. While for elements with low atomic numbers *Z* Auger electron decay is the dominant process, radiative fluorescent decay prevails for elements with high *Z*. Since in this work only the electron yield of the oxygen K-edge was employed, the discussion will be limited to this detection principle.

Auger emissions result from an energy transfer from electron to electron. The process proceeds as follows in case of an OKLL transition (see Figures 1.4 and 1.5): An incident photon releases an electron from the K shell leaving behind a hole. This hole is filled by an electron from the L shell, which transfers its energy to another electron in the L shell. The energy transfer allows this electron to be ejected from the L shell and leave the sample. For each excitation energy, the amount of emitted Auger electrons is proportional to the absorption of X-rays of the material.

The emitted electrons can either leave the sample without further interaction and be detected directly with the analyzer in the fixed analyzer transmission mode. Or alternatively, they can interact with secondary electrons that subsequently also leave the sample and are simultaneously detected with an electron multiplier. The former detection mode is referred to as Auger electron yield (AEY) while the latter is called total electron yield (TEY) since it detects all electrons leaving the sample irrespective of their kinetic energy.

The high interaction of electrons with solids causes the electrons to have short IMFPs, as already discussed for XPS, granting the surface sensitivity of this technique. While for the AEY probing depths on the order of 2 nm - 3 nm result, the probing depth in the TEY mode is slightly higher on the order of 5 nm - 10 nm, since also very slow electrons leaving the sample are detected. In general, the signal-to-noise ratio of the TEY mode is higher than for the AEY mode due to its higher count rate.

1.4.3 Density functional theory (DFT)

Density functional theory (DFT) is a computational quantum mechanical method that relies on the electron density to compute the electronic ground state of a many-electron system in an external potential.⁷³ The advantage of DFT over other quantum mechanical computational methods is that it avoids the solution of the Schrödinger equation of a many-electron system and therefore tremendously reduces computational time and costs. In this work, DFT was used to aid in the interpretation of measured XPS and NEXAFS spectra. Therefore, DFT principles and how it can be used in combination with electronic structure measurements will be shortly outlined.

The Hohenberg-Kohn theorems deliver the foundation of modern DFT.⁷⁴ The theorems show that the ground state of a many-electron system with N electrons and its corresponding Hamiltonian can be solely derived from the electron density of the system. Hence, by using functionals of the electron density, the many-body problem of N electrons with 3N spatial coordinates is reduced to a problem of the only 3 spatial coordinates of the electron density. By a variational principle, the theorems further demonstrate that the correct ground state of a system minimizes its energy density functional.

To obtain the energy density functional, Kohn and Sham assumed that there exists a non-interacting system in a fictitious external potential with the same electron density as the interacting system.⁷⁵ With this assumption, the Schrödinger equation for an N-electron system is translated into N one-particle Schrödinger equations (or the Kohn-Sham equation), where the N independent particles move in an effective potential defined by the electron density. The ground state energy and density can then be solved for, which requires a self-consistent solution because of the effective potential's dependence on the density.

As solid-state systems are the focus of this thesis, the self-consistent solution of the Kohn-Sham equation was accomplished by expanding the Kohn-Sham orbitals in a plane-wave basis set. This approach is widely employed⁷⁶ and made practical by the efficient use of pseudopotentials.⁷⁷ These pseudopotentials replace the Coulomb potential describing the interaction between core electrons and the nucleus by a weaker effective potential that acts on pseudo wave functions. While these pseudo wave functions match the all electron wave functions outside of the core, they lack radial nodes inside the core by construction. This characteristic eases computational costs by drastically reducing the size of the plane-wave basis sets required to reach convergence. With this approach, it is, in principle, possible to find the ground state charge density and energy to an arbitrary accuracy. In practice, however, the Kohn-Sham equation contains an approximate expression for the exchange and correlation potential.

While some limits are known for the exchange and correlation potential, it is not known exactly; thus approximations for this term are unavoidable within the DFT framework. For IrO₂, it has been shown that the approximation by Perdew, Burke, and Ernzerhof (PBE)⁷⁸ recovers the ground state properties best⁷⁹ and is therefore used throughout this work. The PBE functional is a generalized gradient approximation, in which both the density and its local gradient are considered in the approximation of the exchange and correlation potential term. PBE is known to be well suited for metallic conductors since it recovers the uniform electron gas limit.⁸⁰

The aforementioned computational tools help to efficiently calculate atomic and electronic structures. Since these computations use approximations, their validity needs to be thoroughly confirmed. Part of this confirmation can be achieved by comparison of the computed atomic and electronic structures with measured data, e. g. lattice constants and valence band spectra. Once the benchmarking process is successful, additional information on physical properties of the system and its analogous can be computed with confidence in the results.

Of particular interest in this work are calculations of XPS core level binding energies and NEXAFS spectra. For the former, Pehlke and Scheffler⁸¹ showed that using the Δ SCF (self-consistent field) method within DFT recovers initial and final state effects in core level photoemission spectra. Relative binding energies can be calculated and shifted according to well-known calibration points. Hence, electronic structure fingerprints can be assigned to the respective species. When calculating NEXAFS spectra by DFT, however, caution is required since DFT's one-particle approach of solving the Schrödinger equation is not suitable for strongly interacting initial and final states.⁸² Nevertheless, for K-edges, especially OK-edges, which are of interest for this work, multielectronic interactions are weak and it has been demonstrated that DFT using pseudopotentials is able to excellently recover experimental spectra if careful benchmarking is performed.^{82,83} Therefore, DFT can be used to determine the influence of defects in the atomic and electronic structure of iridium oxides.

The exact calculation details and methods used will be given in the respective sections of Chapters 2 to 4.

1.4.4 *In situ* cell to monitor oxygen-evolving surfaces by XPS and NEXAFS

In order to tackle the pressure gap between electrochemical measurements in electrolyte and surface-sensitive spectroscopic investigations in UHV, devices combining these techniques have been developed.^{50–52} The first step towards enabling this combination was made by so-called near-ambient-pressure XPS (NAP-XPS) setups, in which XPS measurements at pressures in the low millibar range can be performed due to a combination of a differential pumping and an electrostatic lens system.⁸⁴ One of these systems is operated by the Fritz-Haber-Institut at the endstation of the ISISS (Innovative station for *in situ* spectroscopy) beam line⁸⁵ at the synchrotron radiation facility BESSY II/HZB (Berliner Elektronenspeicherring für Synchrotronstrahlung/Helmholtz-Zentrum Berlin). All XPS and NEXAFS measurements contained in this thesis were collected at this endstation.

The *in situ* cell for performing electrochemical experiments at this endstation will be described in the following. A similar approach has already been employed by Arrigo *et al.*⁵⁰ to investigate the OER and the active species on Pt for gas-phase water electrolysis. Throughout this thesis, the cell design originally introduced by Arrigo *et al.* was further improved. The two *in situ* cells employed in this work are depicted in Figure 1.6.



Figure 1.6: (left) Two-electrode *in situ* cell with sputtered Ir working and Pt counter electrode. (right) Three-electrode *in situ* cell with sputtered Ir working, Pt wire counter, and Ag/AgCl reference electrode. In both cells, water supplied from the rear diffuses through the desiccation cracks of the sputtered electrodes and the PEM and delivers the reactant molecules to the reaction chamber. While XPS and NEX-AFS are measured, the gas composition is monitored by on-line QMS. Through the connection to an external potentiostat, OER-relevant potentials can be applied to the working electrode.

The principle of the cells relies on the water permeability of proton exchange membranes (PEM), namely Nafion[®], and sputter-deposited metal electrode films. Due to the pressure difference between the liquid on one side of the membrane and the evacuated measurement chamber on the other, water diffuses through the desiccation cracks of the conductive, sputter-deposited electrodes and the PEM and delivers the reactant molecules to the working electrode, in the present case Ir. The pressure in the measurement compartment amounts to 0.1-10 Pa. The electrodes of the system can be connected to an external potentiostat and OER-relevant potentials can be applied while simultaneously recording XPS or NEXAFS. To monitor if oxygen is evolving from the working electrode surface, a quadrupole mass spectrometer (QMS) is attached to the measurement compartment.

Arrigo et al.⁵⁰ started off this measurement technique with a batch-like two-electrode cell in which only a small reservoir of water was supplied on the rear side of the PEM. This configuration led to short measurement times and variable measurement conditions since the reservoir dried out within less than an hour and therefore the amount of water transported through the membrane electrode assembly was not constant. In the first step of cell improvement throughout this work, the water supply of the twoelectrode cell was modified to allow continuous flow (see Figure 1.6 (left)), which increased the measurement times to several hours. In a second improvement step, a Ag/AgCl micro reference electrode was integrated into the cell to work under welldefined potential conditions (see Figure 1.6 (right)). The integration of the reference electrode led to further modifications of the cell setup. To ensure that the reference electrode was located closer to the working electrode than the counter electrode, the sputter-deposited Pt counter electrode film was replaced by an externally inserted Pt wire. The integration of the reference electrode further required the use of an electrolyte instead of water to prevent high ohmic losses between the electrodes. Finally, to enhance the corrosion stability of the cell, the stainless steel of the cell body was replaced by polyether ether ketone (PEEK). In both the two- and three-electrode cells, the electrical contact to the working electrode was achieved by a glassy carbon lid. Glassy carbon has better electrochemical resistivity than stainless steel and was able to prevent the strong corrosion, which had been observed when using stainless steel. Details on the cell and further information on the employed materials, the setup, and measurement techniques will be given in Chapter 4.

The virtue of this approach is that it makes the direct observation of iridium electrode surfaces via XPS and NEXAFS possible while the OER proceeds. Therewith, the cells enables the observation of the fingerprints in the electronic structure of iridium and oxygen species present during the OER, which will give hints about surface species favorable in catalyzing the OER.

1.5 Scientific objective and outline of this work

In order to pave the way for an energy storage system for intermittent renewable sources based on the fuel H_2 , the PEM water electrolysis technology requires major improvements. One of these required improvements is a cost-effective and stable catalyst. The state-of-the-art OER catalyst in acidic media is iridium oxide. Considering the previous research on Ir-based catalysts for the OER outlined in Sections 1.2 and 1.3, it is clear that many indications have been found with respect to the nature of the species in iridium oxides favoring its OER activity. Nevertheless, before being able to efficiently tailor Ir-based OER catalysts, several points concerning iridium and its oxides remain controversial in the literature and require further investigation:

- For being able to identify the type of species contained in different iridium oxide configurations based on XPS measurements, how can the peculiar XPS Ir 4f line shape of iridium oxide be explained? Is the line shape due to a physical/spectroscopic cause or are the reference materials simply composed of multiple species?
- Why are X-ray amorphous iridium oxides more active in catalyzing the OER than crystalline rutile-type IrO₂ and bare metallic iridium?
- What is the nature of the iridium and oxygen species present on iridium oxide surfaces during the OER and how is their presence related to the OER activity?

The objectives of this PhD thesis may be deduced from these unresolved questions:

- To elucidate the electronic structure of iridium and its oxides by combining theoretical calculations with experimental results, thereby resolving the origin of the Ir 4f line shape of iridium oxides and identifying fingerprint features of oxygen and iridium species contained in highly and less OER-active iridium oxides.
- To investigate the reactivity of surface species contained in highly OER-active iridium oxides by using the prototypical probe molecule CO.
- To identify surface species forming on oxygen-evolving Ir surfaces and contribute to a further understanding of the OER reaction mechanism on Ir by making use of *in situ* photoemission and absorption spectroscopy.

The following results part is divided into three chapters addressing these objectives.

Chapter 2* delivers a detailed understanding of the electronic structure of iridium metal and crystalline as well as X-ray amorphous iridium oxides. To gain this understanding and to resolve the controversy in literature about the peculiar Ir 4f line shape of iridium oxides, XPS and NEXAFS are combined with theoretical calculations. First, Chapter 2 describes the thorough characterization of two reference iridium oxide powders, one crystalline and one X-ray amorphous, using X-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), the Brunauer–Emmett–Teller (BET) method, thermogravimetry (TG), differential scanning calorimetry (DSC), temperature-programmed reduction (TPR), and finally linear sweep voltammetry (LSV) to assess their OER performance. Second, Chapter 2 points out the origins of the different Ir 4f line shapes and features in the OK-edges of iridium metal and the two reference iridium oxide powders, which enables a speciation of present iridium and oxygen species. Finally, Chapter 2 discusses *in situ* XRD and XPS/NEXAFS heating experiments of the amorphous iridium oxide powder that document its transformation into a crystalline configuration.

Chapter 3⁺ uses the knowledge about the electronic structure of highly OER-active X-ray amorphous iridium oxides acquired in Chapter 2 to identify reactive oxygen species contained in these materials by employing the prototypical probe molecule CO. First, Chapter 3 demonstrates that, without the addition of external oxygen, highly OER-active X-ray amorphous iridium oxides oxidize CO to CO₂ at room temperature in a stoichiometric reaction. Second, Chapter 3 asserts by a combination of quasi *in situ* XPS/NEXAFS measurements, *ab initio* calculations and a microcalorimetric analysis that the oxygen species spontaneously reacting with CO are those contained in the amorphous iridium oxide that have holes in their O2p states, i. e. the electrophilic O^{I–} species. These electrophiles are susceptible to nucleophilic attack not only by CO to form CO₂ but possibly also by H₂O/OH during the O-O bond formation process of the OER. Finally, Chapter 3 confirms through a quasi *in situ* XPS/NEXAFS experiment

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that these reactive oxygen species can be replenished, which is a prerequisite for their participation in the catalytic OER cycle.

Chapter 4[‡] employs *in situ* XPS/NEXAFS cells enabling the observation of the electronic structure of an iridium (oxide) surface while it evolves oxygen. To interpret the changes in the electronic structure fingerprints during the OER, Chapter 4 combines the findings from Chapters 2 and 3 and fosters that the presence of the reactive oxygen species identified in highly active X-ray amorphous iridium oxides is closely tied to the OER activity of iridium surfaces. First, Chapter 4 shows how the initially metallic iridium surface is almost completely oxidized during the OER at high overpotentials and identifies which types of iridium and oxygen species form during this process. Second, Chapter 4 describes experiments performed at moderate OER overpotentials to determine the presence of which species is correlated with the OER activity of the material. Finally, Chapter 4 draws a parallel to photosystem II and points out that the electrophilic O^{I-} species contained in highly active X-ray amorphous iridium oxides and accommodated during the OER on an initially metallic iridium surface are likely favoring the suggested rate- and potential-determining step of the OER, i. e. the O-O bond formation.

Chapter 5 delivers a final conclusion of the findings obtained throughout this thesis.

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Pfeifer, V., Jones, T. E., Velasco Vélez, J. J., Arrigo, R., Piccinin, S., Hävecker, M., Knop-Gericke, A., and Schlögl, R. 2017 In situ observation of reactive oxygen species on oxygen-evolving iridium surfaces. Chem. Sci., 8, 2143-2149, doi: 10.1039/C6SC04622C

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2 The electronic structure of iridium and its oxides[§]

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2.1 Abstract

Iridium-based materials are among the most active and stable electrocatalysts for the oxygen evolution reaction. Amorphous iridium oxide structures are found to be more active than their crystalline counterparts. Herein, we combine synchrotron-based X-ray photoemission and absorption spectroscopies with theoretical calculations to investigate the electronic structure of Ir metal, rutile-type IrO₂, and an amorphous IrO_x. Theory and experiment show that while the Ir 4f line shape of Ir metal is well described by a simple Doniach–Šunjić function, the peculiar line shape of rutile-type IrO₂ requires the addition of a shake-up satellite 1 eV above the main line. In the catalytically more active amorphous IrO_x, we find that additional intensity appears in the Ir 4f spectrum at higher binding energy when compared with rutile-type IrO₂ along with a pre-edge feature in the OK-edge. We identify these additional features as electronic defects in the anionic and cationic frameworks, namely formally O^{I–} and Ir^{III}, which may explain the increased activity of amorphous IrO_x electrocatalysts. We corroborate our findings by *in situ* X-ray diffraction as well as *in situ* X-ray photoemission and absorption spectroscopies.

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2.2 Introduction

A major challenge facing efforts to transition to a clean and renewable energy supply is finding feasible means of storing excess energy from intermittent resources. Water electrolysis, which converts electrical into chemical energy by the generation of hydrogen and oxygen from water, is a key technology in this field.¹ The hydrogen generated by this method can either be fed into fuel cells or used in the synthesis of chemical feedstocks. However, to date, a sustainable, economic, and stable system for mass production of hydrogen by water electrolysis is lacking. A factor hampering the successful development of such a system is the sluggish oxygen evolution reaction (OER), which requires the transfer of four electrons and four protons. The proton transfer between the electrodes is typically achieved via proton exchange membranes. While this membrane technology is mature, taking advantage of it involves the development of OER electrocatalysts that are both active and stable under the required acidic working conditions. Conducting iridium oxide is the electrocatalyst that represents the best compromise between high activity and stability in acidic environments.^{2,3}

The high activity of iridium oxides for catalyzing the OER, when compared with other materials, has been discussed for decades.^{4,5} Such studies have revealed that upon electrochemical cycling of bulk Ir metal within a specific potential window, a hydrated, amorphous iridium oxide surface layer forms with an accompanying increase in OER activity.^{6,7} The scarcity of iridium has led researchers to refrain from studies on bulk iridium materials and focus on high surface area iridium oxide structures with the aim of optimizing iridium usage.⁸ From these attempts, it was found that amorphous iridium oxide catalysts exhibit higher OER activities than crystalline ones.^{9,10} These findings have prompted studies aimed at identifying and understanding the nature of the active species in iridium oxide catalysts.

Researchers have tried to correlate the electronic structure of iridium oxide with its OER activity by means of X-ray photoemission spectroscopy (XPS) in an effort to identify active surface species.^{6,11–14} Unambiguous speciation, however, has proven elusive because the combined influence of band structure, electron correlation, and spin-orbit coupling on the electronic structure of iridium oxide has not yet been resolved.¹⁵ For example, as a conductor, the core level spectra of rutile-type IrO₂ are expected to be asymmetric, as described by the Doniach–Šunjić (DS) line shape. However, the Ir 4f spectrum of crystalline rutile-type IrO₂ cannot be fit with the conventional DS line profile. The origin of this peculiar line shape has been debated in literature.^{16–18}

In this study, we investigate two reference iridium oxides, one crystalline and one amorphous, and correlate their electrocatalytic activities with their electronic structures. To develop a well-defined reference, we first combine XPS with theoretical calculations to explain the origin of the unusual line shape of rutile-type IrO_2 . Subsequently, we complement XPS with the near-edge X-ray absorption fine structure (NEXAFS) of the OK-edge and identify additional species present in the catalytically more active amorphous IrO_x powder. Finally, we test the robustness of our proposed models by *in situ* X-ray diffraction (XRD) and *in situ* XPS/NEXAFS investigations.

2.3 Experimental

2.3.1 Powder sample characterization methods

Prior to the X-ray photoemission and absorption experiments, two commercially available iridium oxide powders from Sigma-Aldrich (99.9 % trace metals basis) and AlfaAesar (Premion[®], 99.99 %, trace metals basis) were thoroughly characterized.

First, XRD was used to investigate the powders in the as-received state and after calcination at 1073 K for 50 h in 10^5 Pa O₂. XRD was measured in Bragg–Brentano geometry on a Bruker AXS D8 Advance θ/θ diffractometer using Ni-filtered Cu K α radiation and a position-sensitive LynxEye silicon strip detector. The powders were filled into the recess of a cup-shaped sample holder, the surface of the powder bed being flush with the sample holder edge (front loading). Second, the as-received powder morphologies were observed, and their atomic compositions were determined in a scanning electron microscope (SEM) Hitachi S-4800 FEG equipped with a Bruker XFlash detector and an energy dispersive X-ray spectroscopy (EDX) system Quantax. The images were taken with an acceleration voltage of 1.5 kV in SE mode, and the atomic compositions were determined via EDX at 25 kV. After degassing the samples for 3 h at 353 K, the surface area of the powders was measured in N₂ at 77 K by the Brunauer–Emmett–Teller (BET) method using an Autosorb 6-MP from Quantachrome.

Thermal analysis of the samples was carried out via thermogravimetry (TG) and differential scanning calorimetry (DSC) using a Netzsch STA449C Jupiter instrument. The samples were heated to 1073 K at a constant heating rate of 10 K min⁻¹ in 21 vol.% O_2 in Ar (100 mL min⁻¹) at 10⁵ Pa. The resultant gaseous products were analyzed by a Pfeiffer QMS200 OmniStar quadrupole mass spectrometer. The overall iridium oxidation state of the powders was calculated based on a temperature-programmed reduction (TPR). The TPR profile was measured in a home-built plug-flow fixed-bed reactor in 4.92 vol.% H₂ in Ar (80 mL min⁻¹) at a heating rate of 6 K min⁻¹ (end temperature 723 K). The H₂ consumption of 9.8 mg rutile-type IrO₂ and 8.3 mg amorphous IrO_x was measured by a thermal conductivity detector. The detector was calibrated by reducing 34.5 mg of CuO (≈99 %, trace metals basis) prior to the measurements. In the oxida-

tion state determination, we assume a standard deviation of 2 % based on repeated measurements of the reduction of a defined amount of CuO.¹⁹

Finally, the OER performance of the powders was evaluated. For this, catalyst inks were prepared from ground iridium oxide powder, 60 % water, 39.6 % isopropanol, and 0.4 % Nafion (5 % perfluorinated resin solution, Sigma-Aldrich). Defined ink volumes were deposited on glassy carbon ring disk electrodes (Pine Instruments) with a micropipette and dried in air at 333 K for 30 min to achieve a constant loading of $20 \,\mu g_{Ir} \, cm^{-2}$. Electrochemical measurements were performed at a rotational frequency of 1600 rpm in N₂-saturated 0.5 M H₂SO₄. For the linear sweep voltammetry (LSV), the potential was increased at a rate of $5 \, mV \, s^{-1}$ up to 1.8 V versus the standard hydrogen electrode (SHE).

2.3.2 NAP-XPS and NEXAFS

X-ray photoemission and absorption measurements were performed in a nearambient-pressure X-ray photoemission spectroscopy (NAP-XPS) system at the Innovative station for *in situ* spectroscopy beam line at the synchrotron facility BESSY II/HZB (Berlin, Germany). The setup is described in detail elsewhere.²⁰ Monochromatic light was used to investigate the electronic structure of an Ir (111) single crystal (MaTecK, 99.99% trace metals basis) and the two iridium oxide powders, which were pressed into pellets of 8 mm diameter (40 mg powder, 3 t pressing weight). The samples were mounted onto a stainless steel backplate on a sapphire sample holder and fixed by a tantalum wire construction (single crystal) or a stainless steel lid with a 3 mm hole (powder pellets). The sample could be heated via the backplate by an infrared laser. The laser power was adjusted with a proportional integral derivative feedback loop controlled by a K-type thermocouple, which was in contact with the sample surface. The experiments were either performed in UHV ($\approx 10^{-6}$ Pa) or in 25 Pa O₂. The gas flow was controlled by Bronkhorst mass flow controllers, and a constant pressure was ensured by a pressure-regulating value. The exit slit setting of the beam line was $111 \,\mu$ m for all measurements.

In XPS, a pass energy of 10 eV was chosen, which, for the Ir 4f core line, yielded an approximate resolution of 0.2 eV at 130 eV kinetic energy (KE) of the photoelectrons, 0.3 eV at 450 eV KE, and 0.6 eV at 900 eV KE. The associated inelastic mean free paths of the photoelectrons are \approx 0.4 nm, \approx 0.7 nm, and 1.1 nm, according to the model of Tanuma *et al.*²¹ The binding energy was calibrated by measuring the corresponding Fermi edge after each core level measurement.

In NEXAFS, the photon energy was varied from 525 eV to 555 eV by a continuous movement of the monochromator. The Auger electron yield at the OK-edge was mea-

sured with the electron spectrometer to partly suppress the contribution of gas-phase O_2^{22} by setting the KE to 385 eV (pass energy 50 eV). The energy resolution was approximately 0.8 eV.

Prior to the room temperature measurements in UHV, the three types of sample were subjected to different pretreatments. The Ir single crystal was cleaned by cycles of Ar⁺-sputtering ($2x10^2$ Pa, 1.5 kV, 20 mA, 15 min) and subsequent annealing (873 K, 25 Pa O₂, 30 min) before a final flashing in UHV to 873 K. The powder from Sigma-Aldrich was washed in Milli-Q water to reduce the amount of impurities and then calcined at 1073 K in 10^5 Pa O₂ for 50 h to achieve phase purity. The AlfaAesar IrO_x was measured as received.

