Experimental Activity Descriptors for Iridium-Based Catalysts for the Electrochemical Oxygen Evolution Reaction (OER)

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Supporting Information

ABSTRACT: Recent progress in the activity improvement of anode catalysts for acidic electrochemical water splitting is largely achieved through empirical studies of iridium-based bimetallic oxides. Practical, experimentally accessible, yet general predictors of catalytic OER activity have remained scarce. This study investigates iridium and iridium—nickel thin film model electrocatalysts for the OER and identifies a set of general ex situ properties that allow the reliable prediction of their OER activity. Well-defined Ir-based catalysts of various chemical nature and composition were synthesized by magnetron sputtering. Correlation of physicochemical and electrocatalytic properties revealed two experimental OER activity descriptors that are able to predict trends in the OER activity of unknown Ir-based catalyst systems. More specifically, our study demonstrates that the IrIII+- and OH-surface concentration of the oxide catalyst constitute closely correlated and generally applicable OER activity predictors. On the basis of these predictors, an experimental volcano relationship of Ir-based OER electrocatalysts is presented and discussed.

KEYWORDS: electrolysis, OER, electrolyzers, figures of merit, water splitting, catalyst design, volcano relationship, oxide formation and growth

1. INTRODUCTION

With increasing capacities of renewable energies being installed worldwide, one of the most important requirements for industry and research alike is the development of suitable energy-storage solutions. Among the most promising suggestions is (photo)electrochemical water splitting, which can be effectively done in ion exchange membrane electrolyzers. Here, proton exchange membrane (PEM) electrolysis is predicted to be the state-of-the-art technology in short and medium term development. Because of the acidic environment of proton exchange membranes, iridium has been widely accepted as the standard anode catalyst in PEM water electrolysis with the best compromise of activity and stability. However, despite the huge effort, the reaction mechanism as well as the active species or structure have not been fully elucidated and are subject to intense discussion in the field. Besides activity descriptors like the adsorption energy difference between the *OH and *OOH intermediates, as they are often used in density functional theory (DFT) calculations, other catalyst properties can be used as descriptors as well. While the investigation of active species of Ir-based catalysts is crucial, it is restricted to complex in operando measurements. Hence, several approaches to identify activity descriptors from the as-prepared state have been made. The superior activity of electrochemically oxidized iridium over thermally oxidized iridium is usually attributed to a more amorphous and hydrated structure of the former. Recent efforts correlate a three-dimensional reaction regime in the electrochemically oxidized case to the increased activity. Reier et al. have shown that iridium oxide thin films calcined at high and low temperatures retain different ratios of OH-surface species and two chemically distinct oxide types that correlate with the observed activity trend. Özer et al. have indicated that the exposed facets of an iridium catalyst may have an influence on the initial activity. Given that the current understanding of the OER mechanism suggests strong surface amorphization and participation of the lattice oxygen, one can easily assume the loss of a distinct long-range order of...

Received: February 13, 2019
Revised: May 19, 2019
Published: June 13, 2019

DOI: 10.1021/acscatal.9b00648
ACS Catal. 2019, 9, 6653–6663

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surface facets during the reaction. However, Willinger et al. have proposed the importance of short-range order structural motifs for the iridium OER activity. 16 Their amorphous iridium(hyd)oxide catalyst is suggested to consist of tunnel-like hollandite clusters that are stabilized by K+ ions in the tunnels. The flexibility of these short-range motifs is supposed