Following UHV measurements, the XPS and NEXAFS of the AlfaAesar IrO_x were measured *in situ*. These experiments were performed by heating the sample in 25 Pa O_2 to 523 K at 5 K min⁻¹. Spectra were collected under these conditions. Afterwards, the temperature was increased to 673 K, and spectra were recorded at a constant temperature.

The fitting of all core level spectra was performed 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 inevitable inaccuracies evoked by background subtraction and peak area determination of asymmetric peaks. Details on the fit functions can be found in Fairley and Carrick.²³ In brief, $DS(\alpha,n)$ is a DS profile with the asymmetry parameter α that is convoluted with a Gaussian whose width is characterized by an integer $0 \le n \le 499$. The SGL(m) function blends the DS function with a Gaussian–Lorentzian sum form on the low binding energy side of the peak maximum. The ratio of the sum form is given by the parameter m (0 pure Gaussian and 100 pure Lorentzian). The SGL(m) allows the spectra to be less Lorentzian in nature than the DS function would predict.

2.3.3 In situ X-ray diffraction

In situ XRD data were collected on a STOE θ/θ X-ray diffractometer (Cu K α_{1+2} radiation, secondary graphite monochromator and scintillation counter) equipped with an Anton Paar XRK 900 *in situ* reactor chamber. The gas feed was mixed with Bronkhorst mass flow controllers using 21 vol.% O₂ in helium at a total flow rate of 100 mL min⁻¹. The effluent gas composition was monitored with a Pfeiffer OmniStar quadrupole mass spectrometer. Before the thermal treatment, the sample was characterized at 298 K with slow XRD scans (15°–75° 2 θ with 0.02° steps, 10 s per step counting time). During the temperature program, faster scans (1 s per step counting time and 70 min per scan) were performed. The sample was heated to 473 K at $20 \text{ K} \text{min}^{-1}$ and then isothermal XRD scans were recorded every 50 K between 473 K and 873 K with intermediate heating ramps of $20 \text{ K} \text{min}^{-1}$.

2.4 Theoretical background and methods

A major challenge with interpretation of XPS data on iridium oxides stems from their peculiar Ir 4f peak shape, which makes speciation ambiguous. As conductors, electron screening will make the X-ray lines in Ir metal and IrO_2 asymmetric. If, for simplicity, we ignore lifetime, phonon, and instrumental broadening and assume constant excitation matrix elements, the asymmetric line shape is given by

$$I(\omega) = \int_{-\infty}^{\infty} dt \ e^{-i\omega t} \ \exp\left[\int_{0}^{\infty} d\epsilon \frac{N_{\rm eh}}{\epsilon^2} \left(e^{-i\epsilon t} - 1\right)\right],\tag{2.1}$$

where ω is the energy, *t* is the time, $N_{\rm eh}$ is the electron hole pair excitation spectrum, and ϵ is the excitation energy (see reference 24 and references therein). It is well-known that there is no closed-form solution for this line shape. As such, the asymptotic solution is often employed, which can be found by assuming the density of states (DOS) does not vary, resulting in $N_{\rm eh} = \alpha \epsilon$, where α is a constant. This solution, with the appropriate broadening, gives rise to the DS line shape.²⁵ Formally, it holds only in the neighborhood of the Fermi energy $(E_{\rm F})$, but in practice, the asymptotic solution is often an excellent approximation over several electron volts above $E_{\rm F}$, as is the case for Ir metal (see in the succeeding discussions). However, if the DOS is highly structured, $N_{\rm eh}$ may not be linear in ϵ and the DS line shape will be a poor approximation above the threshold energy, as is the case for IrO₂ (see in the succeeding discussions).¹⁶ In principle, it is possible to compute the line shape numerically if N_{eh} is known with high fidelity. However, faithful computation of the electron hole pair excitation spectrum necessitates an extremely accurate DOS,¹⁶ which in turn requires detailed knowledge of the atomic structure. Unfortunately, we lack such information for the amorphous material used in this work. We can instead estimate deviations from the DS line shape using a one-electron picture by recognizing that, within this approximation, the structured DOS introduces additional "shake-up" satellites not predicted by the asymptotic theory. The positions of these satellites can be found using model systems. Thus, a fit model can be developed wherein the DS line shape is augmented with (Gaussian) shake-up satellites centered at their theoretically predicted binding energies. This approach offers a flexible and chemically intuitive means of linking theory and experiment for the speciation of Ir 4f spectra.

To carry out this program, we require the initial and final states in the photoemission process of each material, states in the absence and presence of a core hole, respectively. The shake-up satellites are due to the excitation of an electron (near E_F) in the absence of a core hole into an unoccupied level in the presence of a core hole and are governed by a monopole selection rule, giving $\Delta l=0$ within a central potential approximation.²⁶ As such, we can determine the nature of potential shake-up satellites by examining the occupied l-resolved DOS in the absence of a core hole and the unoccupied l-resolved DOS in the absence of a core hole and the vicinity of a core hole. To compute these DOSs, we projected the wave functions, obtained by way of density functional theory (DFT) with the Perdew, Burke, and Ernzerhof exchange and correlation potential,²⁷ onto orthogonalized atomic wave functions, generating the projected density of states (PDOS) on the ground state and core-ionized iridium atoms.

All DFT calculations were performed with the Quantum ESPRESSO package²⁸ using a kinetic energy cutoff of 50 Ry and a charge density cutoff of 500 Ry. Spin polarization and scalar relativistic corrections were included. Ultrasoft pseudopotentials were taken from the PSLibrary.²⁹ To compute the OK-edge spectra, two gauge-including augmented wave projectors were added to the l = 1 channel of the oxygen pseudopotential. A **k**-point mesh equivalent to (8x8x8) for the 24-atom IrO₂ cell (Figure 2.1) was used in all calculations along with Marzari–Vanderbilt cold smearing³⁰ with a smearing parameter of 0.005 Ry.



Figure 2.1: Twenty-four-atom supercell of IrO₂ used for calculations.

Before calculating the spectroscopic properties, the rutile-type IrO_2 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.³¹ Ionic relaxations were performed until all components of the forces were less than 103 a. u., while the total change in energy was simultaneously less than 104 a. u.

Spectroscopic properties were computed following the approach detailed in Jones *et al.*³² Briefly, core level binding energies were computed using the Δ SCF (self-consistent field) method to accurately recover initial and final state effects.³³ The relative O 1s binding energies computed with the Δ SCF method were shifted to absolute binding energies using a reference calculation on a (4x4x4) supercell of rutile-type IrO₂, for which we took the measured O 1s binding energy to be 530.0 eV. The relative Ir 4f binding energies were shifted to their absolute values using a reference calculation on a (4x4x4) supercell of Ir metal, which we took to have an Ir 4f_{7/2} binding energy of 60.8 eV. We verified that the relative binding energies in IrO₂ were converged to better than 0.1 eV with our computational setup, including supercell size.

OK-edge spectra were computed from Fermi's golden rule using the XSpectra package.^{34,35} 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,³⁶ was used for Γ_0 . The energy dependence was assumed to scale linearly, $\Gamma(E) = 0.1 (E - E_F)$. This empirical energy dependence was chosen as it has previously been shown to be an effective approximation in a range of materials.^{32,37} Gaussian broadening was also included with a full width at half maximum (FWHM) of 0.6 eV for calculations on rutile-type IrO₂ and 0.8 eV for the defective IrO_x spectra, where the increased FWHM of the latter is used to account for the reduced order in the amorphous samples. $E_{\rm F}$ of each computed spectrum was set to the computed O1s binding energy of the absorbing atom. With this method, the OK-edge spectrum of the crystalline bulk oxide, IrO₂, was well reproduced without a core hole on the absorbing atom. As such, we computed all OK-edge spectra without a core hole on the absorbing atom. For a detailed discussion on the core hole effect in DFT, see, for instance, Mauchamp et al.³⁸

2.5 Results and discussion

2.5.1 Powder sample characterization

A routine XRD characterization of the as-received iridium oxide powders revealed considerable differences in the XRD patterns (Figure 2.2). The Sigma-Aldrich powder exhibits the expected reflections of the rutile-type IrO_2 structure; hence, we call it rutile-type IrO_2 . After calcination, the reflections are sharper and more symmetric due to crystallite growth and possibly a higher degree of stoichiometry. In contrast, as received, the AlfaAesar powder exhibits only minor Ir metal reflections. At the diffraction angles corresponding to rutile-type IrO_2 reflections, the diffractogram of

the AlfaAesar powder shows only slight, broad peaks. Therefore, the oxidic part of this powder is X-ray amorphous, and we call the powder amorphous IrO_x . After calcination, sharp rutile-type IrO_2 reflections evolve also in this powder, while the metallic reflections remain unaltered. Thus, only the formerly amorphous part of the sample crystallizes and is possibly further oxidized during the calcination process while the metal remains unchanged. Quantitative Rietveld analysis of the IrO_2/Ir mixture after calcination yields an estimate of 2.4 wt.% Ir metal in the formerly amorphous IrO_x powder.



Figure 2.2: X-ray diffraction (XRD) patterns of the IrO_2 and IrO_x powders as received and after calcination at 1073 K in 10^5 Pa O_2 for 50 h. The initially amorphous powder shows as received broad peaks and crystallizes upon calcination. It contains a minor amount of Ir metal. The crystalline powder shows as received all reflections of rutile-type IrO_2 and becomes more homogeneous upon calcination, which is seen by sharper, more symmetric reflections.

The different morphologies of the as-received samples are shown in the scanning electron microscopy images in Figure 2.3. The rutile-type IrO_2 consists of parallelepiped-shaped particles of various sizes, while the amorphous IrO_x is less ordered and is composed of smaller, fluffy particles. EDX reveals the expected 1:2 atomic ratio of Ir:O in the rutile-type IrO_2 , while an oxygen excess is observed for the amorphous IrO_x . In both samples, iron contamination of $\approx 1\%$ was found. The correspond-



Figure 2.3: Scanning electron microscopy images of (a) the rutile-type IrO_2 powder and (b) the amorphous IrO_x powder. The scale bar applies to both (a) and (b).



Figure 2.4: Thermogravimetry quadrupole mass spectrometry differential scanning calorimetry (TG-QMS-DSC). (a) The TG signal of the rutile-type IrO_2 is constant over the entire temperature range, while the amorphous powder reduces its mass by 6 wt.%. (b) Corresponding water (m=18 a. u.) QMS trace reveals that the weight loss of the amorphous powder is due to physisorbed and chemisorbed water loss. (c) DSC shows by an exothermic peak at 673 K that the amorphous powder crystallizes at this temperature.

ing BET surface area of the crystalline powder is considerably smaller (2.1 m² g⁻¹) than that of the amorphous IrO_x (33.3 m² g⁻¹).

The TG profile and the corresponding mass spectrum and DSC are shown in Figure 2.4. The rutile-type IrO₂ powder does not show an obvious mass loss upon heating, and only a small amount of CO_2 is released (not shown). In contrast, the amorphous IrO_x loses 6 wt.% upon heating. The H₂O quadrupole mass spectrometry trace shows that at around 400 K \approx 2 wt.% physisorbed water is released from IrO_x. From \approx 500 K on, \approx 4 wt.% chemisorbed water is released from the IrO_x sample. The large amount of water contained in the amorphous IrO_x can account for the deviation from the nominal stoichiometry observed in EDX. An exothermic peak in DSC reveals that the IrO_x sample crystallizes at 673 K. The TPR profiles of both powders are shown in Figure 2.5. The two powders display differences in both their reduction profile and temperature. The rutile-type IrO₂ is reduced at around 500 K in a temperature window of \approx 75 K, while the amorphous IrO_x is already reduced at 350 K in a temperature window of only ≈ 15 K. Furthermore, the inset of Figure 2.5 reveals that the amorphous powder already adsorbs hydrogen during initial H₂ exposure at room temperature, which needs to be taken into account when determining the overall H₂ consumption of the amorphous IrO_x. Based on the total H₂ consumption, the overall oxidation state of iridium in the two powders is calculated. For the rutile-type IrO₂ powder, an Ir oxidation state of 4.1 ± 0.1 is obtained. This finding is in line with the EDX measurement and the expected formal Ir oxidation state of IV in stoichiometric IrO₂. To account for only the oxygen-containing iridium species of the amorphous IrO_x, the metallic Ir and physisorbed water contents were subtracted prior to the oxidation state determination of the amorphous IrO_x. In contrast to rutile-type IrO₂, an Ir oxidation state of 3.6 ± 0.1 is found for the oxygen-containing iridium species in the amorphous powder. Hence, the amorphous powder likely contains iridium-oxygen species with iridium in a formal oxidation state of less than IV, e.g. Ir^{III}, in addition to Ir^{IV} species. We note that this presence of multiple iridium oxidation states has been argued to be crucial for enhanced OER activity. 39,40

Indeed, OER activity assessment demonstrates that the amorphous sample is considerably more active than the rutile-type powder (Figure 2.6). The linear sweep voltammetry displays that the onset of the OER is at a lower potential, and the current density shows a steeper increase for amorphous IrO_x . And although the BET surface area of the amorphous powder is larger than that of the crystalline one (16x), it cannot explain the increased activity. It is then likely that the amorphous IrO_x possesses a surface termination that has an intrinsically higher OER activity than that of the surface species of rutile-type IrO_2 .⁹

Our preliminary characterizations have revealed a variety of differences between these commercially available iridium oxide powders: crystalline versus amorphous, no water loss versus 6 wt.% water loss in TG, oxidation state 4.1 versus 3.6 from TPR



Figure 2.5: Temperature-programmed reduction (TPR) of amorphous IrO_x and rutile-type IrO_2 . The amorphous IrO_x already strongly adsorbs H_2 at room temperature (inset) without releasing water (monitored by quadrupole mass spectrometry; not shown). Upon heating, the amorphous powder is reduced in a narrow temperature window at around 350 K, while the rutile-type IrO_2 is reduced in a broader temperature window at around 500 K.



Figure 2.6: The linear sweep voltammetry (LSV) shows a much steeper and earlier OER onset for the amorphous IrO_x than for rutile-type IrO_2 .

measurements, BET surface area $2.1 \text{ m}^2 \text{ g}^{-1}$ versus $33.3 \text{ m}^2 \text{ g}^{-1}$, low versus high catalytic activity. The difference in electrocatalytic performance is of significant interest as understanding which surface species are favorable in catalyzing the OER is a prerequisite to tailor iridium oxide-based catalysts with reduced precious metal contents. The electronic structure of these different iridium oxide powders may provide valuable insights into the nature of such active species. To characterize their electronic structures, we turn to XPS and NEXAFS.

2.5.2 NAP-XPS and NEXAFS

The most striking differences in the electronic structure of the two powders investigated in this work are found in their Ir 4f lines and OK-edges as illustrated in Figures 2.7 and 2.8. The Ir 4f line of the amorphous IrO_x is significantly broader than that of rutile-type IrO_2 . The difference spectrum highlights that in the amorphous IrO_x intensity is shifted away from the positions of maximum intensity in the rutile-type IrO_2 (61.7 eV and 64.7 eV) towards higher binding energy. The increased intensity at higher binding energy is indicative of the presence of additional oxygen-related species in the amorphous powder, which is corroborated by a comparison of the OK-edges of the two samples. The OK-edge of the amorphous IrO_x shows an additional resonance at 529 eV, while the intensity registered at 530 eV is reduced compared with rutile-type IrO_2 .



Figure 2.7: Comparison of the Ir 4f spectra of rutile-type IrO_2 and amorphous IrO_x normalized by area. The difference spectrum highlights that the amorphous IrO_x has less intensity where the rutile-type IrO_2 main lines are located at and more intensity at higher binding energy.

Although multiple species appear to be present in the amorphous powder, a speciation of iridium oxides is not straightforward because of the peculiar Ir 4f line shape in these materials.¹⁶ To advance toward an identification of the species contained in the catalytically more active amorphous iridium oxide, we make use of DFT calculations. By the combination of theory and experiment, we are able to further understand the



Figure 2.8: Comparison of the OK-edges of rutile-type IrO_2 and amorphous IrO_x . The amorphous IrO_x counts with an additional pre-edge feature at 529 eV and less intensity at 530 eV, where rutile IrO_2 has a sharp resonance. The broader resonance at 533 eV in rutile-type IrO_2 is shifted to slightly lower excitation energies in the amorphous IrO_x .

electronic structure of rutile-type IrO_2 and amorphous IrO_x . However, before doing so, we first benchmark our approach in Ir metal.

Single crystal Ir (111)

As XRD had shown a minor amount of Ir metal contained in the amorphous IrO_x, we found it prudent to investigate a metallic reference, for which we chose an Ir (111) single crystal. Ir single crystals have been widely studied by XPS.^{41,42} Hüfner *et al.*⁴³ determined the DS parameter, α , of Ir metal to be 0.12, which enabled a fit of the asymmetric Ir 4f spectrum with a single contribution.

As a first test of our theoretical approach, we computed the PDOS of Ir metal in a 32-atom supercell with and without an Ir 4f core hole on a single excited atom. We found that the PDOS is only weakly structured and, therefore, the Ir 4f peak shape should be fit well by a standard DS function. To illustrate this point, consider that the most prominent shake-up satellites will come from transitions from occupied states at $E_{\rm F}$ to unoccupied states slightly above $E_{\rm F}$, as the energy dependence of the transition probability is $1/\epsilon^2$, where ϵ is the excitation energy. Thus, because the states at $E_{\rm F}$ are principally d character and the shake-up process is governed by a monopole selection rule, we expect satellites will be due to transitions from occupied to unoccupied d states. Figure 2.9 shows the d states on an Ir atom with a 4f core hole, PDOS(d). Clearly, there is no significant structure in the PDOS(d). As a result, the final states are well represented by a flat DOS, and asymptotic theory is predicted to hold.

Figure 2.10 shows the Ir 4f line of an Ir (111) single crystal at three different probing depths. As expected from the theoretical calculations, good agreement between fit



Figure 2.9: Calculated PDOS(d) of Ir metal in the presence of a 4f core hole. The PDOS shows no significant structuring.



Figure 2.10: Ir 4f spectra with fits of an Ir (111) single crystal measured with three different kinetic energies (KE) of the photoelectrons. In the 130 eV and 450 eV KE spectra, the surface core levels (SCL) of the single crystal termination are visible.

and experiment is obtained on the high binding energy side of the peak maximum by using a DS function (Ir⁰) for the Ir $4f_{7/2}$ (Ir $4f_{5/2}$) peak located at 60.8 eV (63.8 eV). The DS parameter α found to best fit the spectra is 0.13, which is in good agreement with the value determined by Hüfner *et al.*⁴³ On the low binding energy side of the peak

maximum, however, an additional peak (Ir⁰ SCL) appears in the 130 eV and 450 eV KE spectra due to the surface core level shift (SCLS) of the single crystal surface termination. This contribution is the most pronounced in the most surface-sensitive measurement and diminishes at larger probing depths. The appearance of such an SCLS has already been reported in the literature both by theory and experiment.^{42,44} These previous studies have found an SCLS of approximately 0.5 eV on Ir (111) surfaces, slightly larger than the 0.4 eV shift we observe. However, accurate measurement of the SCLS requires a dedicated effort to ensure the surface remains clean because even small amounts of contamination, e.g. adsorbed carbonaceous species, will modify or mask this additional contribution.⁴² We further note that the Ir $5p_{1/2}$ peak is located at a binding energy of \approx 63 eV and completely buried by the Ir 4f signal. A determination of the theoretical cross-section ratio between the $5p_{1/2}$ and 4f peaks based on the calculations by Yeh and Lindau⁴⁵ yields at most 2 % for the photon energies employed in this work. Hence, the Ir $5p_{1/2}$ has such a minor contribution to the recorded spectra that we omitted it in our fits in the interest of clarity. This omission will lead to a minor broadening of the Ir 4f peak contributions. The employed fit parameters are listed in Table 2.1. With higher excitation energy, the energy resolution of the beam line deteriorates. Therefore, the Gaussian contributions and the FWHM of the peaks are larger with increasing KE of the photoelectrons, and the peak maxima of the DS function are slightly shifted. Besides these adjustments, the fits remain unaltered for different probing depths.

130 eV KE	$\operatorname{Ir}4f_{7/2}$	$\operatorname{Ir}4\mathbf{f}_{5/2}$	$\operatorname{Ir}4f_{7/2}$	$\operatorname{Ir}4f_{5/2}$		
	Ir^0	Ir ⁰	Ir ⁰ SCL	Ir ⁰ SCL		
line shape	DS(0.13,140)	DS(0.13,140)	DS(0.13,140)	DS(0.13,140)		
	SGL(100)	SGL(100)	SGL(100)	SGL(100)		
area / %	44.6	29.0	16.0	10.4		
FWHM / eV	0.5	0.5	0.6	0.5		
binding energy / eV	60.8	63.8	60.4	63.4		
450 eV KE						
line shape	DS(0.13,160)	DS(0.13,160)	DS(0.13,160)	DS(0.13,160)		
	SGL(95)	SGL(95)	SGL(95)	SGL(95)		
area / %	53.6	40.2	3.6	2.7		
FWHM / eV	0.6	0.6	0.6	0.6		
binding energy / eV	60.8	63.8	60.4	63.4		
900 eV KE						
line shape	DS(0.13,250)	DS(0.13,250)				
	SGL(90)	SGL(90)				
area / %	57.1	42.9				
FWHM / eV	0.9	0.9				
binding energy / eV	60.9	63.9				

Table 2.1: Fit parameters Ir (111) single crystal at three probing depths. KE, kinetic energy; SCL, surface core level; FWHM, full width at half maximum.

Transferring this finding to our measured iridium oxides (Figure 2.7) shows that, although XRD documented the presence of metallic Ir in the amorphous IrO_x powder, neither of the two powders contains metallic Ir in the surface-near region as a peak at 60.8 eV is absent in both cases.

Rutile-type IrO₂

Rutile-type IrO_2 is a metallic conductor, and therefore, an asymmetric line shape similar to the one of metallic Ir is expected. Nevertheless to date, we know of no example of a fit for rutile-type IrO_2 that requires only one component. Earlier studies tried to explain this shortcoming by a compound such as Ir_2O_3 being present in commercially available IrO_2 powders.^{13,46} Recently, Kahk *et al.*¹⁷ described the line shape based on the Kotani model⁴⁷ and proposed that the Ir 4f peak consists of a screened and an unscreened final state. Hence, they deconvoluted the rutile-type IrO_2 Ir $4f_{7/2}$ line into two simple Gaussian–Lorentzian peaks. Importantly, their work showed that the uncommon line shape is inherent to the material and is not connected with stoichiometry deficiencies.

However, predicting the binding energies of a screened and an unscreened state can be cumbersome. For instance, Wertheim and Guggenheim¹⁶ predicted that the unscreened satellite would have a binding energy of \approx 3 eV above the main line, while we find a difference of \approx 10 eV between the computed final and initial state shifts, both of which are well above the values used in the Ir 4f deconvolution of Kahk *et al.*¹⁷ In an effort to develop a simple predictive model to capture the binding energy of the satellite peaks, we use our theoretical approach previously outlined.

To understand the nature of the Ir 4f spectrum in IrO₂, we can again turn to the PDOS of an Ir atom with an Ir 4f core hole, which we computed in a (4x4x4) supercell of IrO₂. The resultant PDOS(d) of the Ir atom with a core hole is shown in Figure 2.11. As with Ir metal, we only show the d states because there are few s and p states near E_F . Unlike the example of the metal, however, the d states on iridium in the oxide can be seen to be highly structured in the presence of a core hole. Inspection of the figure reveals that there is a strong narrow feature at $\approx 1 \text{ eV}$ above E_F in the final state PDOS(d). Excitation of Fermi energy electrons to this unoccupied state will lead to a shake-up satellite at $\approx 1 \text{ eV}$ above the main line in the Ir 4f spectrum of IrO₂. Furthermore, the occupied states (inset in Figure 2.11) have a strong feature at $\approx 2 \text{ eV}$ below E_F because of localized nonbonding iridium d electrons. Excitation of these electrons into the unoccupied states at 1 eV above E_F may lead to the appearance of a second satellite at $\approx 3 \text{ eV}$ above the main line in the Ir 4f spectrum. However, because the transition probability scales as $1/\epsilon^2$ this second shake-up satellite, if visible, will be less prominent than the $\approx 1 \text{ eV}$

satellite. Thus, at a minimum, the IrO_2 Ir 4f line should then be fit using a standard DS function to capture the main line, for which our Δ SCF calculations predict a binding energy of 61.7 eV for the Ir 4f_{7/2}, and a Gaussian at 1 eV higher binding energy to capture the primary shake-up satellite.



Figure 2.11: Calculated PDOS(d) of rutile-type IrO_2 in the presence of a 4f core hole. The PDOS(d) shows a sharp peak at 1 eV above E_F causing a shake-up satellite to appear 1 eV above the main line of the Ir 4f spectrum due to excitation from electrons at E_F into these unoccupied states. The inset shows the calculated occupied DOS without a core hole. The DOS has a strong feature at 2 eV binding energy. Excitation of electrons from these states into the unoccupied states 1 eV above E_F may lead to a second shake-up satellite 3 eV above the Ir 4f main line.

Based on our theoretical predictions, a least square fit of the rutile-type IrO₂ Ir 4f spectra was carried out using one DS component (Ir^{IV}) and one Gaussian satellite (Ir^{IV} sat1) for each, Ir 4f_{7/2} and Ir 4f_{5/2} (Figure 2.12). The fits at both probing depths give good agreement between the measured spectra and the fit envelopes except at a binding energy of $\approx 68 \text{ eV}$, where a minor deviation is observed. To obtain satisfactory agreement between the fit and measurement, the second satellite (Ir^{IV} sat2) of the Ir 4f_{5/2} peak at $\approx 3 \text{ eV}$ above the main line, stemming from the excitation from the localized nonbonding Ir d states 2 eV below $E_{\rm F}$ into the unoccupied states at 1 eV above $E_{\rm F}$ (Figure 2.11), needs to be added. As the corresponding second satellite of the Ir 4f_{7/2} peak is completely buried by the Ir 4f_{5/2} main line, it was not included in the fit. The need for an additional component at around 68 eV has also been observed in previous fits of rutile-type IrO₂.⁴⁸ All fit parameters are found in Table 2.2. In contrast to the Ir single crystal measurement, no SCLS is observed in the surface-sensitive measurement of the rutile-type IrO₂ powder. The absence of the SCLS is potentially due to coverage of the surface by a carbonaceous layer.

The predominance of a single phase of IrO_2 is corroborated by the measured OKedge. As shown in Figure 2.13, the two pronounced resonances at 530 eV and 533 eV are in good agreement with our calculations of the phase-pure rutile-type IrO_2 OKedge, in which all oxygen and iridium are formally O^{II–} and Ir^{IV} , respectively.

In summary, our combination of theory and experiment confirms that the peculiar Ir 4f line shape is inherent to rutile-type IrO_2 and not connected to the presence of additional iridium species. In general, our approach offers a predictive means of identifying the presence of satellites and their binding energies for conductive materials with structured DOSs. For example, to further test our theoretical calculations, we computed the PDOS for RuO_2 and Cu metal (not shown). For both materials, the presence (RuO_2) and the absence (Cu metal) of satellites was correctly predicted by a structured (RuO_2) and flat (Cu metal) PDOS. Finally, for the material studied in this work, iridium oxide, our approach further enables speciation of Ir 4f spectra as shown in the succeeding discussions.



Figure 2.12: Ir 4f spectra of rutile-type IrO₂ measured at two different kinetic energies (KE) and fit with a Doniach–Šunjić main line and Gaussian satellites based on theoretical findings.

130 eV KE	Ir 4f _{7/2}	$\operatorname{Ir}4f_{5/2}$	$\operatorname{Ir}4f_{7/2}$	$\operatorname{Ir}4f_{5/2}$	$\operatorname{Ir}4f_{5/2}$		
	Ir ^{IV}	Ir ^{IV}	Ir^{IV} sat1	Ir^{IV} sat1	Ir ^{IV} sat2		
line shape	DS(0.2,100)	DS(0.2,100)	GL(0)	GL(0)	GL(0)		
	SGL(65)	SGL(65)					
area / %	44.6	34.8	11.2	8.4	1.1		
FWHM / eV	0.6	0.7	2.5	2.6	1.7		
binding energy / eV	61.7	64.7	62.8	65.8	67.8		
900 eV KE							
line shape	DS(0.2,230)	DS(0.2,230)	GL(0)	GL(0)	GL(0)		
	SGL(55)	SGL(55)					
area / %	44.1	35.7	10.4	7.8	2.1		
FWHM / eV	0.9	0.9	2.6	2.6	2.5		
binding energy / eV	61.8	64.8	62.9	65.9	67.9		
ţ	ာ OK-edge rutile-type IrO						

Table 2.2: Fit parameters rutile-type IrO_2 at two probing depths. KE, kinetic energy; FWHM, full width at half maximum.



Figure 2.13: Measured (top) and calculated (bottom) OK-edge of rutile-type IrO_2 containing solely O^{II-} species.

Amorphous IrO_x

As shown in Figure 2.7, the Ir 4f line shape of the amorphous powder is considerably broader than that of rutile-type IrO₂ with additional intensity appearing at higher binding energy than that of the main lines of rutile-type IrO₂. TPR shows that the oxidation state of the amorphous sample is likely a mixture between Ir^{III} and Ir^{IV}; hence, it is tempting to assign this additional intensity to Ir^{III}. The assignment of a higher binding energy feature to a lower oxidation state is, at first, counterintuitive in XPS. Nevertheless, in the case of silver oxides, this phenomenon is well-known.⁴⁹ In addition to this apparent defect in the cationic framework, the OK-edge of the amorphous IrO_x has a pre-edge feature at \approx 529 eV (Figure 2.8), which hints at additional oxygen species. Such pre-edge features are commonly observed in other covalently bound oxides. By way of example, a pre-edge is observed in the OK-edge of superconducting cuprates upon doping due to the creation of holes in the O2p orbitals (formally O^{I-}).^{50,51} To test if these formally Ir^{III} and O^{I-} electronic defects can account for the additional features observed in the XPS and NEXAFS of IrO_x powders, we again turn to theory.


Figure 2.14: Supercell with Ir vacancy in the middle.



Figure 2.15: Scheme of transformations in the anionic and cationic framework upon the introduction of an Ir vacancy.

To study the possibility of O 2p hole and Ir^{III} formation in IrO₂, we used a 24-atom supercell of rutile-type IrO₂ with a single Ir vacancy as a model system (Figure 2.14). As schematically outlined in Figure 2.15, introducing the Ir vacancy transforms the six formally O^{II–} anions surrounding the vacancy to formally O^{I–} species; the remaining O^{II–} anions, those not in the neighborhood of the Ir vacancy, are comparatively unaltered. Thus, six electrons are transferred from O^{II–} to the cationic framework. Of these six electrons, four are removed from the system by the Ir vacancy, Ir^{IV} and 4 e[–]. The remaining two electrons will then reduce neighboring Ir^{IV} to Ir^{III}. In support of this view, our Δ SCF calculations reveal that Ir vacancy formation does lead to the appearance of species with an Ir 4f binding energy of 62.2 eV, which we attribute to the formally Ir^{III} cations. Inspection of the PDOS(d) (not shown) reveals that these Ir^{III} are expected to have a satellite at ≈1 eV higher binding energy in the Ir 4f spectrum, leading to the fit shown in Figure 2.16. Evidence for the formally O^{I–} species can be found in the computed OK-edge spectrum, where the O^{I–} species introduce a strong resonance at ≈529 eV (Figure 2.17), in good agreement with experiment.



Figure 2.16: Ir 4f spectra of amorphous IrO_x measured at two different kinetic energies (KE) with Ir^{IV} and Ir^{III} Doniach–Šunjić main lines and corresponding Gaussian satellites based on theoretical findings.

Based on our theoretical findings, we developed a fit for the Ir 4f line of amorphous IrO_x , which is shown for two probing depths in Figure 2.16. We employed the established Ir^{IV} fit functions from rutile-type IrO_2 and added the Ir^{III} components found in our model calculations with DS functions (62.3 eV and 65.3 eV) and corresponding Gaussian satellites. To account for a less regular order in the amorphous sample when compared with the crystalline one, we chose a higher FWHM value for the DS components of Ir^{IV} . The separation between Ir^{IV} and Ir^{III} leading to the best fit is 0.56 eV, which is slightly larger than what our calculations predict. When taking into account both the intensities of the main lines and corresponding satellites, the fits show that the subsurface region of the amorphous IrO_x powder contains roughly 80 % Ir^{IV} and 20 % Ir^{III} species. At the outmost surface (130 eV KE measurement), the defect density is slightly (\approx 5 %) larger. The fit parameters of all peaks and their intensities can be found in Table 2.3.

130 eV KE	$\operatorname{Ir}4f_{7/2}$	$\operatorname{Ir}4f_{5/2}$	$\operatorname{Ir}4f_{7/2}$	$\operatorname{Ir}4f_{5/2}$	$\operatorname{Ir}4f_{5/2}$	$\operatorname{Ir}4f_{7/2}$	$\operatorname{Ir}4f_{5/2}$	$\operatorname{Ir}4f_{7/2}$	$\operatorname{Ir}4f_{5/2}$
	$\mathrm{Ir}^{\mathrm{IV}}$	$\mathrm{Ir}^{\mathrm{IV}}$	Ir^{IV} sat1	Ir^{IV} sat1	Ir^{IV} sat2	Ir ^{III}	Ir ^{III}	Ir ^{III} sat1	Ir^{III} sat1
line shape	DS(0.2,100)	DS(0.2,100)	GL(0)	GL(0)	GL(0)	DS(0.2,100)	DS(0.2,100)	GL(0)	GL(0)
	SGL(50)	SGL(50)				SGL(50)	SGL(50)		
area / %	32.6	24.8	8.2	6.2	0.8	13.4	10.1	2.3	1.7
FWHM /	0.8	0.9	2.5	2.6	1.8	0.9	1	2.4	2.6
eV									
binding en-	61.7	64.7	62.8	65.8	67.8	62.3	65.3	63.3	66.3
ergy / eV									
900 eV KE									
line shape	DS(0.2,230)	DS(0.2,230)	GL(0)	GL(0)	GL(0)	DS(0.2,230)	DS(0.2,230)	GL(0)	GL(0)
	SGL(45)	SGL(45)				SGL(45)	SGL(45)		
area / %	33.8	27.4	7.9	6.0	2.0	10.9	8.8	1.9	1.4
FWHM /	1.1	1.1	2.6	2.6	2.5	1	1.1	2.6	2.6
eV									
binding en-	61.8	64.8	62.9	65.9	67.9	62.4	65.4	63.4	66.4
ergy / eV									

Table 2.3: Fit parameters amorphous IrO_x as received at two probing depths. KE, kinetic energy; FWHM, full width at half maximum.

The OK-edge of the amorphous IrO_x has resonances at 529 eV and 530 eV. Hence, our calculations predict that it contains both formally O^{I-} and O^{II-} species. Because the O2p hole is a localized defect, we can take a linear combination of the computed OK-edge spectra of O^{I-} and O^{II-} to estimate the amount of O^{I-} in the probing depth of the experiment. Doing so, we find that a spectrum with approx. 40 % O^{I-} and 60 % O^{II-} results in a good agreement between measurement and theory (Figure 2.17).



Figure 2.17: Measured (top) and calculated (bottom) OK-edge of amorphous IrO_x containing both O^{I-} and O^{II-} species. For the calculated spectrum a share of 40 % O^{I-} yielded the best agreement with the measured spectrum.

In the model outlined in Figure 2.15, per each one Ir^{III} , three O^{I-} are created. In line with this prediction, we find a higher concentration of electronic defects in the anionic than in the cationic framework of the amorphous material. A ratio as high as 1:3, though, does not result. This observation shows that as expected, the atomic structure of the amorphous IrO_x will be more complex than our model system. Nevertheless, the local defects in the atomic structure present in our model capture both kinds of

electronic defects observed in the amorphous IrO_x . Hence, these types of local defects are likely to be present in the amorphous framework. Furthermore, the calculations and fits based thereon allow us to estimate the defect concentrations in the surface and subsurface region, which are probed by XPS/NEXAFS and likely crucial for heterogeneous catalytic reactions.

2.5.3 In situ XRD, XPS, and NEXAFS

To substantiate our proposed fit for the amorphous IrO_x , we performed *in situ* XRD and XPS/NEXAFS heating experiments of the powder. In XRD, we already know that the initial pattern shows only broad peaks, compare Figure 2.2. Upon heating, the pattern in Figure 2.18 starts to show rutile-type IrO_2 reflections at 623 K. Crystallization appears to start roughly at this temperature under 10^5 Pa in synthetic air as we had similarly observed in DSC. When heating to higher temperatures, the reflections become sharper hinting at a higher degree of homogeneity of the sample with increasing temperature.



Figure 2.18: *In situ* XRD heating experiment at 10^5 Pa in 21 vol.% O₂ of amorphous powder that initially does not show rutile-type IrO₂ reflections but only metallic ones. Upon heating, rutile-type IrO₂ reflections evolve.

In both XPS and NEXAFS, the changes in the spectra upon heating in 25 Pa O_2 are obvious (Figures 2.19 and 2.20). The contributions of Ir^{III} to the Ir 4f line at 62.3 eV



Figure 2.19: *In situ* XPS heating experiment of the amorphous powder. The intensity at higher binding energy than the main line of IrO_2 is reduced with increasing temperature. A comparison with the rutile-type IrO_2 Ir 4f spectrum and the measurement of the amorphous IrO_x at 673 K still shows a slightly broader spectrum.



Figure 2.20: In situ NEXAFS heating experiment of the amorphous IrO_x powder. Spectra are corrected by the O_2 gas phase transmission. The intensity of the resonance at 529 eV is reduced with increasing temperature. A comparison with the rutile-type IrO_2 OK-edge still shows that a slightly larger contribution of the 529 eV resonance is still present at 673 K.



Figure 2.21: Ir 4f spectra of amorphous IrO_x measured at 673 K in 25 Pa O_2 at two different kinetic energies (KE) with theory-based fit models. Compared with the measurement at room temperature, the Ir^{III} component is decreased.

and 65.3 eV are reduced with a concomitant decrease in the intensity of the 529 eV component in the OK-edge and an increase in the intensity of the resonance at 530 eV. To remove the distortion of the NEXAFS spectra by photon absorption in the gas phase, the spectra shown in Figure 2.20 were reconstructed by taking into account the O_2 gas phase transmission as described in detail in Hävecker *et al.*²² At 673 K, a comparison with spectra of phase pure rutile-type IrO_2 still shows discrepancies, which are likely a result of the incomplete oxidation and crystallization under the applied conditions (Figure 2.20). This view is further supported by the aforementioned observation from *in situ* XRD that heating to 673 K might not be sufficient to obtain a homogeneous sample (Figure 2.18). Therefore, a fraction of the structural and electronic defects might still be present in the IrO_x sample after heating.

The continued presence of electronic defects in the cationic framework is corroborated by a fit of the Ir 4f region. Figure 2.21 shows the fit of the Ir 4f line measured at 673 K in O_2 based on the model developed in this section. Note that the area ratio between the DS lines and the corresponding satellites is fixed to a constant value to ensure comparability between different fits. Fit parameters are listed in Table 2.4. As anticipated, the contribution of Ir^{III} is smaller than for the sample in the as-received state (7 % vs. 20 %) but has still not completely vanished. The Ir^{IV} component increases and, as a result of partial crystallization, is more ordered than in the initial state, which is reflected by a slightly decreased FWHM even though measured at an elevated temperature. Also for this state of the powder, good agreement is obtained for the measured spectra and the fit using our newly introduced model.

130 eV KE	$\mathrm{Ir}4\mathrm{f}_{7/2}$ $\mathrm{Ir}^{\mathrm{IV}}$	$\frac{\mathrm{Ir}4\mathrm{f}_{5/2}}{\mathrm{Ir}^{\mathrm{IV}}}$	$\mathrm{Ir}4\mathrm{f}_{7/2}$ $\mathrm{Ir}^{\mathrm{IV}}\mathrm{sat1}$	${ m Ir}4{ m f}_{5/2}$ ${ m Ir}^{ m IV}$ sat1	${ m Ir}4{ m f}_{5/2}$ ${ m Ir}^{ m IV}$ sat2	$\frac{\mathrm{Ir}4\mathrm{f}_{7/2}}{\mathrm{Ir}^{\mathrm{III}}}$	$\frac{\mathrm{Ir}4\mathrm{f}_{5/2}}{\mathrm{Ir}^{\mathrm{III}}}$	Ir 4f _{7/2} Ir ^{III} sat1	$\mathrm{Ir}4\mathrm{f}_{5/2}$ $\mathrm{Ir}^{\mathrm{III}}\mathrm{sat1}$
line shape	DS(0.2,100)	DS(0.2,100)	GL(0)	GL(0)	GL(0)	DS(0.2,100)	DS(0.2,100)	GL(0)	GL(0)
	SGL(55)	SGL(55)				SGL(55)	SGL(55)		
area / %	41.2	32.1	10.3	7.9	1.3	3.5	2.6	0.6	0.4
FWHM /	0.8	0.9	2.5	2.6	2	0.9	1	2.3	2.4
eV									
binding en-	61.7	64.7	62.8	65.8	67.8	62.3	65.3	63.3	66.3
ergy / eV									
900 eV KE									
line shape	DS(0.2,230)	DS(0.2,230)	GL(0)	GL(0)	GL(0)	DS(0.2,230)	DS(0.2,230)	GL(0)	GL(0)
	SGL(50)	SGL(50)				SGL(50)	SGL(50)		
area / %	40.2	32.6	9.5	7.1	2.3	4.0	3.2	0.7	0.5
FWHM /	1	1.1	2.6	2.6	2.5	1	1.1	2.6	2.6
eV									
binding en-	61.8	64.8	62.9	65.9	67.9	62.4	65.4	63.4	66.4
ergy / eV									

Table 2.4: Fit parameters amorphous IrO_x at 673 K in 25 Pa O_2 at two probing depths. KE, kinetic energy; FWHM, full width at half maximum.

2.6 Conclusion

In conclusion, we describe the electronic structure of Ir metal, rutile-type IrO_2 , and an amorphous IrO_x . We confirm that the line shape of Ir metal is well-described by a simple DS function. For iridium oxides, however, a shake-up satellite is identified at 1 eV above the main Ir 4f line. This satellite accounts for the peculiar line shape of phase-pure rutile-type IrO_2 . As we have probed our samples at different information depths, we can exclude that the observed phenomena are solely due to surface effects but are also present in the subsurface region. Our theoretical models explain formerly unidentified features observed in the OK-edge and the Ir 4f line of amorphous IrO_x . O 2p hole states, which are formally O^{I-} , cause a resonance at 529 eV in the OK-edge NEXAFS. A compensatory Ir^{III} species exhibits a reverse binding energy shift in XPS. This reverse shift is responsible for the increased intensity in the Ir 4f line at higher binding energy than the rutile-type IrO_2 Ir 4f signal. Hence, our calculations show that caution is required when assigning oxidation states based solely on binding energy shifts. Finally, our investigation enables an estimation of the concentration of the electronic

defects in the anionic and cationic framework of the more active catalyst studied in this work. These electronic defects may account for the increased electrocatalytic activity observed in such amorphous iridium oxide systems. For a deeper understanding of how such highly defective termination layers evolve on surfaces under the influence of applied potentials, XPS and NEXAFS investigations of oxygen-evolving iridium catalysts are needed.

2.7 Supplementary Information[¶]

2.7.1 Calculated PDOS and measured valence band spectra

To further investigate the differences in the electronic structure of rutile-type IrO_2 , amorphous IrO_x , and the contained O^{I-} and O^{II-} species, we explored the occupied electronic states of the materials near the Fermi energy (E_F) by comparing measured valence band (VB) spectra with the computed projected density of states (PDOS). Though the PDOS and VB spectra are not exactly comparable because of, for instance, matrix element effects and lifetime broadening, the main peak positions should still be in good agreement. By using a projected density of states, it is possible to extract information about which element gives rise to the states associated with a given peak, making a combination of the measured VB spectra and the computed PDOS an excellent complement to the OK-edge NEXAFS, which effectively measures the unoccupied part of the projected Op states, PDOS(p).

The calculations were performed using the cells shown in Figures 2.1 and 2.14. The geometry of the three iridium atoms surrounding one oxygen atom in the defect-free IrO_2 cell is shown in Figure S2.7.1. In the cell that contains an Ir vacancy, for six of the oxygen atoms one of these surrounding iridium atoms is missing.

Figure S2.7.2 shows a comparison of the PDOS of only the $O2p_y$ and all O2p orbitals of single O^{I-} and O^{II-} species, respectively. The $O2p_y$ orbitals are those mainly involved in π -bonding and -anti-bonding as may be inferred from Figure S2.7.1. Their PDOS is shown separately since we observe a shift of these states towards more positive energies, i. e. a deoccupation, when comparing O^{I-} and O^{II-} . This deoccupation is also reflected by an increased splitting of the overall PDOS of the O2p states near E_F of O^{I-} when compared to O^{II-} .

[¶]This section was partly reproduced from the Supplementary Information to

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Figure S2.7.1: Geometry of the three iridium atoms surrounding one oxygen atom in the defect free IrO_2 cell. The Ir and O atoms are in the xz-plane



Figure S2.7.2: Projected density of states of (left) $O 2p_y$ and (right) all O 2p orbitals for O^{I-} and O^{II-} species.

Figures S2.7.3 and S2.7.4 show comparisons of all Ir 5d and O2p states calculated for the entire rutile-type IrO₂ cell without (see Figure 2.1) and with (see Figure 2.14) Ir vacancy. Introduction of the Ir vacancy leads to the creation of O^{I–} and Ir^{III}. While the increased splitting of the O2p orbitals near $E_{\rm F}$ may still be seen, it is significantly washed out when compared to the presentation in Figure S2.7.2 for only single O^{I–} and O^{II–} species.



Figure S2.7.3: Projected density of states of all (left) Ir 5d and (right) O 2p orbitals for rutile-type IrO₂ without and with Ir vacancy, calculated using cells shown in Figures 2.1 and 2.14.



Figure S2.7.4: Projected density of states of all Ir 5d and O2p orbitals for rutiletype IrO_2 without (left) and with (right) Ir vacancy, calculated using cells shown in Figures 2.1 and 2.14.

Figure S2.7.5 shows a comparison of the measured valence bands and oxygen Kedges of rutile-type IrO₂ and amorphous IrO_x. It may be seen that the valence band of amorphous IrO_x has reduced intensity at 2 eV and 0.5 eV binding energy when compared to the prominent features in the rutile-type IrO₂ at these energies. The intensity loss near E_F may allude to the deoccupation of O 2p states and the formation of additional O 2p hole states as suggested by the PDOS of O^{I–} (see Figure S2.7.2). Nevertheless, since the valence band consists of contributions of both the Ir 5d and the O 2p states, it is rather difficult to explicitly disentangle the respective contributions. However, when we consider the element-specific NEXAFS O K-edge of amorphous IrO_x, we are indeed able to confirm the deoccupation of O 2p states and the presence of additional O 2p hole states in amorphous IrO_x by an additional resonance at 529 eV that is absent in rutile-type IrO_2 . Therefore, monitoring the element-specific O K-edge presents a more direct and unequivocal way of observing the deoccupation of electronic states near E_F than the unspecific valence band measurements. Techniques to investigate changes in the occupied states near E_F in future investigations may be element-specific X-ray emission spectroscopies.



Figure S2.7.5: (left) Comparison of the measured valence band spectra of rutile-type IrO_2 and amorphous IrO_x normalized by maximum intensity. (right) Comparison of the OK-edges of rutile-type IrO_2 and amorphous IrO_x .

2.7.2 Literature survey of Ir 4f line shape interpretations

The Ir 4f line shape of iridium oxides and species contained in different types of iridium oxide have been heavily discussed in literature. The intrinsic asymmetric shape of stoichiometric rutile-type IrO₂ was interpreted by Wertheim *et al.*¹⁶ as well as Kahk *et al.*¹⁷ Wertheim *et al.* do a full many body calculation of the line shape expected for rutile-type IrO₂ while Kahk *et al.* reason their proposed screened and unscreened states by the Kotani model.⁴⁷ Although Wertheim *et al.* predicted that in such an approach the unscreened state would have a binding energy \approx 3 eV above the main line, Kahk *et al.*'s fits use significantly lower values (\approx 0.6 eV).

Table S2.7.1 gives a general overview of previously published XPS studies on iridium oxides (including both crystalline and amorphous forms) and one reference for IrCl₃ with the proposed line shapes, contained species, and binding energy positions. In general, for rutile-type IrO₂ 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.*⁴⁶ claim to have a considerable amount of Ir^{III} in commercially available IrO₂ powder and suggest a binding energy of 62 eV for Ir^{III} and 63.7 for Ir^{IV}. Similarly, Augustynski *et al.*⁵² attribute a binding energy of 61.6 eV to Ir^{III} in a compound of Ir_2O_3 , for which no crystallographic data is available, though, and a binding energy of 62.7 eV to Ir^{IV} in IrO_2 .

Several groups deconvoluted the recorded Ir 4f spectra and proposed a wealth of different line shapes and interpretations of present Ir species.^{8,12,14,17,46,48,52} Especially the spectra of anodized iridium and of iridium oxyhydroxides were found to be broader and therefore suspected to contain more species than those of rutile-type IrO₂.

By way of example, Augustynski et al.⁵² fitted an additional peak at 1.6 eV above the main line of rutile-type IrO₂ and attributed this to Ir^{VI}, which they suggested to be present in commercially available IrO₂ due to surface oxidation. Similarly, Atanasoska *et al.*⁴⁸ fitted peaks at 1.4 eV and 6.3 eV above the main line of rutile-type IrO_2 . These additional features have similar binding energies as those of the fit proposed in this work. However, in Atanasoska et al.'s⁴⁸ fits, symmetric line shapes were used for the main line, which is unexpected for metallic conductors. In addition, they ascribed 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 $\approx 1 \text{ eV}$ above the main line is a shake-up satellite of Ir^{IV} species. Furthermore, Casalongue et al.¹⁴ assign an oxidation state of V to species appearing during OER at 0.7 eV above their asymmetric main line. This assignment encouraged Nong et al.8 to also mention that the species they observe at higher binding energy after OER might be Ir with an oxidation state higher than IV. Finally, Kim et al.⁵³ also discussed about the presence of Ir^{VI} on anodized Ir electrodes since they observed intensity at binding energies 2.5 eV above the main line. This small literature overview already witnesses the large discrepancies between the interpretation of different Ir 4f spectra.

It needs to be noted that all assignments of iridium oxidation states higher than IV were simply based on shifts of these components to higher binding energies, although Kötz *et al.*⁶ and Hall *et al.*¹² had pointed out that there might be no correlation between a higher oxidation state and a 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-type IrO_2 with Ir in oxidation state IV (62.6 eV vs. 61.8 eV). Due to the lack of a well-defined reference material with Ir in oxidation state V, such a material could not be characterized via XPS.

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.

	sample type	BE/ eV	type/ fit shape	BE/ eV	type/ fit shape	BE/ eV	type/ fit shape
Atanasoska et al. ⁴⁸	IrO ₂ (thermal decomposition IrCl ₃)	61.2	Ir ^{IV} /GL	62.6	lr ^{>IV} /GL	67.5	unknown/ GL
Augustynski	IrO ₂	62.7	Ir ^{IV} /GL	64.3	Ir ^{VI} /GL		
et al. ³²	Ir_2O_3	61.6	Ir ^{III} /GL				
	anodic IrO _x	62.9	Ir ^{IV} /GL	64.3	Ir ^{VI} /GL		
Casalongue et al. ¹⁴	Ir ^{IV} oxide nanoparticles	61.5	Ir ^{IV} /G-DS	62.2	Ir ^V (only present during OER)/G-DS		
Hall et al. ¹²	anodic IrO _x	61.2	Ir ^{IV} /GL	63.1	oxide- hydroxide/GL		
Hara et al. ⁴⁶	IrO ₂ powder	62	Ir ^{III} / not specified	63.7	$ m Ir^{IV}/$ not specified		
Kahk et al. ¹⁷	IrO ₂ powder	61.7	Ir ^{IV} screened/GL	62.4	Ir ^{IV} unscreened/GL	74.5	satellite/ GL
Kim et al. ⁵³	IrO ₂ powder/ anodized Ir electrode	61.9	Ir ^{IV} /no fit	63.4	Ir ^{VI} /no fit		
Kötz et al. ⁶	IrO ₂ (reactively sputtered)	61.8	$\mathrm{Ir}^{\mathrm{IV}}$ no fit				
	anodic IrO _x	62.4	not specified/ no fit				
Peuckert et al. ¹³	IrO ₂ (thermally oxidized Ir)	61.9	$\mathrm{Ir}^{\mathrm{IV}}/\mathrm{no}$ fit				
	anodic IrO _x	61.2	not specified/ no fit				
Wertheim et al. ¹⁶	IrO ₂ single crystal	61.6	Ir ^{IV} /calcu- lated asym.				
Folkesson ⁵⁴	IrCl ₃	62.6	Ir ^{III}				

Table S2.7.1: Literature values of $Ir 4f_{7/2}$ binding energies of IrO_x and $IrCl_3$. Fit shape abbreviations: GL:Gaussian-Lorentzian, G-DS: Gaussian convoluted Doniach-Šunjić, BE: binding energy 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.^{55–57} For electrodeposited, hydrated Ir oxyhydroxide 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.

2.8 Acknowledgments

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2.9 References

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3 Reactive oxygen species in iridium-based OER catalysts¹¹

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3.1 Abstract

Tremendous effort has been devoted towards elucidating the fundamental reasons for the higher activity of hydrated amorphous $Ir^{III/IV}$ oxyhydroxides (IrO_x) in the oxygen evolution reaction (OER) in comparison with their crystalline counterpart, rutile-type IrO_2 , by focusing on the metal oxidation state. Here we demonstrate that, through an analogy to photosystem II, the nature of this reactive species is not solely a property of the metal but is intimately tied to the electronic structure of oxygen. We use a combination of synchrotron-based X-ray photoemission and absorption spectroscopies, *ab initio* calculations, and microcalorimetry to show that holes in the O 2p states in amorphous IrO_x give rise to a weakly bound oxygen that is extremely susceptible to nucleophilic attack, reacting stoichiometrically with CO already at room temperature. As such, we expect this species to play the critical role of the electrophilic oxygen involved in O-O bond formation in the electrocatalytic OER on IrO_x . We propose that the dynamic nature of the Ir framework in amorphous IrO_x imparts the flexibility in Ir oxidation state required for the formation of this active electrophilic oxygen.

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3.2 Introduction

Ir-based materials are promising candidates to catalyze the oxygen evolution reaction (OER) in acidic media. Iridium oxides, both anhydrous rutile-type IrO_2 and hydrated X-ray amorphous forms, have been widely considered as possible OER catalysts.^{1–8} Of these, the amorphous and nanostructured Ir-based catalysts have been shown to exhibit higher OER activities than rutile-type IrO_2 .^{9,10} Although numerous studies exist on such amorphous structures, and activity descriptors like mixed iridium oxidation states^{11,12} and the surface OH-concentration¹³ have been proposed, a convincing explanation for the enhanced activity of amorphous structures over crystalline ones is lacking. While many studies concentrated on investigating active metal centers and the iridium oxidation state,^{11,12,14} by analogy with the well-studied biological water splitting, an investigation of preactivated oxygen species contained in OER catalysts seems appropriate.

Oxygen preactivated for O-O bond formation is essential in photocatalytic water splitting over the tetranuclear Mn water oxidation complex (WOC) of photosystem II (PS II).^{15,16} A proposed mechanism of O-O bond formation in PS II is the nucleophilic attack of oxygen adsorbed in the WOC (O*) by a (preadsorbed) water molecule/hydroxide^{17,18}:

$$WOC - O^* + H_2O_{(ads)} \rightarrow WOC - O - O - H + H^+ + e^-.$$
(3.1)

In this mechanism water acts as the nucleophile, donating electrons to the reactive oxygen, which can alternatively be formulated $WOC \equiv O^+$ to emphasize its susceptibility to nucleophilic attack.¹⁵ Within this mechanism, the ability of Mn to accommodate different oxidation states enables the preparation of the electrophilic oxygen.

Nucleophilic attack of adsorbed oxygen by water/hydroxide has also been proposed to describe the mechanism of O-O bond formation on transition metal oxides during the OER.^{4,19} For iridium oxide, the importance of reactive oxygen is evident from isotope labeling experiments,⁵ which suggest the outer layers of the catalyst are involved directly in the electrocatalytic OER. Thus, O-O bond formation can be written as:

$$IrO_xO_{(ads)} + H_2O \to IrO_x - O - O - H + H^+ + e^-,$$
 (3.2)

with $IrO_xO_{(ads)}$ representing the iridium oxide matrix with an adsorbed oxygen. The oxidation state of the surrounding Ir metal centers must be flexible to allow this adsorbed oxygen to become an electrophilic species that is susceptible to nucleophilic attack. In line with this assumption, our previous study revealed that highly electrochemically active X-ray amorphous iridium oxides contain electronic defects in their

cationic (Ir^{III}) and anionic frameworks (O^{I–}) that are nearly absent in less active rutiletype IrO₂.¹⁰ The holes in the O 2p states of IrO_x may make the O^{I–} an electrophile that, in analogy to the biological cycle, may lead to the enhanced OER activity of amorphous IrO_x. To test this hypothesis, we need to understand the chemistry of these O^{I–} species.

A powerful means of uncovering the chemistry of the O^{I-} is through CO oxidation, a reaction that has proven essential in developing a fundamental understanding of heterogeneous processes.²⁰ Herein we use this probe to test if the O^{I-} in X-ray amorphous IrO_x can act as a strong electrophile. If this species is sufficiently electrophilic, we expect it to readily react with CO by accommodating the electron density of the partially negatively charged carbon atom of CO.^{20,21}

The sample investigated is a commercially available, hydrated, X-ray amorphous Ir^{III/IV} oxyhydroxide (IrO_x, Premion[®], AlfaAesar). In a control experiment, a less active, crystalline rutile-type IrO₂ (Sigma-Aldrich) was examined. The properties of both materials have been extensively described elsewhere.^{10,22} Therein, we showed that O^{I–} is identifiable by an excitation energy resonance at 529 eV in the near-edge X-ray absorption fine structure (NEXAFS) of the OK-edge that is not present in pristine rutile-type IrO₂. Herein, the spectroscopic features corresponding to these O^{I–} species were monitored by quasi *in situ* X-ray photoemission spectroscopy (XPS) and NEXAFS before and after CO exposure to observe whether O^{I–} reacts with CO during titration of the IrO_x surface. This approach ensures high-quality artifact-free oxygen spectra by preventing alterations of the sample during air exposure between measurements and CO exposure and eliminating gas-phase contributions of CO and CO₂ to the oxygen absorption spectra. The results are compared to theoretical calculations and a microcalorimetric analysis.

3.3 Results and discussion

In a preliminary experiment, we tested the general activity of the two iridium oxide powders towards a stoichiometric oxidation of CO to CO_2 at room temperature and atmospheric pressure in a standard flow-through reactor (details in Section 3.5.1). To ensure reaction of CO was exclusively with active oxygen from the iridium oxide samples, we did not add O_2 to the gas feed and had oxygen filters attached to the gas dosing lines.

We observe that introducing CO into the reactor filled with rutile-type IrO_2 leads to no change in the CO₂ signal (Figure 3.1). In contrast, when introducing CO into the reactor loaded with IrO_x , the CO₂ signal shows a sharp increase followed by a decline towards the baseline (Figure 3.1). Such full CO conversion at \approx 300 K is extremely unusual, having only been observed in a few novel systems, such as oxide-supported



Figure 3.1: CO₂ concentration in effluent gas stream over time after CO is introduced (0 min) in He stream (100 mL min⁻¹ CO:He 1:99, 298 K) for IrO_x and rutiletype IrO₂. IrO_x in contact with CO results in up to 0.2 vol.% CO₂ in the effluent gas stream. The inset shows the QMS signal for CO₂ during the CO exposure of the IrO_x sample in the near-ambient-pressure XPS chamber.

gold catalysts,²³ and reveals the high reactivity of the IrO_x . As there is no external oxygen source available in the present experiment, the effluent CO_2 must be due to the stoichiometric reaction of CO with an oxygen species present in IrO_x and nearly absent from the rutile-type powder. Because only IrO_x has an abundance of O^{I-} , this type of oxygen is a likely candidate for that active in CO oxidation. To test this hypothesis, we employ XPS/NEXAFS and monitor the regions characteristic for O^{I-} (\approx 529 eV).

In a quasi *in situ* experiment, we first measured the powder in vacuum as received (base pressure 10^{-6} Pa). We then exposed the IrO_x to pure CO in the NAP-XPS chamber (25 Pa, 2 mL min⁻¹) for 3 h and observed a CO₂ profile similar to that seen in the standard reactor (see inset Figure 3.1). Finally, we evacuated the chamber and without air contact measured the sample after CO (details see Section 3.5.2).

When comparing the XPS core lines recorded before and after CO exposure, the Ir 4f spectra show no obvious changes (Figure S3.5.3). In contrast, the intensity at low binding energies (529 eV-530 eV) in the O 1s spectrum is slightly reduced after CO exposure (Figure S3.5.3), indicating the potential loss of O^{I-} . The corresponding O K-edge NEX-AFS collected in the surface-sensitive Auger electron yield mode (AEY) corroborate this finding. Here we see CO exposure leads to a loss in intensity at excitation energies around 529 eV (Figure 3.2). A comparison of the difference spectrum of the O K-edges before and after CO exposure with that calculated for O^{I-} (see Figure 3.2) supports this conclusion, suggesting O^{I-} is consumed from IrO_x by oxidizing CO to CO_2 at room temperature.

Interestingly, more bulk sensitive total electron yield (TEY) measurements of the OK-edge also show reduced 529 eV intensity after CO exposure (see Figure S3.5.5).



Figure 3.2: OK-edge of IrO_x measured in Auger electron yield (AEY) mode before and after CO exposure (25 Pa, 2 mLmin^{-1} CO, 298 K). The difference spectrum shows the considerable decrease of the 529 eV feature and is in good agreement with the calculated spectrum of O^{I-} species.

Hence, subsurface O^{I-} species migrating to the surface also appear to be involved in the reaction with CO. This observation alludes to the dynamic mobility of O^{I-} in the porous structure¹⁰ of IrO_x. Nevertheless, since the CO₂ signal in the standard reactor and the NAP-XPS chamber declines immediately after the initial increase, the reservoir of mobile O^{I-} species seems to be rapidly exhausted. However, since the 529 eV component does not vanish completely in either AEY and TEY, part of the O^{I-} seem unavailable for reaction with CO over the time scale of our experiment.

Though comparison of our theoretical and experimental OK-edge spectra supports the conclusion that O^{I-} participates in stoichiometric room temperature CO oxidation, we have not demonstrated such a reaction is feasible. To do so, we begin by considering the thermodynamics of the reaction of gas-phase CO with oxygen, in oxidation state n (O^{n-}), in an IrO_x matrix (IrO_xOⁿ⁻):

$$IrO_xO^{n-} + CO_{(g)} \rightarrow IrO_x + CO_{2(g)} + n e^-.$$
 (3.3)

The liberated $n e^-$ may reduce adjacent Ir or O. We have assumed the product desorbs from the surface after forming, an assumption we will show to be valid. It is then straightforward to compute the heat of reaction for this process for different types of oxygen species by way of DFT (see Section 3.5.4 for details), as the energies of the gas-phase reactant and product are constants and only the adsorption energy of the oxygen species involved in the reaction changes the heat evolved (using the positive sign convention of microcalorimetry). And while we do not know the structure of the amorphous IrO_x , we can use model systems to gain useful insights into the relationships between the electronic structure of oxygen and its adsorption energy. To investigate the reaction of $CO_{(g)}$ with surfaces species, we employed IrO_2 (110) and IrO_2 (113) surfaces as model structures, using both oxygen-terminated and partially reduced (110) surfaces along with a partially reduced (113) surface (see Section 3.5.4 for full details). Both types of surface have under coordinated O atoms whose simulated O K-edge spectra agree with that measured for O^{I-} (see Section 3.5.4). The reduced surfaces also have under coordinated Ir atoms that can adsorb CO with adsorption energies of $\approx 180-210 \text{ kJ} \text{ mol}^{-1}$ (see Section 3.5.4).

As a first consideration, we computed the minimum energy path for the reaction of $CO_{(g)}$ with an oxygen-terminated (110) surface. This surface contains three unique types of oxygen, an O^{II-} like species, an O^{I-} like species, and oxygen on the coordinatively unsaturated site (CUS), the last of which was not observed experimentally (Figure S3.5.14). The O^{I-} has a barrier for reaction (3.3), $\approx 10 \text{ kJ mol}^{-1}$, that is slightly larger than $k_{\rm B}T$ at room temperature, and the reaction is $\approx 90 \text{ kJ mol}^{-1}$ exothermic. In contrast, the activation energy associated with the reaction of $CO_{(g)}$ directly with O^{II-} is significantly larger than the energy available at room temperature, 170 kJ mol⁻¹, and is exothermic by $\approx 50 \text{ kJ mol}^{-1}$.

To test the reaction of adsorbed CO with an O^{I-} like species, we computed minimum energy paths on the partially reduced (113) surface (see Section 3.5.4 for details). In this case, CO oxidation by an O^{I-} has a slightly higher barrier, 50 kJ mol⁻¹, than was observed on the fully oxidized (110) surface. Also, the initial product on the reduced surface is a strongly adsorbed CO₂, not CO_{2(g)}. Overall reaction (3.3) is \approx 160 kJ mol⁻¹ exothermic on the reduced (113) surface, which is in agreement with the 165 kJ mol⁻¹ computed for the reaction of CO_(g) with O^{I-} on a partially reduced (110) surface with an Ir vacancy.

These results suggest that, if present, surface O^{I-} species are highly electrophilic, with the fully oxidized surface perhaps showing higher reactivity. These electrophilic anionic defects are, in fact, predicted to be so reactive that they should not persist except under ultra-high vacuum, which may explain the their absence in rutile-type IrO₂ loaded from air¹⁰ and the lack of CO₂ formation when rutile-type IrO₂ is exposed to CO (see Figure 3.1). However, we know from the TEY measurements that, unlike the rutile-type oxide, the amorphous oxides contain a significant concentration of potentially mobile O^{I-} in the subsurface/bulk region. These subsurface species are depleted during CO oxidation (see Figure S3.5.5). If we assume that once on the surface any O^{I-} will behave in a manner analogous to the aforementioned surface species, we can focus on the bulk as a thermodynamic source of oxygen and compute its associated heat of reaction with CO_(g).

We find that reaction with the bulk O^{II-} of rutile-type IrO_2 is thermoneutral, whereas reaction with bulk O^{I-} species¹⁰ is 110-120 kJ mol⁻¹ exothermic, depending on the



Figure 3.3: The schemes summarize the CO titration of different oxygen species in iridium oxides with respect to their calculated activation barriers and reaction enthalpies. Exothermic processes are given by positive values (positive sign criterion of microcalorimetry). Energetically, the reaction of CO with O^{I–} seems feasible at room temperature while reaction with O^{II–} does not.

atomic structure around the anionic defect. As with the surfaces, we see that bulk O^{I–} species are more weakly bound, hence more electrophilic, than the bulk O^{II–}. These results are summarized schematically in Figure 3.3.

When the heats of reaction for all the oxygen species studied in this work are considered, we find that the O^{I-} type generally gives rise to higher heats of reaction than the formally O^{II-} . Remarkably, in the absence of major structural relaxations of the surface after reaction, there is a rough linear relationship between the position of the white line in the calculated OK-edge spectrum of an oxygen species and its corresponding heat of reaction with CO (see Figure S3.5.15). Thus, the OK-edge spectra appear to offer a means of probing the electrophilic character of the oxygen. From this measure, we would predict the heat of reaction of the dominant O^{I-} species present in our experiments (O K \approx 529 eV) is 100 kJ mol⁻¹.

To validate the calculated heats of reaction for room temperature CO oxidation on IrO_x , we titrated IrO_x with CO at 313 K using *in situ* microcalorimetry.²⁴ A gas phase analysis after the experiment confirmed the predominant presence of $CO_{2(g)}$, supporting our assumption in equation (3.3) and alluding to complete oxidation of the dosed CO (see Figure S3.5.11). Hence, in the determination of the differential heat of reaction, we took into account the entire dosed CO. Doing so, and averaging over three measurements, we obtain an exothermic heat of reaction of $125 \text{ kJ mol}^{-1} \pm 40 \text{ kJ mol}^{-1}$ for the 2 mmol g⁻¹ of reacted CO (see Figure 3.4). These measured differential heats of reaction agree with those calculated for $CO_{(g)}$ oxidation by O^{I-} species (see Figure 3.4), whereas they are much larger than the thermoneutral reaction of $CO_{(g)}$ with O^{II-} . In fact, the mean measured value (125 kJ mol^{-1}) is similar to the heats calculated for reaction with bulk O^{I-} , while the upper and lower ends of the standard deviation window agree with the calculated reaction enthalpies for $CO_{(g)}$ with O^{I-} on the partially reduced (113) and fully oxidized (110) surfaces, respectively. In addition, we observe a



Figure 3.4: Differential heats over the amount of reacted CO in the microcalorimeter for three experiments with IrO_x . An average heat of reaction of $125 \text{ kJ mol}^{-1} \pm 40 \text{ kJ mol}^{-1}$ is determined. The dotted lines show the calculated heats of reaction for CO with different oxygen species of IrO_x .

broadening of the thermosignal time profiles with increasing amount of reacted CO (see Figures S3.5.8 to S3.5.10), which could be an indication for the involvement of subsurface O^{I–} liberated by the reaction heat evolved in the surface region.

Hence, the calculations corroborate our assumption that during the exposure of IrO_x to CO, O^{I-} reacts with CO at room temperature. Combining our NEXAFS and microcalorimetric measurements with our theoretical calculations therefore suggests that the O^{I-} is a stoichiometric oxidant of CO to CO_2 , and therefore strongly electrophilic.

Now that we have demonstrated the reactivity of the O^{I-} species, it seems appropriate to consider their regeneration since for the OER cycle to be catalytic, reactive oxygen must be replenished. To test whether O^{I-} can be replenished on IrO_x , we performed additional quasi *in situ* XPS and NEXAFS experiments. Following the CO titration, we exposed the sample successively to different gas atmospheres (25 Pa O_2 , 25 Pa H_2O , and 25 Pa $O_2:O_3$ (99:1)) in the NAP-XPS chamber for 20 min each to discern whether any of these gases can replenish the reactive oxygen sites. After each gas treatment, we evacuated the chamber and measured XPS and NEXAFS in UHV without allowing the samples to contact air.

We observed distinct changes in the OK-edge only after the exposure of the sample to the ozone-containing gas mixture. A comparison of the OK-edges after CO and after subsequent ozone exposure indicates a replenishment of O^{I-} by a more intense 529 eV feature after ozone exposure, see Figure S3.5.6. However, we found that the formally O^{I-} species replenished by ozone were not stable, as indicated by a reduction in the 529 eV resonance after 30 min in vacuum. This observation suggests that parts of the matrix stabilizing these O^{I-} species are lost during the oxidation of CO and cannot be restructured under such low pressure at room temperature. Nevertheless, ozone, as a source of atomic oxygen, seems to be capable of at least temporarily refilling the O^{I–} vacancies formed during reaction with CO. Hence, we have demonstrated that the replenishment of these reactive oxygen species is feasible, which makes them relevant for the catalytic OER cycle.

The local structure of the O^{I-} species considered in our work can be characterized as a μ_2 -oxo bridge, which can be seen to arise naturally when defects are introduced into the cationic framework of the parent rutile-type structure, thereby transforming μ_3 oxo into μ_2 -oxo bridges. This process gives rise to holes in the O 2p states, due to the removal of Ir^{IV} and 4 e⁻, making the μ_2 -oxo bridges charge deficient.^{10,22} Such μ_2 -oxo bridged atomic structures have been identified as key motifs in amorphous IrO_x thin films²⁵ and as active centers in liquid-phase iridium oxidation catalysts²⁶ by extended X-ray absorption fine structure (EXAFS) measurements, which are able to resolve the local atomic structure of amorphous materials. It is worth noting, however, that the electrophilic O^{I–} species seen in XPS and NEXAFS need not exclusively be due to such μ_2 -oxo bridges. Instead, they may also emerge when substituting an Ir^{IV} with a lowervalent element, such as Ni^{II}, ¹³ as the holes formed by replacing Ir^{IV} and 4 e⁻ with Ni^{II} and 2 e⁻ can localize on neighboring oxygen atoms. Thus, both types of environment, the under-coordinated and the lower-valent, can result in the emergence of an electron deficiency on oxygen. And while other potentially electron deficient oxygen species, in particular Ir=O, can also be imagined, we find no evidence for them in the OK-edge spectra of the rutile-type IrO_2 or amorphous IrO_x samples, see Figure S3.5.14.

3.4 Conclusion

In conclusion, we showed that the O^{I–} species adsorbed on the surface and in the subsurface of OER-active Ir^{III/IV} oxyhydroxides are extremely electrophilic. By combining advanced experimental and theoretical techniques we found that this electrophilic oxygen can even oxidize CO to CO₂ at room temperature, with a portion of the reacting oxygen coming from the subsurface region of the amorphous catalyst. The exceptional reactivity of the formally O^{I–} species is suspected to play a critical role in the OER by reacting with OH/H₂O to form the OOH intermediate, which, when considering that weakly OER-active crystalline rutile-type IrO₂ is nearly devoid of this reactive oxygen, explains the exceptional reactivity of amorphous Ir^{III/IV} oxyhydroxides. Like in biological water splitting, the electrophilic oxygen in Ir^{III/IV} oxyhydroxides is an optimal precursor site for the nucleophilic attack of (preadsorbed) water during the O-O bond formation. The creation of electrophilic oxygen in PS II is enabled by the easy accommodation of different oxidation states of the coordinated Mn ions. Likewise flexibility in the oxidation state for iridium is needed for electrophilic oxygen formation in iridium, which is apparently found in the Ir^{III/IV} oxyhydroxides.

3.5 Supplementary Information

3.5.1 CO exposition of iridium oxides in flow-through reactor

CO oxidation experiments over iridium oxide powders were first performed in a glasslined steel, U-shaped tube reactor with an inner diameter of 5 mm. 25 mg of iridium oxide powder were diluted in 250 mg inert SiC powder with a particle diameter of 250 μ m - 355 μ m. Prior to CO exposure, the samples were dried in a He flow of 100 mL min⁻¹ (controlled by Bronkhorst mass flow controllers) for 1 h at room temperature. The subsequent switch from inert He to a 1 % CO in He flow (100 mL min⁻¹) was realized via a 6-port switch valve (Valvo, Vici), which excluded dead volumes. The effluent gas was monitored on line with an X-Stream, Emerson/Rosemont gas analyzer to quantify CO and CO₂ concentrations. The catalyst temperature was recorded by an analog connection to the gas analyzer. To ensure gas purity, the CO line was equipped with a carbonyl remover (consisting of a tube filled with inert SiC heated to 573 K) as well as a CO₂-trap (crushed KOH-filled cartridge). The He line had water as well as oxygen filters. The iridium oxide samples were an X-ray amorphous $\rm Ir^{\rm III/IV}$ oxyhydroxide (IrO_x, 99.99 % metals basis, AlfaAesar Premion[®]) and a crystalline rutile-type IrO_2 (99.9 % metals basis, Sigma-Aldrich). Details on the materials' properties can be found elsewhere. 10,22



Figure S3.5.1: CO_2 concentration in effluent gas stream over time during CO dosage in inert gas stream (CO:He 1:99) for IrO_x and rutile-type IrO_2 . The left graph shows both the CO and CO₂ traces for the two samples. The right graph shows only the CO₂ traces zoomed in and includes a second CO dosage after having exposed the sample to a He flow for 20 min after the first CO dosage. During the second CO dosage, starting at 183 min, the CO₂ concentration is two orders of magnitude smaller than during the first CO dosage, starting at 0 min.

Figure S3.5.1 shows that upon initial CO introduction into the reactor loaded with IrO_{x} , a strong CO₂ signal is measured that declines to a value close to the baseline

within 50 min. In a second dosage of CO, after 20 min of pure He exposition, the recorded CO_2 signal of IrO_x is smaller by two orders of magnitude, which corroborates the assumption that the majority of reactive oxygen surface species was consumed during the first CO exposure. For the rutile-type IrO_2 sample, no CO_2 is registered upon the exposition of the sample to CO (Figure S3.5.1).

3.5.2 CO exposition of IrO_x in near-ambient-pressure XPS setup

The near-ambient-pressure X-ray photoemission spectroscopy (NAP-XPS) system at the ISISS (Innovative station for *in situ* spectroscopy) beam line²⁷ in the synchrotron radiation facility BESSY II/HZB (Berlin, Germany) was used to perform quasi *in situ* photoemission and absorption experiments. The iridium oxide powder (IrO_x, 99.99% metals basis, AlfaAesar Premion[®]) was pressed into a self-supporting pellet (40 mg, 3 t, 90 s, $\emptyset = 8$ mm). After a measurement of the sample as received in UHV ($\approx 10^{-6}$ Pa), the sample was exposed to 25 Pa CO at a flow rate of 2 mL min⁻¹ for 3 h and afterwards measured again in UHV. The advantage of comparing spectra measured in vacuum is that there is no interference from the gas-phase contributions. This approach is especially important for the OK-edge, which would otherwise have a significant contribution from the gas-phase signals of CO and CO₂.

Successively, 25 Pa O₂ (3 mL min⁻¹), 25 Pa H₂O (3 mL min⁻¹) and 25 Pa O₂:O₃ (99:1) were dosed each for 20 min and NEXAFS was measured in between without air contact. For the ozone generation, a commercially available ozone generator TC-1KC was used. Oxygen was passed through Teflon tubing at a rate of 1 L min⁻¹. The effluent gas contained a mixture of \approx 1 % ozone and 99 % molecular oxygen and was dosed into the measurement compartment via a leak valve.

In the XPS measurements, a pass energy (PE) of 10 eV and an exit slit setting of 111 μ m was used, which led to an approximate resolution of 0.2 eV for the Ir 4f core line and 0.4 eV for the O1s core line at 130 eV and 150 eV kinetic energy of the photoelectrons (KE), respectively. With the model of Tanuma *et al.*,²⁸ an inelastic mean free path (IMFP) of the photoelectrons of \approx 0.4 nm is estimated. The binding energy calibration was carried out after evaluating each corresponding Fermi edge.

In NEXAFS, the photon energy was varied between 525 eV and 560 eV by a continuous movement of the monochromator. The Auger electron yield (AEY) of the OK-edge was collected with the electron spectrometer at a fixed KE of 385 eV (PE 50 eV). The probing depth of this measurement is $\approx 2 \text{ nm} - 3 \text{ nm}$. Simultaneously, the total electron yield (TEY) of the OK-edge was collected via a Faraday cup with an accelerating voltage applied. In this case the measurement depth is $\approx 5 \text{ nm} - 10 \text{ nm}$.



Figure S3.5.2: QMS traces of CO, CO₂, H₂O, and O₂ recorded in the NAP-XPS chamber during the CO exposure of the IrO_x (top, lower left (zoomed in)) and rutile-type IrO₂ (lower right (zoomed in)). Over the course of the entire experiment of the IrO_x sample (top), the shape of the CO₂ profile for the IrO_x is considerably different to the traces of H₂O and O₂, confirming that the observed formation of CO₂ is not simply a reaction of CO with residual gas-phase oxygen or water. The figures in the lower part show a comparison of the active (IrO_x, left) and inactive (rutile-type IrO₂, right) samples. In both experiments, when introducing the sample at t = 0 min into the chamber filled with CO also the H₂O and the O₂ traces increase since more surface area of the setup (i.e. load lock in which sample was stored) was exposed which led to a slightly different background signal of the QMS traces. Nevertheless, it is evident that the change in the CO₂ trace of the IrO_x is not just a change in background signal but the actual formation of CO₂.



Figure S3.5.3: Ir 4f spectra (left) and O 1s spectra (right) of IrO_x before and after CO and after ozone exposure. While the Ir 4f spectrum is affected neither by CO nor by ozone, the intensity of the O 1s spectrum at low binding energies slightly decreases after CO exposure. The intensity increase in the O 1s spectrum at \approx 531 eV after ozone exposure is most likely due to carbonate formation at the surface (compare to C 1s spectrum in Figure S3.5.4 (left)). This carbonate formation at the surface might mask the replenishment of O^{I–} in the top layer of IrO_x.



Figure S3.5.4: C 1s spectra (left) and S 2p spectra (right) of IrO_x before and after CO and after ozone exposure. After the CO exposure, mainly the intensity at around 284.5 eV corresponding to graphitic carbon increases, a phenomenon commonly observed in near-ambient-pressure XPS chambers due to the "high" base pressure (10^{-6} Pa) of such systems when compared to UHV-only systems (10^{-8} Pa) .²⁹ This phenomenon also occurs when keeping the sample in vacuum without dosing CO as shown in Figure S3.5.7. After the ozone exposure a slight increase of intensity at around 286 eV may be seen due to oxidation of carbon forming carbonates (as also indicated in the O1s spectrum Figure S3.5.3) during the presence of ozone. The S2p spectra show that the amount of S on the sample is slightly increasing during the course of the experiment. Since similar concentrations of C and S are observed before and after ozone, it can be excluded that the decrease/increase of the 529 eV feature after CO/after ozone is simply the result of carbon or sulfur species covering the O^{I-} species.



Figure S3.5.5: O K-edge of the IrO_x sample measured in total electron yield (TEY) mode before and after CO exposure. Like in AEY mode, the spectra witness a relative decrease of the 529 eV feature compared to the 530 eV feature upon CO dosage.



Figure S3.5.6: OK-edge of the IrO_x sample measured in Auger electron yield (AEY) (left) and total electron yield (TEY) mode before and after ozone exposure. The spectra witness a relative increase of the 529 eV feature compared to the 530 eV feature upon ozone exposure. The additional contribution in the AEY spectra between 548 eV and 558 eV is due to the S 2p XPS peak interfering with the AEY spectrum.



Figure S3.5.7: C 1s core level (left) and OK-edge (right) of an IrO_x sample in its initial state and after 4 h in vacuum (base pressure 10^{-6} Pa). The "high" base pressure of the NAP-XPS system leads to graphitic carbon accumulation at the sample surface as evidenced by the increased contribution to the C 1s core level at \approx 284.5 eV. The shape of the low excitation energy region of the OK-edge is not affected by sole carbon accumulation.

3.5.3 CO titration in SETARAM MS70 Calvet microcalorimeter

The heats of reaction of CO with reactive oxygen species from IrO_x were determined using a SETARAM MS70 Calvet microcalorimeter with a custom-designed highvacuum and gas-dosing apparatus described in detail elsewhere.²⁴ A calibration of the heat-voltage constant of the instrument was done prior to the experiments via the Joule effect. In three runs of the experiment, IrO_x powder volumes between 400 mg and 500 mg were dispensed into the microcalorimeter with a total volume of 274.608 mL. Prior to CO exposure, the powders were dried in vacuum ($<10^{-6}$ Pa) for 72 h to release loosely physisorbed water. When a constant heat signal was reached, the cell was closed. Subsequently, defined amounts of CO 3.7 (Westfalen) were introduced into the initially evacuated measurement volume. The corresponding differential heats of reaction can be calculated by converting the signal area into a heat using the preliminarily determined calibration factor and dividing by the number of involved molecules. For an exothermic process, positive energetic quantities are obtained (calorimetric sign criterion). Figures S3.5.8 to S3.5.10 show the time-dependent line profiles of the thermosignals for the individual dosing steps performed in the three microcalorimetry experiments. For an easier comparison of the line shapes, the signals are normalized and only shown up to 70 min after the initial CO introduction to the microcalorimeter. In the experiment, prior to the following dosing step, we waited for the signal to completely decay to the thermosignal base line, which could take up to 10 h (not shown). In all three experiments, we observe a broadening of the thermosignal with increasing pressure and amounts of reacted CO, as well as a shift of the maximum of the thermosignal to longer times after the initial CO introduction. The latter trend is only reversed towards the end of the experiment, i.e. the last dosing steps. The broadening and tailing of the signal with higher pressures might be an indication for the deeper layer desorption of O^{I–}, liberated by the reaction heat evolved in the surface reaction.

In a postanalysis, the gas phase present in the microcalorimeter after experiment 3 was examined. For this postanalysis, the closed microcalorimeter container was connected to a Varian CP-4900 micro gas chromatograph (microGC) with 4 channels (channel 1: mole sieve 5A, channel 2:Al₂O₃, channel 3: CP-Sil 19CB, channel 4: PoraPlot Q). After opening the connecting valve, the gas volume in the microcalorimeter was flushed out by a He stream of initially 1 mL min⁻¹ and subsequently 5 mL min⁻¹ (Figure S3.5.11). In the effluent gas, we found no residual CO but only CO₂ (see Figure S3.5.11). This finding suggests that the vast majority of CO introduced to the measurement volume was consumed by reactive oxygen species of IrO_x. Therefore, in the calculation of the differential heats of reaction, the entire dosed amount of CO was taken into account. There might be, of course, some residual, unreacted CO molecules



Figure S3.5.8: Normalized time-dependent line profiles of the evolved heat in microcalorimetry experiment 1 for different amounts of reacted CO measured at 313 K. At time 0 min the CO was introduced to the microcalorimeter. For better comparison of the line shapes, the recorded heat signals are normalized to 1 and are only shown up to 70 min. In the experiment, the next dosing step was only performed once the thermosignal base line was reached (for higher amounts of reacted CO not shown). The low signal-to-noise ratio for the first dosing steps is due to the very small thermosignals registered.



Figure S3.5.9: Normalized time-dependent line profiles of the evolved heat in microcalorimetry experiment 2 for different amounts of reacted CO measured at 313 K. At time 0 min the CO was introduced to the microcalorimeter. For better comparison of the line shapes, the recorded heat signals are normalized to 1 and are only shown up to 70 min. In the experiment, the next dosing step was only performed once the thermosignal base line was reached (for higher amounts of reacted CO not shown).



Figure S3.5.10: Normalized time-dependent line profiles of the evolved heat in microcalorimetry experiment 3 for different amounts of reacted CO measured at 313 K. At time 0 min the CO was introduced to the microcalorimeter. For better comparison of the line shapes, the recorded heat signals are normalized to 1 and are only shown up to 70 min. In the experiment, the next dosing step was only performed once the thermosignal base line was reached (for higher amounts of reacted CO not shown). The low signal-to-noise ratio for the first dosing steps is due to the very small thermosignals registered.

that were possibly not detected by the microGC. Unfortunately, due to the measurement setup, it was not possible to measure the composition of the gas phase after each CO pulse in order to determine the exact number of molecules that reacted in each step. The reported value for the reaction enthalpy is therefore given with a considerable error bar and has to be viewed as a lower limit for the reaction enthalpy per molecule. The large standard deviation of this measurement shows that the equipment was operated at its limits since it is usually used only for monitoring adsorption and not reaction events.



Figure S3.5.11: CO_2 and CO concentrations of the postanalysis of the gas mixture in the microcalorimeter after CO titration of IrO_x . The profiles confirm a predominant presence of CO_2 , which suggests that the dosed CO was completely oxidized.

3.5.4 Calculation details

All density functional theory (DFT) calculations were performed using the Quantum ESPRESSO package version 5.3.0.³⁰ The Perdew, Burke, and Ernzerhof (PBE) exchange and correlation potential³¹ was employed as it has been shown to recover the correct ground state electronic structure of IrO2³² and has been used to effectively describe the defect states present in the amorphous IrO_x.^{10,22} The present calculations were performed using scalar relativistic corrections and without spin polarization. Ultrasoft pseudopotentials taken from the PS library³³ were employed for all total energy calculations. Two Gauge-Including Augmented Wave (GIPAW) projectors were included for the l=1 channel of the oxygen pseudopotential to allow us to compute the OK-edge spectra. A plane wave basis set was employed with a kinetic energy cutoff of 30 Ry and a charge density cutoff of 300 Ry. Bulk calculations were performed using a k-point mesh equivalent to (8x8x8) for the 24 atom cell shown in Figure S3.5.12 and previously described.^{10,22} Slab calculations were performed using 10 layers of the crystallographic unit cell for the (110) and (113) surface with approximately 15 Å of vacuum separating periodic images and a k-point mesh equivalent to (8x4x1) for the surface unit cells. Climbing image nudged elastic band calculations (see below) used the full (113) slab but were performed with only 5 layers of the crystallographic unit cell for reactions on the (110) surface. Marzari-Vanderbilt cold smearing³⁴ was used with a smearing parameter of 0.01 Ry.

Climbing image nudged elastic band calculations were performed to identify the transition states for the reaction of CO on the (110) and (113) surfaces. These were performed using 8 images of the system until the forces on the images were less than $0.05 \text{ eV} \text{ Å}^{-1}$. The Δ SCF (self-consistent field) method was used to compute core level


Figure S3.5.12: The bulk rutile-type IrO_2 cell used in the present work is identical to that employed in Pfeifer *et al.*^{10,22}

binding energies (BE) to ensure both initial and final state effects were captured.³⁵ The resultant relative O 1s BEs were shifted to absolute BEs using a reference calculation on a (4x4x4) supercell of IrO_2 . We took the measured O 1s BE of the reference system as 530.0 eV. Previously,^{10,22} we have verified that the relative BEs in IrO_2 were converged to better than 0.1 eV with our computational setup.

OK-edge spectra

Oxygen K-edge spectra were computed in two ways, which proved to be nearly identical, see Figure S3.5.13. In the first we approximated the X-ray absorption process using a one-electron Fermi's golden rule expression as implemented in the XSpectra package.^{36,37} Here we neglected the core-hole and used the ground state results from the USPP calculations. We previously found this approach to give good agreement with experiment for rutile-type IrO₂ when the computed spectra were convoluted using a Lorentzian with an energy dependent linewidth, $\Gamma(E) = \Gamma_0 + \Gamma(E)$, to account for lifetime broadening.^{10,22}

In an effort to ensure this one-electron approximation remains valid for the defect structures giving rise to the O^{I-} state, we also employed a resolvent-based Bethe-Salpeter Equation (BSE) approach to capture the screened core-hole potential and electron-hole dynamics.^{38,39} These calculations were carried out by combining the Kohn-Sham wave functions from QE (Quantum Espresso) with the NIST core-level BSE solver (NBSE) through the OCEAN package.^{40,41} For these calculations, however, we employed norm conserving pseudopotentials generated with the FHI98PP package.⁴² The exchange and correlation was treated with the local density approximation

(LDA) based on Perdew and Wang's parametrization of Ceperely and Alder's data.⁴³ We found the results were converged using a kinetic energy cutoff of 100 Ry (400 Ry) for wave functions (charge density) with ground and final state **k**-point meshs equivalent to those used in the total energy calculations. Methfessel-Paxton smearing⁴⁴ was used with a width of 0.002 Ry during the self-consistent field calculations. The screening calculations were performed including bands to capture states over 100 eV above the Fermi energy. All spectra were broadened with a Lorentzian with a constant width of 0.2 eV to account for lifetime broadening.



Figure S3.5.13: O K-edges computed using the BSE (blue curve) and one-electron (black curve) approaches for rutile-type IrO_2 (left) and O^{I-} and O^{II-} (right).

For both the BSE and one electron calculations the spectra of the symmetry unique oxygen atoms were aligned relative to one another using their corresponding Δ SCF binding energy. Gaussian broadening (FWHM=0.6 eV) was also introduced to account for instrument resolution and phonon broadening.

Figure S3.5.13 shows the BSE and one-electron OK-edge spectra of IrO_2 (left) and the IrO_x -type oxide discussed earlier (right).^{10,22} Both calculations are shown without Gaussian broadening to highlight their differences. The spectrum calculated with the one-electron approximation can be seen to capture all the features present in the BSE approach. While there are slight differences, the remarkable agreement is a consequence of the fact that the 1s core hole is energetically isolated from other states on the atom, which tends to diminish the importance of core-hole dynamics. As a result, the primary differences in the spectra are due to the two treatments of lifetime broadening and core-hole potential, e.g. linear response within the random phase approximation for the BSE calculation compared to the DFT ground state without a core hole.

Heats of reaction

By assuming that the reactant CO and product CO_2 are gas-phase species, as indicated by gas-phase analysis, the heat of reaction can be computed as:

$$\Delta H_{\rm rxn} = E_{\rm IrO_x} - E_{\rm IrO_x - O^*} + E_{\rm CO_2} - E_{\rm CO}$$
(S3.5.1)

where E_{IrO_x} is the total energy of the IrO_x system missing one oxygen, $E_{\text{IrO}_x-O^*}$ is the total energy of the parent IrO_x-O^{*} system, and E_{CO_2} (E_{CO}) is the total energy of an isolated CO₂ (CO) molecule computed at the Γ -point in a 30 Å x 30 Å x 30 Å box. The $E_{\text{CO}_2} - E_{\text{CO}}$ term is a constant that sets the energy of the oxygen atom in the product. Thus, Equation (S3.5.1) could be rewritten:

$$\Delta H_{\rm rxn} = E_{\rm O,vac}^f + E_{\rm O}^{\rm CO_2} \tag{S3.5.2}$$

where $E_{O,vac}^{f}$ is the oxygen vacancy formation energy and $E_{O}^{CO_{2}}$ is the energy of an oxygen atom in CO₂. (Note that the heat of $CO + \frac{1}{2}O_{2} \rightarrow CO_{2}$ was computed to be - 311 kJ mol⁻¹ compared to the -283 kJ mol⁻¹ found experimentally due to the significant errors in reactions with changing bond orders associated with the PBE calculations.⁴⁵) From Equation (S3.5.2) it is clear that the oxygen vacancy formation energy sets the heat of reaction under the assumption that the reactant CO and product CO₂ are gas-phase species.

We computed the heat of reaction by Equation (S3.5.2) for oxygen from the 24 atom bulk rutile-type IrO_2 cell shown in Figure S3.5.12, both with and without an Ir vacancy. In the case of the Ir vacancy we considered the under coordinated and fully coordinated O atoms. We also examined the same vacancy structure with two hydroxyls in place of two under coordinated O atoms. For surfaces we examined bridging oxygen, oxygen on the coordinatively unsaturated sites (CUS), and oxygen in the plane of a (2x1) (110) surface both with and without an Ir vacancy in the surface, see Figure S3.5.14. Inspection of the figure reveals that the OK-edge of the CUS oxygen has a resonance below any observed experimentally whereas the unoccupied states of bridging oxygen are like that of bulk O^{I-} and those of the oxygen in the (110) plane are like that of O^{II-} . We also considered the heat of reaction of CO with oxygen on a (113) surface of rutile-type IrO_2 . For this purpose we took the heat of reaction from the surface.

The computed heats of reaction are shown graphically in Figure S3.5.15, where they are plotted against the position of the white line of the computed OK-edge spectrum of the corresponding oxygen. A linear trend can be seen for cases where Ir-Ir bond formation does not accompany oxygen removal from the surface, as is the case in the



Figure S3.5.14: Oxygen sites considered for heat of reaction on pristine (110) surface. The corresponding OK-edges (computed with one-electron approximation) are also shown.

bulk and for the (110) surface. The more open (113) surface allows significant surface rearrangement after oxygen abstraction, which, in some cases, is resulting in the formation of Ir-Ir bonding, see for example Figure S3.5.16. The resultant drop in energy leads to points that lie off the linear trend in Figure S3.5.15. These points are shown as open circles.



Figure S3.5.15: Correlation between the approximate position of the white line in the computed OK-edge spectrum of an oxygen species and its calculated heat of reaction with CO. Solid circles show results when oxygen loss does not lead to Ir-Ir bond formation, empty circles show results when Ir-Ir bonds are formed after oxygen loss. The dashed line shows the 529 eV excitation energy oxygen is predicted to have a heat of reaction of $\approx 100 \text{ kJ mol}^{-1}$ if no additional Ir-Ir bonds are formed after reaction.



Figure S3.5.16: Example of Ir-Ir bond formation during ionic relaxation of (113) surface after O vacancy formation.

Reactions on (110)

We considered the reaction of $CO_{(g)}$ with O on the (110) CUS, bridge, and lattice sites. In this case, we used the fully oxidized surface, as shown in Figure S3.5.14. However, we employed a (1x1) cell for computational efficiency.

Reaction with the CUS oxygen had a barrier of $158 \text{ kJ} \text{ mol}^{-1}$ and a heat of reaction of $-245 \text{ kJ} \text{ mol}^{-1}$. The high barrier may be tied to the symmetry constraint imposed on the

incoming CO, e. g. the CO axis was aligned with the Ir-O_{CUS} axis. Because we saw no spectroscopic evidence for CUS oxygen we did not explore this further.

Conversely, $CO_{(g)}$ reaction with the bridging oxygen had a barrier of 15 kJ mol^{-1} and heat of 87 kJ mol^{-1} . We could not identify a minimum energy path for reaction with the in-plane oxygen.

Thus, only the O^{I–} like species was found to react with gas-phase CO.

Reactions on (113)

We considered the reaction of CO with oxygen on a partially reduced (113) surface, Figures S3.5.17 and S3.5.18. The surface has two types of under coordinated Ir atoms that can adsorb gas-phase CO, one is coordinated by 3 oxygen atoms and one by 4 oxygen atoms. Of these, a 4-fold site binds CO the strongest at 237 kJ mol^{-1} . Thus, we explored the reaction of CO with surface oxygen from this site.



Figure S3.5.17: Side view of the (113) surface used in this work. The Ir atoms are shown as yellow spheres and the oxygen as red.



Figure S3.5.18: Three (left) and four (right) coordinate Ir atoms on the IrO_2 (113) surface.

The carbon side of the CO adsorbed on a 4-fold site is 3 Å from an O^{I-} site, where the nature of the site was determined by BSE calculation, see Figure S3.5.19. We saw that after CO adsorption the (113) surface could distort, thereby forming an Ir-Ir bond, see Figure S3.5.20. The barrier for this distortion was only 10 kJ mol⁻¹. It is not clear if the distortion is related to CO adsorption or a property of the clean surface. When CO is present, the systems total energy is lowered by 97 kJ mol⁻¹ through this Ir-Ir bond formation. From this state the barrier for CO_{ads} reaction was 50 kJ mol⁻¹. The product CO_2 was adsorbed by 163 kJ mol⁻¹.



Figure S3.5.19: Two views of CO bound to a four coordinate Ir site on the (113) surface and the simulated OK-edge of the neighboring O^{I-} species (black curve) as compared to the bulk O^{I-} species (blue curve) without Gaussian broadening.



Figure S3.5.20: Side view of the (113) surface before and after Ir-Ir bond formation.

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4 *In situ* observation of reactive oxygen species forming on oxygen-evolving iridium surfaces**

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4.1 Abstract

Water splitting performed in acidic media relies on the exceptional performance of iridium-based materials to catalyze the oxygen evolution reaction (OER). In the present work, we use *in situ* X-ray photoemission and absorption spectroscopy to resolve the long-standing debate about surface species present in iridium-based catalysts during the OER. We find that the surface of an initially metallic iridium model electrode converts into a mixed-valent, conductive iridium oxide matrix during the OER, which contains O^{II-} and electrophilic O^{I-} species. We observe a positive correlation between the O^{I-} concentration and the evolved oxygen, suggesting that these electrophilic oxygen sites may be involved in catalyzing the OER. We can understand this observation by analogy with photosystem II; their electrophilicity renders the O^{I-} species susceptible to nucleophilic attack by water during O-O bond formation, i. e. the likely potential-and rate-determining step of the OER. The ability of amorphous iridium oxyhydroxides to easily host such reactive, electrophilic species can explain their superior performance when compared to plain iridium metal or crystalline rutile-type IrO₂.

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4.2 Introduction

In addition to needing renewable energy technologies, an economy based on sustainable resources requires efficient energy storage options. Water electrolysis presents an attractive solution to the latter requirement; it stores excess energy from renewable sources in chemical bonds.^{1,2} To be effective, electrolyzers must be capable of adapting to the varying power inputs of intermittent renewable sources like wind and solar power. While electrolyzers based on proton exchange membranes (PEM) meet this demand, they require a corrosive acidic working environment. Therefore, current research on water electrolysis is driven by the need for efficient, stable, and cost-effective electrocatalysts for the sluggish oxygen evolution reaction (OER) in acidic media.³

While iridium oxide is rare and precious, it remains the state-of-the-art OER catalyst in acidic media owing to its high activity, low overpotential, and good stability.⁴ To uncover the reason for iridium oxide's increased activity, surface scientists have long examined its electronic structure. By combining electrochemical measurements with *ex situ* X-ray photoemission spectroscopy (XPS), they provided chemical information about oxidation states and elemental abundance present after emersion at various potentials.^{5,6} The major drawback of such *ex situ* experiments is that the active state of the electrode cannot be observed under reaction conditions. Furthermore, since the active iridium surface state is likely a hydrated and hydroxylated amorphous form of iridium oxide,^{5,7,8} the electrode's surface morphology and composition likely change when emersed from the electrolyte and brought into a UHV environment.^{5,9} Thus, the active sites may be lost or modified, and since Fierro *et al.*'s¹⁰ isotope-labeling experiments showed that the reactive oxygen species contained in the iridium-oxide matrix are directly involved in the catalytic OER cycle, an *in situ* investigation elucidating the chemical nature of these reactive species is highly desirable.

Significant effort has been invested in the development of *in situ* methodology to assess the active state of electrode materials under working conditions. Owing to these efforts, it is now possible to drive electrochemical reactions and simultaneously record XPS^{11–13} and X-ray absorption spectroscopy (XAS)^{14,15} to monitor the electronic structure of oxygen-evolving surfaces *in situ*. Nevertheless, the interpretation of XPS and XAS measurements of iridium oxides, especially *in situ*, remains challenging. While the literature agrees that hydrated and hydroxylated amorphous forms of iridium oxide with mixed iridium oxidation states have intrinsically higher OER activities than pristine iridium metal and crystalline rutile-type IrO_2 ,^{7,12,15,16} dissent remains about which types of iridium surface species are present during the catalytic OER cycle.^{12,15}

The difficulties in pinpointing iridium oxidation states partly originate from the lack of well-defined oxidic iridium reference materials other than the tetravalent Ir in rutile-type IrO_2 .¹⁷ Drawing parallels with iridium species with different oxidation states present in non-conductive, non-oxidic reference materials is hampered by the fact that these species often have only small^{18,19} or reverse²⁰ shifts in excitation or binding energy in NEXAFS and XPS and usually overlap to a large extent. Therefore, while *in situ* XPS investigations were interpreted to show the presence of iridium species with oxidation states of IV and V during the OER,¹² *in situ* XAS measurements were deconvoluted into contributions of Ir^{III} and Ir^V.¹⁵

In contrast to the difficult identification of the iridium species present, oxygen species (formally O^{I–} and O^{II–}) contained in highly OER-active X-ray amorphous iridium oxide structures show clear fingerprints in the near-edge X-ray absorption fine structure (NEXAFS) of the OK-edge.^{8,16,21} These fingerprint features are highly sensitive to changes in the electronic structure of iridium oxides.²² Hence, the identification of oxygen species in iridium oxide structures presents a key to interpret features in the electronic structure of active iridium oxide surfaces and to shed light on iridium oxide's remarkable activity. For the oxygen species contained in the highly active, amorphous iridium oxide catalysts, for example, the formally O^{I–} species has recently been identified as a highly reactive, electrophilic oxygen.²²

Such electrophiles are prone to nucleophilic attack. This susceptibility to attack by water or OH likely makes O^{I–} active in O-O bond formation, which is often described as both the potential-determining²³ and rate-limiting²⁴ step of the OER. Since we know the electronic structure fingerprints of electrophilic O^{I–} species,^{16,21} we can test if they are indeed forming in oxygen-evolving iridium surfaces by *in situ* NEXAFS and XPS.

On this account, we make use of a proton exchange membrane (PEM)-based *in situ* technique¹¹ for investigating gas-phase water electrolysis. This technique enables us to record XPS and NEXAFS while a model iridium electrode evolves oxygen. An advantage of our approach is that, by keeping the oxygen chemical potential in our system low, we are able to investigate the initial stages of oxide formation on iridium surfaces during the OER. To ensure these low oxygen chemical potentials yield relevant results, we first demonstrate at high overpotentials how iridium is oxidized during the OER and identify the nature of the iridium and oxygen species formed during the reaction. In the second step, we conduct a controlled experiment near the onset of the OER activity of iridium to identify a correlation between the amount of evolved oxygen and the concentration of oxygen species present on oxygen-evolving iridium surfaces.

4.3 Experimental

The discrepancies between electrochemical measurements in electrolyte and surfacesensitive spectroscopic investigations in UHV have been bridged in recent years by setups combining both techniques.^{11–13} The present study uses an *in situ* cell for investigating gas-phase water electrolysis described in detail by Arrigo *et al.*¹¹ In this cell concept (see Figure S4.6.1), a Nafion[®] proton exchange membrane (PEM) is used to separate a continuous flow of liquid water/electrolyte from the evacuated measurement chamber of the near-ambient-pressure XPS (NAP-XPS) endstation of the ISISS beam line²⁵ at the synchrotron facility BESSY II/HZB, Berlin, Germany. The cell concept is described in detail in Section 4.6.2.

In brief, water diffuses through the desiccation cracks of the ≈ 10 nm thick, sputterdeposited electrodes and the PEM due to the pressure difference between the liquid on one side of the membrane and the evacuated measurement chamber on the other (see Figures S4.6.2 to S4.6.4). The water both hydrates the PEM, ensuring good ion conductivity, and delivers the reactant molecules to the working electrode with the resultant equilibrium pressure reaching 0.1-10 Pa. By connecting the working (Ir) and the counter (Pt) electrodes to an external potentiostat, OER-relevant potentials can be applied. A quadrupole mass spectrometer (QMS) monitors the gas composition online to test if oxygen is evolving from the iridium surface.

With this setup, we are able to record XPS and NEXAFS of the X-ray-exposed model iridium working electrode while the OER proceeds. To work under more controlled conditions, in the second part of our study, we equipped the cell with a Ag/AgCl reference electrode (see Figure S4.6.1).

4.4 Results and discussion

Oxygen production on the iridium working electrode is a requirement for our PEMbased approach to deliver relevant observations. Our on-line QMS confirms this OERactive condition of the electrode (see Figure 4.1a). When switching the potential from E_{oc} (open circuit potential) to 2 V, we observe an increase in the oxygen QMS trace. When further increasing the potential to 2.5 V, we detect an additional increase in the oxygen QMS trace. As expected, higher potentials lead to a higher OER activity. By contrast, if we introduce a PEM without Ir coating into the cell, the oxygen QMS trace does not increase when we apply OER-relevant potentials (see Figure S4.6.7). Hence, the oxygen detected in the case of the Ir-coated sample must be produced at the Ir working electrode.



Figure 4.1: a) Oxygen QMS trace, b) Ir 4f spectra and c) OK-edges of Ir-coated PEM (120 s Ir sputtered) recorded in the two-electrode cell with the indicated potentials applied (p=5 Pa, H_2 O).

Ir 4f and OK-edge spectra (probing depths of $\approx 2 \text{ nm}$ and 2 nm - 3 nm, respectively) were collected at each of the potentials applied to the Ir working electrode of the two-electrode system to monitor changes in the present iridium and oxygen species (see Figure 4.1b and c). A deconvolution of the Ir 4f spectra, i.e. a speciation of the Ir species, can be done employing the fit model for iridium oxides introduced in our previous work.^{16,21} Good agreement is obtained between the recorded spectra and the fit envelope for all core level spectra (for fit parameters see Table S4.6.1).

At E_{oc} , the Ir 4f spectrum (see Figure 4.1b) is dominated by the contribution of metallic Ir at 60.8 eV, which has an asymmetric line shape typical for metallic conductors.²⁶ In addition, a minute oxidic component is present at higher binding energy, likely due to surface oxidation of the sputtered Ir nanoparticles. Increasing the potential to 2 V to start the OER produces only subtle changes in the Ir 4f spectrum. The metallic contribution remains nearly unchanged and the oxidic component grows slightly. Further increasing the potential to 2.5 V leads to pronounced changes, with substantially more intensity emerging at higher binding energies in a broad feature.

The Ir4f spectrum recorded during the OER at 2.5V consists of three major contributions. First, there is a residual of the initially metallic Ir at 60.8 eV binding energy. Second, the largest contribution centered at 61.7 eV originates from iridium in the formal oxidation state IV (as in the well-defined reference rutile-type IrO_2). This peak has an asymmetric line shape and appears in combination with a satellite at 1 eV higher binding energy.^{16,21} Finally, there is an additional component at 62.3 eV, i.e. at higher binding energy than Ir^{IV} , not found in rutile-type IrO_2 . The appearance of this higher binding energy iridium oxide feature during OER was also observed by Casalongue et al.¹² Based on the shift to higher binding energy, they intuitively assigned this feature to Ir^V. Nevertheless, in our previous work we combined XPS with theoretical calculations and concluded that Ir^{III} species can exhibit a reverse binding energy shift and that these species are also expected to be found at higher binding energies than Ir^{IV}, namely 62.3 eV.^{16,21} Such Ir^{III} species are present in amorphous, highly OER-active iridium oxyhydroxides. In these materials, Ir^{III} appears in conjunction with formally O^{I–} species. Hence, an identification of the oxygen species formed during OER may help us shed light on the nature of these additional Ir species present during the OER at 2.5 V

We can assess the nature of the oxygen species present in the near-surface region of the catalyst by inspecting the OK-edges collected at the different potentials (see Figure 4.1c). In the OK-edge spectrum recorded at E_{oc} , we mainly see contributions of carbonaceous contamination of the surface (532 eV - 535 eV) and possibly sulfonic or sulfate groups of the PEM (>537 eV) (see Figure S4.6.8). In accordance with the Ir 4f spectrum collected at E_{oc} , we observe no clear contribution of iridium oxide species in the corresponding OK-edge. By contrast, at 2 V where we only registered a small contributions appearing in the low excitation energy region of the OK-edge. The excitation energy values of these two contributions, namely 529 eV and 530 eV, match the main resonances of formally O^{I–} and O^{II–} species identified in the amorphous iridium oxyhydroxide reference material exactly.^{16,21} When further increasing the potential to 2.5 V, the O^{I–} and O^{II–} contributions to the OK-edge grow in intensity.

Since the spectral features seen in the iridium surface oxidized during OER coincide with those observed in the amorphous Ir^{III/IV} oxyhydroxide reference, we suggest that these materials are of a similar nature. We tentatively identify the iridium species present on oxygen-evolving iridium surfaces as Ir^{III} and Ir^{IV}. Further, we confirm the formation of O^{I–} and O^{II–} species during the OER over iridium. Hence, we have witnessed *in situ* that, during the OER, electrophilic O^{I–} species form in an amorphous, mixed-valent iridium phase.

The observed formation of O^{I–} species during the OER not only strengthens our previous suggestion that such electrophilic O^{I–} species may be crucial for the OER reactivity^{16,21,22} but may also explain the long-standing question about the origin of the oxidation signal observed at \approx 1.4 V vs. SHE in the CV of iridium (see Figure 4.2a). Whereas in the past this signal was often assigned to further oxidation of the metal center, i.e. the transition of Ir^{IV} to Ir^V,^{5,27,28} we suggest that it reflects the oxidation of oxygen from O^{II–}, contained in the IrO_x matrix in form of adsorbed OH groups, to O^{I–}:

$$IrO_{x}O^{II-}H \rightleftharpoons IrO_{x}O^{I-} + H^{+} + e^{-}$$
(4.1)

To test this assertion, we used density functional theory (see Section 4.6.6) to compute the potential at which O^{I-} forms from surface OH groups, the latter of which give resonances at 532 eV in the OK-edge (see Figure S4.6.28). The computed value of 1.2 V - 1.3 V supports the hypothesis that O^{I-} formation accounts for the \approx 1.4 V oxidation signal observed experimentally. While such a redox-active, non-innocent ligand^{29,30} may at first glance contrast with common intuition, the diffuse nature of the Ir 5d orbitals and the metal's high oxidation state (IV) in IrO₂ suggest it is energetically favorable for the oxide to accommodate holes in the O2p states rather than further oxidize Ir^{IV} to Ir^V.³¹

With these experiments, we have illustrated the OER-active surface state of an iridium electrode likely consists of an $Ir^{III/IV}$ matrix with oxygen species in the formal oxidation states I– and II–. A comparison of our observations from the recorded Ir 4f spectra and OK-edges highlights that although we only observe subtle changes in the Ir 4f spectrum at 2 V during the OER, the appearance of iridium oxygen compounds is clearly mirrored by the presence of O^{I-} and O^{II-} species in the OK-edge. Hence, the OK-edge is more sensitive to changes in the electronic structure of iridium oxides than the Ir 4f core line. This higher sensitivity may be connected to the slightly higher information depths of the NEXAFS measurements and the sample morphology: The OK-edges likely contain information from regions closer to the triple-phase boundary of water, electrolyte, and iridium where the reaction takes place. Therefore, we use the OK-edge as basis for the subsequent investigation to determine which species are present near the onset of the OER and how they correlate with activity.

What remains to be clarified is in how far the presence of the observed oxygen species is related to iridium's OER activity. For this aim, the reaction needs to be driven under exact potential control at moderate overpotentials. To conduct such experiments near the onset of iridium's OER activity, we upgraded the cell into a three-electrode system by adding a Ag/AgCl reference electrode (see Figure S4.6.1), which ensures that the potential applied to the working electrode has exactly the desired value.



Figure 4.2: a) Cyclic voltammogram, b) normalized O^{I-} and O^{II-} concentrations over QMS oxygen ion current, and c) zoomed and fitted low excitation energy regions of OK-edges recorded in the three-electrode cell (indicated potentials vs. SHE, ring current=60 mA, p=0.3 Pa, 0.1 M H₂SO₄).

Figure 4.2a shows the redesigned device works under relevant conditions. The CV of a sputter-deposited Ir electrode displays the characteristic oxidation waves at 1 V vs. SHE (commonly attributed to and oxidation of Ir^{III} to Ir^{IV 27,28}) and 1.4 V vs. SHE (oxidation of oxygen from O^{II–} to O^{I–}, see the preceding discussion) and the OER onset at 1.5 V vs. SHE. The additional feature visible at 0.6 V vs. SHE originates from the cell itself (see Figure S4.6.6). After a series of 35 CVs to precondition the iridium electrode surface, the potential applied to the working electrode was stepwise increased by 0.05 V starting from 1.6 V vs. SHE. Figure S4.6.18 shows the expected concomitant increase of both the current density and the oxygen concentration in the gas phase. A plot of oxygen concentration over current density shows their linear relationship (see Figure S4.6.18) excluding that, within the measured potential region, the ratio between currents due to simple corrosion and oxygen production changes. Furthermore, an estimation of the amount of present Ir atoms ($\approx 10^{16}$) and the overall number of electrons passed across the electrode ($\approx 10^{19}$) excludes a major contribution to the measured current by simple Ir dissolution/corrosion. By these potential steps, we have created iridium oxide surfaces that evolve different amounts of oxygen. To see whether this increase in oxygen production also shows a correlation with the concentration of the present oxygen species, we recorded the OK-edge at each applied potential (see Figure S4.6.19).

Figure 4.2c shows the low excitation energy region of the OK-edge at successively applied potentials. We deconvoluted these regions using the calculated spectra for the O^{I-} and O^{II-} species^{16,21} to quantify their respective contributions to the overall signal. We used the resulting fits to determine the dependence of the O^{I-} and O^{II-} concentrations on the current density and oxygen QMS ion current (see Figure 4.2b and Figures S4.6.16 and S4.6.21). While we observe a linear correlation between the oxygen evolution activity and the O^{I-} concentration ($R^2 = 0.96$), we see only a weak correlation with the O^{II-} concentration ($R^2 = 0.87$). Hence, the concentration of O^{I-} seems to be tied to the magnitude of the OER reactivity of iridium catalysts whereas the concentration of O^{II-} does not.

If, as we hypothesize, the O^{I-} species in these experiments are stabilized by the applied potential, their concentration should decrease once the potential is reduced below 1.4 V vs. SHE. Aiming to relate the presence of these reactive species to the presence of an applied, OER-relevant potential, we alternatively turned on and off the potential using another fresh sample (see Figures S4.6.22 to S4.6.24). In the recorded and fitted spectra, we clearly observe that turning on and off the potential also reversibly turns on and off the major contribution to the intensity of the O^{I-} species (see Figure 4.3a). The difference of the spectra recorded during and after OER (labeled during-after in Figure 4.3b) yields close agreement with the calculated O^{I-} spectrum.

The disappearance of the O^{I–} species once the potential is switched off is likely due to their protonation and shift to higher excitation energies (\approx 532 eV, see Figure S4.6.28). Unfortunately, owing to the high background signal in this excitation energy region, we are not able to verify such an increase in intensity. Nevertheless, such a protonation and subsequent increase in concentration of hydroxyl groups is in agreement with Reier et al.'s observation that postreaction, highly active OER catalysts have high concentrations of OH-groups at the surface.⁸ The small residual of O^{I-} still present in our experiments after the potential is turned off is likely due to subsurface sites that are not accessible for protonation. As the thickness of the amorphous oxide layer increases, we would then expect a concomitant increase in the amount of residual O^{1–}, in agreement with its ex situ presence in highly active amorphous iridium oxyhydroxide powders.^{16,21} However, the fraction of residual O^{I–} in our thin oxide films is minute when compared to the large O^{I-} signal in such bulk amorphous powder catalysts with signal contributions from deeper, possibly inaccessible subsurface O^{I-} species. Hence, while in the present experiment the majority of O^{I-} is likely protonated and forms OH-groups once the potential is switched off, many of the O^{I-} hosted by the bulk oxyhydroxides seem to be unprotonated.



Figure 4.3: a) Low excitation energy region of OK-edges of Ir-coated PEM (60 s Ir sputtered), consecutively recorded (bottom to top) in the three-electrode cell with the indicated potentials vs. SHE applied and b) difference spectrum of two consecutively recorded OK-edges and comparison with calculated O^{I-} spectrum (ring current=13 mA, p=0.45 Pa, 0.1 M H₂SO₄).

If we assume that the increase in O^{I–} concentration with increasing oxygen evolution activity is not a mere side reaction, we can combine our in situ observations to address the original hypothesis that the electrophilic O^{I–} species participates in O-O bond formation during the OER on iridium. This idea stems from a comparison to photosystem II (PS II). Although in this heavily studied biological system for oxygen generation from water the O-O bond formation process has not yet been finally resolved, theory and experiment strongly agree on the involvement of an electron deficient oxygen species, either electrophilic oxygen or an oxyl radical, in O-O bond formation.^{32–37} While, so far, we have not obtained direct experimental evidence for the formation of radicals in the iridium oxide matrix, our previous study²² demonstrated the O^{I-} species, shown in the present study to also form in oxygen-evolving iridium surfaces, to be strong electrophiles. In a mechanism proposed for PS II, which involves such electrophilic oxygen species, an oxygen contained in the Mn water oxidation complex (WOC) transforms into an electrophile (O*) that is subsequently attacked by nucleophilic (bound) water or hydroxides to form the O-O bond.³⁵⁻³⁷ In a simplified form, this part of the OER process in PS II can be written as:

$$WOC - O^* + H_2O \longrightarrow WOC - O^{I-} - O^{I-} - H + H^+ + e^- \longrightarrow WOC + O_2 + 2H^+ + 3e^-$$
(4.2)

Under the assumption that a similar mechanism with a ligand-centered oxidation prior to O-O bond formation applies to the OER over iridium oxides, we may write for the reaction between water and the electrophilic O^{I–} species present on iridium oxides during the OER:

$$IrO_xO^{I-} + H_2O \longrightarrow IrO_xO^{I-} - O^{I-} - H + H^+ + e^- \longrightarrow IrO_x + O_2 + 2H^+ + 3e^-$$
 (4.3)

The electrophilic nature of the O^{I–} makes this nucleophilic attack of water possible, whereas the additional charge on O^{II–} makes that species less susceptible to such an attack. After the evolution of oxygen, the catalytic cycle can be closed by regenerating IrO_xO^{I-} from IrO_x and water under the influence of the applied potential. In our experiments, we are not able to see the OOH intermediate of reaction (4.3) due to its short lifetime once the O-O bond is formed. Nevertheless, a reaction path through this intermediate has been suggested both by theory²³ and ultra-fast infra-red measurements.³⁸ The suggested OER mechanism then rationalizes the high activity observed for amorphous iridium oxyhydroxide powder catalysts, since they tend to form large amounts of highly reactive O^{I–} species.^{16,21,22} In contrast to these highly active IrO_x powders, rutile-type IrO_2 does not tend to form a high concentration of O^{I–} and is significantly less active in the OER.^{16,21} Thus, a catalyst's propensity to accommodate electrophilic O^{I–} species appears to be essential in its ability to catalyze O-O bond formation.

4.5 Conclusion

In conclusion, using *in situ* X-ray photoemission and absorption spectroscopies, we have demonstrated for the first time that reactive electrophilic O^{I–} oxygen species form in a mixed-valent iridium^{III/IV} matrix during the OER. The observed formation of these O^{I–} species implies that iridium oxide contains redox-active, non-innocent ligands accounting for the redox chemistry of the material. We further found the O^{I–} concentration to increase with the measured oxygen evolution activity and to virtually disappear from our thin oxyhydroxide films in the absence of an applied potential. Both observations agree with our hypotheses that electrophilic O^{I–} species are active in catalyzing the OER on iridium oxides and that enhanced OER performance of iridium oxyhydroxides can be achieved by the accommodation of large amounts of reactive oxygen species serving as precursor sites for the O-O bond formation. In the quest for less expensive materials to catalyze the OER, these findings can guide the way for the design of new high-performance catalysts comprising such reactive oxygen species.

4.6 Supplementary Information

4.6.1 In situ X-ray photoemission/absorption spectroscopy setup

All *in situ* photoemission and absorption measurements were collected with the nearambient-pressure X-ray photoemission spectroscopy (NAP-XPS) system at the ISISS (Innovative station for *in situ* spectroscopy) beam line²⁵ located at the synchrotron radiation facility BESSY II/HZB (Berlin, Germany). In contrast to conventional UHV-based XPS systems, in this setup spectra can be collected at gas-phase pressures of up to several hundreds of pascals due to a sophisticated differential pumping and electrostatic lens system.³⁹ In the present experiments, the pressure was adjusted between 0.1 Pa and 10 Pa depending on the measurement requirement as will be stated in more detail in the respective sections. All measurements were collected at room temperature.

For all XPS measurements, a pass energy (PE) of 20 eV and an exit slit setting of the beam line of 111 μ m were used, which led to an approximate resolution of the Ir 4f core line of 0.5 eV at 450 eV kinetic energy (KE) of the photoelectrons. The corresponding inelastic mean free path of the photoelectrons is \approx 0.7 nm according to the model of Tanuma *et al.*⁴⁰ A binding energy calibration of the spectra was realized by measuring the Fermi edge after each core level scan.

For all near-edge X-ray absorption fine structure (NEXAFS) measurements, the photon energy was varied between 525 eV and 552 eV by continuously moving the monochromator. Both the Auger and total electron yield (AEY and TEY) were registered. The AEY was measured with the electron spectrometer. To partly suppress the contribution of gas-phase oxygen and water,⁴¹ the KE of the collected electrons was set to 385 eV with a PE of 50 eV. The TEY was collected via a Faraday cup via the first aperture of the differential pumping system with an applied accelerating voltage. While AEY is slightly more surface sensitive than TEY (probing depths of 2 nm - 3 nm vs. 5 nm - 10 nm),⁴² TEY usually provides better signal-to-noise ratios which becomes important when measuring low intensities. When comparing NEXAFS spectra of a series of measurements, the spectra were normalized to 0 in the pre-edge region between 523 eV and 527 eV and a linear fit function of the same region was used to subtract the slightly linearly increasing background of the spectra.

The NAP-XPS system is equipped with an on-line quadrupole mass spectrometer (QMS, Prisma, Pfeiffer Vacuum, Inc., Germany). The QMS was used to continuously record the traces of H_2O , H_2 , O_2 , CO_2 , and their fragments during the measurements.

The measurements reported here were collected during different operation modes of the synchrotron. When denoted with top-up mode, the storage ring current was held constant at 300 mA by continuous injections. To reduce beam damage of the sample, measurements were also collected during a low-alpha operation mode of the synchrotron, in which the storage ring current was in decay mode starting from 100 mA or 15 mA. The used mode and storage ring current will be denoted in the respective paragraphs.

4.6.2 Proton exchange membrane-based in situ cells

In the present work, the design of an *in situ* cell described by Arrigo*et al.*¹¹ based on the water permeability of a proton exchange membrane (PEM) was further developed. Due to the modular approach of the ISISS endstation, such cells can be easily inserted into the system.



Figure S4.6.1: (left) Two-electrode *in situ* cell with sputtered Ir working and Pt counter electrode. (right) Three-electrode *in situ* cell with sputtered Ir working, Pt wire counter, and Ag/AgCl reference electrode. In both cells, water supplied from the rear diffuses through the desiccation cracks of the sputtered electrodes and the PEM and delivers the reactant molecules to the reaction chamber. While XPS and NEXAFS are measured, the gas composition is monitored by an on-line QMS. Through the connection to an external potentiostat, OER-relevant potentials can be applied to the working electrode.

In a first advancement, we upgraded the water supply from a batch reservoir to a continuous flow (see Figure S4.6.1 (left)). This continuous flow of water prevents the PEM from drying out and ensures a stable supply of reactant molecules to the working electrode throughout the experiments. This first upgrade permits measurement durations of several hours.

In a second advancement, we equipped the cell with a Ag/AgCl micro reference electrode (DRIREF-2SH, World Precision Instruments, USA) to work under well-defined potential conditions (see Figure S4.6.1 (right)). During this second upgrade, we needed to slightly modify the cell design: To allow the reference electrode to be lo-

cated closer to the working electrode than the counter electrode, we replaced the sputtered Pt film by an externally inserted Pt wire. In addition, instead of water, the threeelectrode cell requires an electrolyte for proton conductivity. We used 0.1 M H_2SO_4 prepared from concentrated sulfuric acid (EMSURE[®], 95-97 %, Merck KGaA, Darmstadt, Germany) and ultra-pure Milli-Q water (18.2 M Ω). For better corrosion stability, we replaced the stainless steel of the cell body by polyether ether ketone (PEEK).

For both cells, we realized the electrical contact to the working electrode (WE) via a glassy carbon lid. The use of this electrochemically resistant material prevents the strong corrosion of the lid material, which we had observed for a previously used stainless steel lid. In the two-electrode cell, we contacted and grounded the counter electrode (CE) via the stainless steel body while in the three-electrode cell, we contacted the CE directly with the Pt wire. The Ag/AgCl reference electrode (RE) was directly connected to the potentiostat.

As potentiostat, we used an SP-300 modular research grade device from Bio-Logic Science Instruments SAS, France. For the two-electrode cell, we operated the potentiostat in floating mode, since the CE was grounded via the stainless steel cell body in contact with the spectrometer. By this electrical connection between the CE and the spectrometer, their Fermi levels were aligned. Shifts observed in the BE of the recorded spectra could therefore be directly related to the potential difference between the WE and CE during the chronoamperometric (CA) measurements. For the three-electrode setup, we used the potentiostat in grounded mode.

For the samples, we used Nafion[®] 117 (AlfaAesar) as PEM throughout all of our experiments. The diameter of the circular samples was 12 mm. Prior to the deposition of the electrode materials, the Nafion[®] 117 was first purified in 3 vol.% H_2O_2 (prepared from 30 % H_2O_2 ROTIPURAN[®], Carl Roth, Germany and Milli-Q water) for 2 h at 80 °C and then activated in 0.5 M H_2SO_4 (prepared from H_2SO_4 EMSURE[®], 95-97 %, Merck KGaA, Darmstadt, Germany and ultra-pure Milli-Q water) for 2 h at 80 °C. Between and after these steps, the membranes were rinsed with Milli-Q water and finally dried and stored in air between clean filter paper.

We sputter-deposited the Ir and Pt films from metallic targets (Ir 99.99% and Pt 99.99%, Elektronen-Optik-Service GmbH, Germany) in 10 Pa Ar at 40 mA using a Cressington 208HR sputter coater. The deposition time was 180 s or 60 s for Ir and 120 s for Pt, resulting in film thicknesses ranging from 10 nm - 20 nm. The areas of the circular Ir and Pt electrodes were 6 mm and 9 mm, respectively. We used the working electrode size of 6 mm to determine the current densities from the measured currents. This determination is obviously just an approximation since we do not know the electrochemically active surface area from this electrode size.

We determined the morphologies of the sputtered films and their metallic distribution in a scanning electron microscope (SEM) Hitachi S-4800 FEG equipped with a Bruker XFlash detector and an energy dispersive X-ray spectroscopy (EDX) system Quantax. The images were taken with an acceleration voltage of 1.5 kV in SE mode and the metallic distribution was determined via an X-ray map at 15 kV. We further investigated their nanostructure by TEM using an FEI TITAN 80-300 with an acceleration voltage of 200 kV. The SEM images in Figure S4.6.2 display the Ir and Pt films that have desiccation cracks, which enable the water transport across the electrode-membrane assembly. The X-ray scans in Figure S4.6.3 confirm the homogeneous distribution of the electrode materials on the Nafion[®] 117. The TEM images confirm the Ir film thickness of $\approx 20 \text{ nm}$ and that the nanostructure of the film is composed of interconnected nanoparticles. These connected nanoparticles ensure the conductivity necessary for driving electrochemical experiments and measuring XPS.



Figure S4.6.2: SEM images of (left) Ir and (right) Pt sputter-deposited on Nafion[®] 117. The images clearly show the desiccation cracks of the sputter-deposited films allowing for an efficient water transport through the metallic films.

Figure S4.6.5 shows an XPS survey of such a sputter-deposited Ir film on Nafion[®] 117. Apart from the iridium core levels, we also detect fluorine, oxygen, carbon and sulfur signals. These signals mainly originate from Nafion[®] 117 and the fluid electrolyte H_2SO_4 . The reason for Nafion[®] 117 to contribute to the XPS signal is the mud-crack type structure of the sputter-deposited Ir film. In the desiccation cracks, the membrane is directly exposed to the X-rays and its emitted photoelectrons contribute to the overall signal, hence we are partly probing the triple phase boundary (electrolyte, water, iridium) of interest. Nevertheless, parts of the oxygen and carbon signal will also originate from surface oxidation of the Ir nanoparticles and carbonaceous contamination on the Ir surface. Since we do not observe any (differential) charging of the surface, we can be sure that the Ir islands are interconnected and form a conductive film.



Figure S4.6.3: X-ray map of (left) Ir and (right) Pt sputter-deposited on Nafion[®] 117. The images show the homogeneous distribution of the electro-active materials.



Figure S4.6.4: TEM cross sections of the sputter-deposited Ir in different magnifications.



Figure S4.6.5: XPS survey of Ir-coated Nafion[®] 117 (60 s Ir sputtered, sample 23898) with an identification of the observed core levels. Recorded in the three-electrode cell at E_{oc} (ring current=13 mA, p=0.45 Pa, 0.1 M H₂SO₄).

4.6.3 Control investigation of uncoated PEM

To ensure that the registered signals and main spectral regions of interest were neither distorted nor affected by signals of the substrate Nafion[®] 117 membrane, uncoated membranes were investigated in control experiments.

For the first investigation, a purified and activated plain Nafion[®] 117 was mounted in the three-electrode cell. In a first step, a cyclic voltammogram (CV) was recorded (see Figure S4.6.6 (left)). The CV shows reversible oxidation/reduction waves at 0.6 V vs. SHE and 0.5 V vs. SHE, respectively. In the OER-relevant region of the CV starting from 1.5 V vs. SHE only a slight current increase is observed. For comparison, the CV of an Ir-coated sample is shown in Figure S4.6.6 (right). Comparing these CVs, on the one hand, we see that the reversible oxidation/reduction signals of Nafion[®] 117 are still slightly visible for Ir-coated sample. On the other hand, we see that, in addition, the characteristic oxidation signals of iridium at \approx 1 V vs. SHE and \approx 1.4 V vs. SHE are present and that both the capacitative currents and the current increase in the OER region are almost one order of magnitude higher when Ir is present.



Figure S4.6.6: Cyclic voltammograms of (left) uncoated Nafion[®] 117 (sample 23879, p=16.5 Pa) and (right) Ir-coated Nafion[®] 117 (180 s Ir sputtered, sample 23878, p=5.8 Pa) recorded in the three-electrode cell prior to chronoamperometry (scan rate=100 mV s⁻¹, 0.1 M H₂SO₄).

A similar observation holds for the comparison of the current density and oxygen QMS traces measured during different applied potentials to uncoated and Ir-coated Nafion[®] 117 (see Figure S4.6.7): The current density measured for the uncoated is considerably lower than for the Ir-coated Nafion[®] 117. The oxygen QMS trace of plain Nafion[®] 117 is not perturbed when the potential is raised above OER-relevant values, i. e. no oxygen evolves from the uncoated Nafion[®] 117, while the oxygen QMS signal considerably increases for the Ir-coated Nafion[®] 117 with each potential increase.



Figure S4.6.7: (bottom) Chronoamperometry and (top) oxygen QMS signal of (left) uncoated Nafion[®] 117 (sample 23879, p=16.5 Pa) and (right) Ir-coated Nafion[®] 117 (180 s Ir sputtered, sample 23878, p=5.8 Pa) recorded in the three-electrode cell with the indicated potentials vs. SHE applied ($0.1 \text{ M H}_2\text{SO}_4$).

Finally, the OK-edge of plain Nafion[®] 117 was measured at the different applied potentials. Figure S4.6.8 shows the collected AEY (left) and TEY (right) data. In the AEY, the signal at \approx 532 eV may result from carbonaceous contamination while the large signal at \approx 537 eV originates from sulfates from the Nafion[®] 117 and the used electrolyte H₂SO₄. In the TEY, the most prominent signals descend from the gas-phase resonances of water vapor.⁴³ From both graphs, we observe that our main region of interest, the excitation energy values of 529 eV and 530 eV, seems to be unaffected by the background signals. A zoom into this region confirms the absence of disturbing background signals (see Figure S4.6.9).



Figure S4.6.8: (left) AEY and (right) TEY signals of the OK-edges of uncoated Nafion[®] 117 (sample 23879), consecutively recorded (bottom to top) in the three-electrode cell with the indicated potentials vs. SHE applied (ring current=70 mA, $p=16.5 \text{ Pa}, 0.1 \text{ M H}_2\text{SO}_4$).



Figure S4.6.9: Zoomed low excitation energy regions of the (left) AEY and (right) TEY signals of the OK-edges of uncoated Nafion[®] 117 (sample 23879), consecutively recorded (E_{oc} to 1.8 V) in the three-electrode cell with the indicated potentials vs. SHE applied (ring current=70 mA, p=16.5 Pa, 0.1 M H₂SO₄).

Although the water supply from the back of the membrane is continuous, we always observe slight alterations of the pressure in the measurement compartment and therefore also in the amount of water present in the gas phase. Especially when comparing a sequence of measurements, the tails of the water signals may affect the background and distort the iridium oxide signals. Hence, the water vapor background signals observed in the TEY measurement may still become disturbing to the interpretation of the spectra, even though Nafion[®] 117 and water do not have disturbing signals exactly at the excitation energies of interest. To minimize the influence of differing background signals on the spectra, we reduced the pressure in the measurement compartment by increasing the applied pumping speed of the NAP-XPS system. At a pressure of ≈ 0.1 Pa, the contribution of the water gas phase is no longer visible in the TEY measurement of pure Nafion[®] 117 (see Figure S4.6.10) and therefore the signal background is no longer dependent on the gas-phase water pressure and less sulfate is expected to deposit on the surface.

The advantage of using the TEY instead of the AEY signal is the increased signalto-noise ratio of the TEY measurements. Therefore, for the controlled measurements collected near the onset of iridium's OER activity with low ring currents to prevent beam damage, it is necessary to rely on the TEY measurements. As will be shown later, we still observe the evolution of oxygen at these reduced pressure conditions by means of QMS, hence the device is still working under relevant conditions at these reduced pressures.



Figure S4.6.10: (left) AEY and (right) TEY signals of the OK-edges of uncoated Nafion[®] 117 (sample 23896), consecutively recorded (bottom to top) in the three-electrode cell with the indicated potentials vs. SHE applied (ring current=50 mA, p=0.1 Pa, $0.1 \text{ MH}_2\text{SO}_4$).



Figure S4.6.11: Zoomed low excitation energy regions of the (left) AEY and (right) TEY signals of the OK-edges of uncoated Nafion[®] 117 (sample 23896), consecutively recorded (E_{oc} to 1.6 V) in the three-electrode cell with the indicated potentials vs. SHE applied (ring current=50 mA, p=0.1 Pa, 0.1 M H₂SO₄).

4.6.4 Ir 4f fit parameters

The fitting of the Ir 4f spectra shown in Figure 4.1 was done using the fit model previously derived for iridium and its oxides.^{16,21} The parameters employed for the fits shown in Figure 4.1 are given in Table S4.6.1.

Table S4.6.1: Fit parameters of Ir 4f spectra recorded *in situ* at the indicated potentials with a kinetic energy of the photoelectrons of 450 eV. FWHM, full width at half maximum; BE, binding energy; E_{oc} , open circuit potential; DS, Doniach-Šunjić; GL, Gauss-Lorentz; SGL, Gaussian-Lorentzian sum form.

	$_{\rm Ir4f_{7/2}}^{\rm Ir4f_{7/2}}$	$_{\rm Ir4f_{5/2}}^{\rm Ir4f_{5/2}}$	$_{\rm Ir^{4f_{7/2}}}^{\rm Ir^{4f_{7/2}}}$	$_{\rm Ir^{4f_{5/2}}}^{\rm Ir^{4f_{5/2}}}$	$\frac{\mathrm{Ir}4\mathrm{f}_{7/2}}{\mathrm{Ir}^{\mathrm{IV}}\mathrm{sat1}}$	$\frac{\mathrm{Ir}4\mathrm{f}_{5/2}}{\mathrm{Ir}^{\mathrm{IV}}\mathrm{sat1}}$	$\frac{\mathrm{Ir}4\mathrm{f}_{5/2}}{\mathrm{Ir}^{\mathrm{IV}}\mathrm{sat2}}$	$_{\rm Ir^{4f_{7/2}}}^{\rm Ir4f_{7/2}}$	$_{\rm Ir^{4f_{5/2}}}^{\rm Ir4f_{5/2}}$	$\frac{\mathrm{Ir}4\mathrm{f}_{7/2}}{\mathrm{Ir}^{\mathrm{III}}\mathrm{sat1}}$	$\frac{\mathrm{Ir}4\mathrm{f}_{5/2}}{\mathrm{Ir}^{111}}\mathrm{sat1}$
$E_{\rm oc}$											
line shape	DS(0.132,163) SGL(100)	DS(0.132,163) SGL(100)	DS(0.2,100) SGL(45)	DS(0.2,100) SGL(45)	GL(0)	GL(0)					
area/%	54.0	38.0	3.8	2.9	0.7	0.6					
FWHM/eV	0.8	0.7	0.9	1.0	3.1	3.1					
BE/eV	60.8	63.8	61.8	64.8	62.8	65.8					
2 V											
line shape	DS(0.132,163) SGL(100)	DS(0.132,163) SGL(100)	DS(0.2,100) SGL(45)	DS(0.2,100) SGL(45)	GL(0)	GL(0)					
area / %	45.9	32.3	10.4	7.9	2.0	1.5					
FWHM/eV	0.8	0.8	0.9	1.0	3.1	3.1					
BE/eV	60.8	63.8	61.8	64.8	62.8	65.8					
2.5 V											
line shape	DS(0.132,163) SGL(100)	DS(0.132,163) SGL(100)	DS(0.2,100) SGL(45)	DS(0.2,100) SGL(45)	GL(0)	GL(0)	GL(0)	DS(0.2,100) SGL(45)	DS(0.2,100) SGL(45)	GL(0)	GL(0)
area/%	7.2	5.1	36.1	27.2	7.0	5.3	0.2	5.8	4.7	0.8	0.6
FWHM/eV	0.7	0.8	1.1	1.1	2.9	2.9	2.5	0.7	0.8	2.9	2.9
BE/eV	60.8	63.8	61.8	64.8	62.8	65.8	67.8	62.3	65.3	63.3	66.3

4.6.5 In situ investigation near the onset of iridium's OER activity

The controlled measurements near the onset of iridium's OER activity were all performed with the three-electrode cell at reduced pressures (≈ 0.1 Pa). To minimize the beam damage of the beam sensitive 529 eV feature of the O^{I–} species, we performed these measurements in the low-alpha mode of BESSY II with reduced ring currents. The pressure and exact ring current conditions will always be denoted in the figure captions. To precondition and activate the Ir films on Nafion[®] 117, we always performed a sequence of 35 CVs between 0.1 V vs. SHE and 1.6 V vs. SHE prior to all other measurements. Subsequently, we recorded a scan of the OK-edge, an XPS survey and the Ir 4f, C 1s, and O 1s core levels at E_{oc} to capture the initial state of the Ir electrode surface. Finally, we applied OER-relevant potentials, monitored the corresponding current densities of the WE and oxygen QMS traces and recorded NEXAFS and XPS to observe changes in the electronic structure of the iridium electrodes. In the following, we will show three examples of typical experiment results and how the oxygen evolution rate and current density are related with the presence of O^{I–} species on the Ir electrode surface.



Figure S4.6.12: Cyclic voltammogram of Ir-coated Nafion[®] 117 (180 s Ir sputtered, sample 23894) recorded in the three-electrode cell with the indicated potentials vs. SHE applied (p=0.5 Pa, 0.1 M H₂SO₄).



Figure S4.6.13: (left) Chronoamperometry (bottom) and oxygen QMS signal (top) and (right) linear correlation between current density and evolved oxygen of Ir-coated Nafion[®] 117 (180 s Ir sputtered, sample 23894) recorded in the three-electrode cell with the indicated potentials vs. SHE applied (p=0.5 Pa, 0.1 M H₂SO₄).

Figures S4.6.12 and S4.6.13 show the CV and the subsequently recorded CA of sample 23894, a Nafion[®] 117 that was sputter-coated for 180 s with metallic Ir. The CV mainly shows the oxidation/reduction signal of Nafion[®] 117 at \approx 0.6 V vs. SHE, a slight indication of the Ir-oxidation signals at 1 V vs. SHE and 1.4 V vs. SHE and the OER onset at around 1.5 V vs. SHE. When OER-relevant potentials are applied, the current density in the CA increases stepwise with each potential increase. A concomitant stepwise increase is observed in the oxygen evolution rate as mirrored in the the oxygen QMS signal. We observe a linear relation between the current density and the oxygen evolution activity. When the potential is turned off, the oxygen signal immediately drops back to its original value.



Figure S4.6.14: OK-edges of Ir-coated Nafion[®] 117 (180 s Ir sputtered, sample 23894), consecutively recorded (bottom to top) in the three-electrode cell with the indicated potentials vs. SHE applied (ring current=70 mA, p=0.5 Pa, 0.1 M H_2SO_4).

Figure S4.6.14 displays the OK-edges recorded at consecutively applied potentials. At the pressure established during this experiment, the OK-edge still shows minor resonances of gas-phase water. Nevertheless, these resonances do not severely influence the spectra. In this representation, we observe nearly no changes in the spectra in dependence of the applied potential. However, when we zoom into the region of interest at low excitation energies, we do observe clear changes depending on the applied potential (see Figure S4.6.15). To quantify the observed changes, we used the spectra calculated ¹⁶ for O^{I–} and O^{II–} (shown in Figure S4.6.27) to fit the low excitation energy region of the OK-edge. We obtain good agreement between the measured spectra and the resulting fit envelope (see Figure S4.6.15).

In a next step, we wanted to identify the relation between the observed oxygen species and the oxygen evolution activity of the electrode. For this purpose, we plotted the relative concentration of O^{I–} and O^{II–} against the current density recorded with the potentiostat and the oxygen ion current registered by QMS, respectively (see Fig-



Figure S4.6.15: Zoomed and fitted low excitation energy regions of O K-edges of Ircoated Nafion[®] 117 (180 s Ir sputtered, sample 23894) consecutively recorded (left to right, top to bottom) in the three-electrode cell with the indicated potentials vs. SHE applied (ring current=70 mA, p=0.5 Pa, 0.1 M H₂SO₄).

ure S4.6.16). The determined error values originate from the fluctuations in measured current densities (x-error) and the uncertainties in peak height determination (y-error). We observe a linear relationship between the O^{I-} -species and both the current density measured with the potentiostat and the oxygen ion current registered by QMS (R²-values of 0.94 and 0.95). In contrast, we observe only a loose dependence of the O^{II-} concentration on current density and ion current (R²-values of 0.66 and 0.67).



Figure S4.6.16: Normalized O^{I-} and O^{II-} concentrations over (left) current density and (right) QMS oxygen ion current of Ir-coated Nafion[®] 117 (180 s Ir sputtered, sample 23894) at consecutively applied potentials between 1.6 V vs. SHE and 1.9 V vs. SHE.
To confirm the results obtained with sample 23894, we repeated the experiments with sample 23895, which was also a 180 s Ir-sputtered Nafion[®] 117 from the same batch of sample. Figures S4.6.17 to S4.6.21 show the same features and trends as observed in the previous experiment: The CV in Figure S4.6.17 counts with the oxidation waves of iridium oxides at 1 V vs. SHE and 1.4 V vs. SHE and the additional reversible oxidation/reduction feature of Nafion[®] 117 at \approx 0.6 V vs. SHE. The CA and the QMS oxygen ion current in Figure S4.6.18 show a linear increase with increasing potential applied to the Ir WE. While the overview spectrum of the OK-edge in Figure S4.6.19 does not show marked changes during the experiment, a zoom in the low excitation energy region and the corresponding fits in Figure S4.6.20 shows a clear increase of O^{I–} concentration with increasing potential.



Figure S4.6.17: Cyclic voltammogram of Ir-coated Nafion[®] 117 (180 s Ir sputtered, sample 23895) recorded in the three-electrode cell with the indicated potentials vs. SHE applied (p=0.3 Pa, 0.1 M H₂SO₄).



Figure S4.6.18: (left) Chronoamperometry (bottom) and oxygen QMS signal (top) and (right) linear correlation between current density and evolved oxygen of Ir-coated Nafion[®] 117 (180 s Ir sputtered, sample 23895) recorded in the three-electrode cell with the indicated potentials vs. SHE applied ($p=0.3 Pa, 0.1 M H_2 SO_4$).



Figure S4.6.19: OK-edges of Ir-coated Nafion[®] 117 (180 s Ir sputtered, sample 23895), consecutively recorded (bottom to top) in the three-electrode cell with the indicated potentials vs. SHE applied (ring current=60 mA, p=0.3 Pa, $0.1 \text{ M H}_2\text{SO}_4$).



Figure S4.6.20: Zoomed and fitted low excitation energy regions of OK-edges of Ir-coated Nafion[®] 117 (180 s Ir sputtered, sample 23895), consecutively recorded (left to right, top to bottom) in the three-electrode cell with the indicated potentials vs. SHE applied (ring current=60 mA, p=0.3 Pa, $0.1 \text{ M H}_2\text{SO}_4$).

A quantification of the relative O^{I-} and O^{II-} concentrations and their plots against the current density measured with the potentiostat and the oxygen ion current determined by QMS in Figure S4.6.21 confirm the linear dependence of oxygen evolution activity and O^{I-} concentration.



Figure S4.6.21: Normalized O^{I-} and O^{II-} concentrations over (left) current density and (right) QMS oxygen ion current of Ir-coated Nafion[®] 117 (180 s Ir sputtered, sample 23895) at consecutively applied potentials between 1.6 V vs. SHE and 2 V vs. SHE.

In a final *in situ* investigation, we tested the stability of the O^{I-} species and alternatively switched on and off the potential applied to the Ir WE. We first confirmed the similar behavior of the Ir-coated Nafion[®] 117 (sample 23898, 60 s Ir sputtered) in cyclic voltammetry and obtained a similar CV shape as for the previous samples (see Figure S4.6.22 (left)).



Figure S4.6.22: (left) Cyclic voltammogram and (right) chronoamperometry (bottom) and oxygen QMS signal (top) of Ir-coated Nafion[®] 117 (60 s Ir sputtered, sample 23898) recorded in the three-electrode cell with the indicated potentials vs. SHE applied (p=0.45 Pa, 0.1 M H₂SO₄).

We then applied OER-relevant potentials of 1.6 V vs. SHE, 1.7 V vs. SHE, and 1.9 V vs. SHE and turned off the potential in between. The resulting current densities and QMS oxygen ion currents are shown in Figure S4.6.22 (right). At 1.9 V vs. SHE the current density and the corresponding oxygen ion current increase sharply for a short period of time, in which the electrode possibly reaches a highly active state. Due to the short time period, it was not possible to record the corresponding OK-edge. The measurement at 1.9 V vs. SHE was recorded from 80 min onwards.

In the overview spectra of the OK-edge, we can observe already in this representation that the 529 eV species is switched on and off with the applied potential (see Figure S4.6.23). This observation becomes even clearer when considering the zoomed in and fitted low excitation energy region in Figure S4.6.24.



Figure S4.6.23: O K-edges of Ir-coated Nafion[®] 117 (60 s Ir sputtered, sample 23898), consecutively recorded (bottom to top) in the three-electrode cell with the indicated potentials vs. SHE applied (ring current=13 mA, p=0.45 Pa, 0.1 M H₂SO₄).



Figure S4.6.24: Zoomed and fitted low excitation energy regions of O K-edges of Ircoated Nafion[®] 117 (60 s Ir sputtered, sample 23898), consecutively recorded (left to right, top to bottom) in the three-electrode cell with the indicated potentials vs. SHE applied (ring current=13 mA, p=0.45 Pa, 0.1 M H₂SO₄).

Figures S4.6.25 and S4.6.26 show the corresponding Ir 4f and O 1s spectra of sample 23898 recorded at the different applied potentials. The major change observed in the Ir 4f spectrum occurs at the first application of an OER-relevant potential of 1.7 V vs. SHE. We observe slightly more intensity at higher binding energy, suggesting a slight surface oxidation, which is in line with the observation of the increasing contribution of O^{I–} and O^{II–} at this applied potential (see Figure S4.6.24). Subsequent potential cycles of turning the applied potential on and off have nearly no impact on the shape of the Ir 4f spectrum. In the O 1s spectra, complementary to the OK-edge, we observe an increased intensity at lower binding energies of 529 eV, where the O^{I–} are located, while the OER proceeds. Since this sample was measured at a low storage ring current of 13 mA, the signal-to-noise ration of these spectra is rather poor and we concentrated our interpretation on the OK-edge. Nevertheless, the O 1s spectra confirm the trends observed in the OK-edge.



Figure S4.6.25: Ir 4f signals of Ir-coated Nafion[®] 117 (60 s Ir sputtered, sample 23898) recorded in the three-electrode cell with the indicated potentials vs. SHE applied (p=0.45 Pa, 0.1 M H₂SO₄).



Figure S4.6.26: O1s signals of Ir-coated Nafion[®] 117 (60 s Ir sputtered, sample 23898) recorded in the three-electrode cell with the indicated potentials vs. SHE applied (p=0.45 Pa, 0.1 M H₂SO₄).

4.6.6 Calculation details

As described in detail in our previous work,^{16,21} density functional theory (DFT) calculations were performed using the Quantum ESPRESSO package version 5.3.0⁴⁴ with the Perdew, Burke, and Ernzerhof (PBE) exchange and correlation potential.⁴⁵ Ultrasoft pseudopotentials were taken from the PSlibrary for all total energy calculations.⁴⁶ A kinetic energy cutoff of 30 Ry and a charge density cutoff of 300 Ry was used in all calculations. A **k**-point mesh equivalent to (8x4x1) was employed for the surface unit cells. Surfaces were modeled using 5 layers of the crystallographic unit. Oxygen K-edge spectra were computed using a one-electron Fermi's golden rule expression as implemented in the XSpectra package.⁴⁷ A Lorentzian with an energy dependent linewidth, $\Gamma(E) = \Gamma_0 + \Gamma(E)$, was employed to account for lifetime broadening. The Δ SCF (self-consistent field) method was used to compute O 1s binding energies.



Figure S4.6.27: Calculated OK-edges of bulk O^{I-} and O^{II-} species.^{16,21}

Figure S4.6.27 shows the calculated OK-edges of bulk O^{I–} and O^{II–} spectra^{16,21} used to fit the low excitation energy region of the *in situ* measurements.

The potential at which O^{I-} forms on an iridium surface was computed using the DFT energies along with the well-known concept of a theoretical standard hydrogen electrode (SHE).²³ In this approach, we assume the surface is in thermodynamic equilibrium with protons and liquid water at 298 K at a fixed applied potential and pH. Thus, the surface can exchange oxygen and hydroxyl with the water. The potential and pH dependence of the free energy can be captured through the chemical potential of the proton and electron by writing:

$$2\mathrm{H}^{+}_{(\mathrm{aq})} + 2\mathrm{e}^{-} \leftrightarrow \mathrm{H}_{2(\mathrm{g})}, \tag{S4.6.1}$$

with $\Delta G^0 = 0$ at pH=0 and 10⁵ Pa H₂ pressure. This allows us to set U=0 V vs. SHE. With this definition it is now straightforward to compute changes in Gibbs Free Energies as:

$$\Delta G = \Delta G_0 + \Delta G_U + \Delta G_{pH}$$
(S4.6.2)

where ΔG_0 , ΔG_U , and ΔG_{pH} take their standard definitions:

$$\Delta G_0 = \Delta E + \Delta Z P E - T \Delta S, \qquad (S4.6.3)$$

$$\Delta G_{\rm U} = -eU, \qquad (S4.6.4)$$

and

$$\Delta G_{pH} = -k_B T \ln 10 pH. \tag{S4.6.5}$$

Here ΔE is the reaction energy computed from DFT, ΔZPE and ΔS are the changes in zero point energy and entropy due to reaction, respectively. For the zero point energy (ZPE) term the vibrational modes of the solid are computed using DFT while the molecular ZPE and S are taken from tabulated data.

We investigated O- and OH-groups on the (110) and (100) surfaces of rutile-type IrO₂. Here we found that the μ_2 -OH bridges are predicted to be deprotonated at \approx 1.3 V vs. SHE on the (110) surface when μ_1 -O is also present and \approx 1.2 V vs. SHE when a μ_1 -OH is present. In both cases μ_2 -O is predicted to form, see OK-edges below. Similarly, at an applied potential of \approx 1.2 V vs. SHE the μ_2 -OH bridges on the (100) surface are predicted to transform into μ_2 -O when a μ_1 -OH is present. Deprotonation of the μ_1 -OH is predicted to occur at \approx 1.8 V vs. SHE on the (110) surface and \approx 1.6 V vs. SHE on the (100) surface.

The simulated OK-edge spectra corresponding to the aforementioned structures suggest that the μ_2 -O is seen during our experiments, which gives rise to a resonance at \approx 529 eV, see Figures S4.6.28 and S4.6.29. The exact position of the resonance depends on surface termination and the nature of the coadsorbed species, with the resonance shifting to lower excitation energies when μ_1 -OH or μ_1 -O are also present. While we cannot rule out the presence of μ_1 -OH (giving a resonance at \approx 530 eV), we do not see any resonance at 528 eV in the experiments that would be indicative of μ_1 -O.



Figure S4.6.28: OK-edges computed for a subsurface O^{II-} in the third layer beneath the (110) surface (solid red) and a μ_2 -O (dashed blue), a μ_2 -OH (black dotted), and a μ_1 -OH (dotted-dashed orange) on the (110) surface.



Figure S4.6.29: O K-edges computed for a μ_1 -OH (dotted-dashed orange), a μ_2 -O (dashed blue) and a μ_1 -O (solid green) species on the (100) surface of rutile-type IrO₂.



Figure S4.6.30: Ball and stick models of (110) surface with μ_2 -OH (left) and μ_2 -O (center) along with a model of a (100) surface with μ_1 -OH and μ_2 -O (right).

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5 Summary and final conclusion

Replacing fossil fuels and establishing an economy relying on renewable energies entails the provision of sufficient energy storage capacities for intermittent renewable resources. Part of these storage capacities can be based on chemical energy conversion with hydrogen obtained from water electrolysis being the basic fuel. For this aim, electrolyzers need to tolerate the varying power inputs from intermittent sources. Although this flexibility criterion is met by electrolyzers based on proton exchange membranes (PEM), the technology is not yet mature and competitive. One factor hampering the successful implementation of PEM electrolyzers for hydrogen generation is the lack of cost-effective catalyst materials with long-term stability for the sluggish oxygen evolution reaction (OER). Owing to the acidic conditions prevailing in PEM electrolyzers, only noble-metal-based catalysts, the best of which is iridium oxide, are able to withstand the corrosive environment present at the oxygen-evolving anode. In order to tailor cost-effective and stable catalysts with minimized precious metal content and prolonged lifetimes, an identification of favorable surface configurations for the anode material and surface modifications occurring during the OER is required. Such an identification can be obtained from the electronic structure fingerprints of involved species. The principle goal of this thesis was therefore to provide a deeper understanding of the electronic structure fingerprints of iridium oxide surface configurations favoring the OER by X-ray photoemission and near-edge X-ray absorption fine structure spectroscopy (XPS & NEXAFS).

In a first step, a reference library was created to thoroughly understand the inherent differences in different iridium oxide structures. For this aim, two reference iridium oxide powders, one X-ray amorphous (IrO_x) and the other crystalline in the rutile-type structure (IrO₂), were investigated with standard powder characterization methods. From a combination of thermogravimetry and temperature-programmed reduction, a formal Ir oxidation state of 4.1 ± 0.1 for rutile-type IrO₂ was deduced while the formal Ir oxidation state of the amorphous powder was found to be only 3.6 ± 0.1 . This finding suggested the presence of multiple iridium species in the amorphous powder, some of which having an oxidation state of less than four. Finally, linear sweep voltammetry measurements assessed the OER activity of the two reference samples and found the amorphous IrO_x to be considerably more active than rutile-type IrO₂.

In a second step, electronic structure fingerprints of the reference iridium oxide powders were investigated by a combination of theory, XPS and NEXAFS. A prerequisite for the speciation of the recorded XPS measurements was to understand the peculiar line shape of the Ir 4f core level of iridium oxides. By calculating the d projected density of states of an Ir atom in rutile-type IrO₂ with an Ir 4f core hole, it was found that there exists a strong narrow feature at 1 eV above the Fermi energy giving rise to a shake-up satellite. From this point on, a robust fit model for the Ir 4f line shape of Ir in oxidation state four could be developed. For the amorphous powder, not only a broader Ir 4f line shape was observed but also an additional pre-edge feature in the NEXAFS of the OKedge at an excitation energy of 529 eV. Since such pre-edge features can emerge when hole doping materials, rutile-type IrO₂ was intentionally hole-doped in theoretical calculations by inserting Ir vacancies. From these calculations, it was found that the holes localize on oxygen forming formally O^{I-} species. These O^{I-} species have their main resonance in the OK-edge at 529 eV. Furthermore, it was seen that this hole-doping also leads to a reduction of neighboring Ir^{IV} to Ir^{III}. The binding energy of these Ir^{III} was calculated to be higher than that of Ir^{IV}. Although counterintuitive, this finding is able to explain the broader Ir 4f line shape of the amorphous IrO_x and is in line with the previous finding of mixed Ir oxidation states in the amorphous material. These investigations showed that rutile-type IrO_2 is composed only of formally $\mathrm{Ir^{IV}}$ and $\mathrm{O^{II-}}$ while the amorphous IrO_x contains both Ir^{IV} and Ir^{III} as well as O^{I–} and O^{II–} species.

Since the amorphous IrO_x was observed to have a higher OER activity than the crystalline rutile-type IrO₂, the additionally present species in IrO_x, namely O^{I-} and Ir^{III}, were suspected to play a key role in catalyzing the OER. Since the O^{I–} are electron deficient, they were hypothesized to be electrophilic. To test their reactivity and electrophilicity, CO oxidation experiments were performed at room temperature. In a standard reactor at ambient pressure, the amorphous IrO_x reacted stoichiometrically with CO to CO₂ while rutile-type IrO₂ was inactive. To monitor surface modifications on IrO_x induced by this reaction , a quasi in situ XPS/NEXAFS experiment was performed and it was found that the O^{I-} concentration diminished upon CO exposition confirming that CO reacts stoichiometrically with accessible O^{I–} species. By a combination of theoretical calculations and a microcalorimetric analysis, it was found that this reaction is not only thermodynamically feasible but also that the measured reaction enthalpies and those calculated for a reaction of CO with O^{I-} coincide. These observations confirmed the assumption of O^{I-} being an electrophilic species. In addition, quasi in situ NEXAFS experiments employing ozone yielded that the O^{I-}, which had reacted with CO, could be replenished. The possibility of replenishing the O^{I-} species is a prerequisite for them to take part in the catalytic OER cycle.

In the final investigation, it was tested whether the observed O^{I-} were actually present during, and potentially involved in, the OER. To do so, in situ XPS and NEX-AFS experiments were performed to monitor changes in the electronic structure of an oxygen-evolving model iridium surface. For these investigations, a PEM-based electrochemical cell was introduced into a near-ambient-pressure XPS setup, OER-relevant potentials were applied, the evolution of oxygen was witnessed by on-line quadrupole mass spectrometry, and simultaneously XPS and NEXAFS were recorded. At high overpotentials, the previously derived fit model and reference measurements were used to show that reactive electrophilic O^{I-} species form in a mixed-valent Ir^{III/IV} matrix during the OER. Hence, one peculiarity about iridium oxide was deduced to be its ability to readily accommodate electrophilic O^{I-} species, which are redox-active, non-innocent ligands, instead of further oxidizing Ir to oxidation state V. At moderate overpotentials, the O^{I–} concentration present on the initially metallic Ir surface was observed to scale linearly with the oxygen evolution activity. Furthermore, the O^{1–} contribution to the OK-edge spectrum could be reversibly turned on and off when turning on and off the applied potential. These observations further indicate the intimate relationship between the presence of O^{I-} species and the OER activity of iridium oxides. From these indications, it was concluded that the O-O bond formation in electrocatalytic water splitting on iridium may proceed through a nucleophilic attack of water or hydroxyls, similarly as has been proposed in biological water splitting in photosystem II, over a reactive, electrophilic oxygen species accommodated in a flexible, mixed-valent iridium matrix. This finding finally explains the superiority of amorphous IrO_x containing O^{I-} over rutile-type IrO_2 lacking these species.

In conclusion, this thesis contributes to a better understanding of the suitability of iridium oxide as OER catalyst. In particular, it provides a fundamental comprehension of the electronic structure fingerprints of iridium and its oxides that may serve as reference for further investigations of promising catalyst candidates. Furthermore, it identifies the ability of materials to form electrophilic oxygen species as key parameter when tailoring high-performance OER catalysts with minimized noble metal loadings. Thus, with its ability to host such electrophilic O^{I–} species instead of further oxidizing the metal centers to Ir^V, iridium oxide is a role model in this effort. The knowledge obtained may be used to design novel cost-effective catalysts for PEM-based electrolyzer systems needed for a paradigm shift in the energy supply of the future. In fact, in a parallel PhD thesis prepared at the Fritz-Haber-Institute, a family of highly active Irbased OER catalysts containing such electrophilic O^{I–} species could be synthesized.⁺⁺

⁺⁺Massué, C., Iridium oxohydroxide electrocatalysts for the oxygen evolution reaction, dissertation, TU Berlin, 2016

Indeed it was found that the OER activity both scaled with the amount of comprised O^{I–} species and was reduced after their consumption by CO titration of the samples.

An interesting extension to the *in situ* studies performed during this thesis would be to move away from iridium metal as model test system and to investigate actual iridium oxide catalysts with different OER activities. From such an investigation, the role of reactive electrophilic O^{I–} species could be further determined. In a final step, these *in situ* measurements can be translated from gas-phase to liquid-phase water electrolysis to reduce the mass transport limitation of reactants and to compare the results with classical electrochemical investigations in liquid electrolytes. For this aim, a different cell concept based on the electron transparency of graphene may be used. In this concept, a graphene instead of a proton exchange membrane is employed to separate the liquid electrolyte from the evacuated measurement chamber. Such a cell has already been developed at the Fritz-Haber-Institute and proof-of-principle measurements have confirmed its suitability to monitor the electronic structure of solid/liquid interfaces during electrochemical processes.^{#‡}

^{‡‡}Velasco Vélez, J. J.; Pfeifer, V.; Hävecker, M.; Weatherup, R. S.; Arrigo, R.; Chuang, C.-H.; Stotz, E.; Weinberg, G.; Salmeron, M.; Schlögl, R.; Knop-Gericke, A., Photoelectron Spectroscopy at the Graphene-Liquid Interface Reveals the Electronic Structure of an Electrodeposited Cobalt/Graphene Electrocatalyst. *Angew. Chem. Int. Ed.* **2015**, 54, 14554-14558.

Appendix

List of publications

Pfeifer, V.; Jones, T. E.; Wrabetz, S.; Massué, C.; Velasco Vélez, J. J.; Arrigo, R.; Scherzer, M.; Piccinin, S.; Hävecker, M.; Knop-Gericke, A.; Schlögl, R., Reactive oxygen species in iridium-based OER catalysts. *Chem. Sci.* **2016**, *7*, 6791-6795.

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Li, X.; Lunkenbein, T.; Kröhnert, J.; <u>Pfeifer, V.</u>; Girgsdies, F.; Rosowski, F.; Schlögl, R.; Trunschke, A., Hydrothermal synthesis of bi-functional nanostructured manganese tungstate catalysts for selective oxidation. *Faraday Discuss.*, **2016**, 188, 99-113.

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Pfeifer, V.; Jones, T. E.; Velasco Vélez, J. J.; Massué, C.; Arrigo, R.; Teschner, D.; Girgsdies, F.; Scherzer, M.; Greiner, M. T.; Allan, J.; Hashagen, M.; Weinberg, G.; Piccinin, S.; Hävecker, M.; Knop-Gericke, A.; Schlögl, R., The electronic structure of iridium and its oxides. *Surf. Interface Anal.* **2016**, 48, 261-273.

Pfeifer, V.; Jones, T. E.; Velasco Vélez, J. J.; Massué, C.; Greiner, M. T.; Arrigo, R.; Teschner, D.; Girgsdies, F.; Scherzer, M.; Allan, J.; Hashagen, M.; Weinberg, G.; Piccinin, S.; Hävecker, M.; Knop-Gericke, A.; Schlögl, R., The electronic structure of iridium oxide electrodes active in water splitting. *Phys. Chem. Chem. Phys.* **2016**, 18, 2292-2296.

Velasco Vélez, J. J.; <u>Pfeifer, V.</u>; Hävecker, M.; Weatherup, R. S.; Arrigo, R.; Chuang, C.-H.; Stotz, E.; Weinberg, G.; Salmeron, M.; Schlögl, R.; Knop-Gericke, A., Photoelectron Spectroscopy at the Graphene–Liquid Interface Reveals the Electronic Structure of an Electrodeposited Cobalt/Graphene Electrocatalyst. *Angew. Chem. Int. Ed.* **2015**, 54, 14554-14558.

Talks at conferences

- May 2016 Bunsentagung 2016, 115th General Assembly of the German Bunsen Society for Physical Chemistry, Rostock, Germany;
 Title: The Electronic Structure of Iridium Oxides Active in Water Splitting
- Sep 2015 EuropaCat2015, 12th European Congress on Catalysis, Kazan, Russia; Title: Development of *in situ* techniques to monitor oxygen-evolving electrocatalyst surfaces

Poster contributions at conferences as presenting author

Jul 2016	Materials for Energy and Sustainability - 5 th course and EPS-IPS Interna- tional School in Energy - 3 rd course, Summer School, Erice, Italy; Poster title: Reactive oxygen species in iridium-based OER catalysts
Dec 2015	Seventh joint BER II and BESSY II User Meeting, Berlin, Germany; Poster title: The Electronic Structure of Iridium Oxide Electrodes Active in Water Splitting
Mar 2015	48. Jahrestreffen Deutscher Katalytiker, Weimar, Germany; Poster title: NAP-XPS Studies of Iridium during the Oxygen Evolution Reaction
Nov 2014	3 rd Ertl Symposium "Surface Analytics and Dynamics", Berlin, Germany; Poster title: Near-Ambient-Pressure-XPS Studies of Iridium during the Oxygen Evolution Reaction
Sep 2014	Deutsche Tagung für Forschung mit Synchrotronstrahlung, Neutronen und Ionenstrahlen an Großgeräten 2014, Bonn, Germany; Poster title: Investigation on the electrolysis of water by <i>in situ</i> NAP-XPS
May 2014	562 nd Wilhelm and Else Heraues-Seminar: From Sunlight to Fuels - Novel Materials and Processes for Photovoltaic and (Photo)Catalytic Applica- tions, Bad Honnef, Germany; Poster title: Investigation of water electrolysis by <i>in situ</i> NAP-XPS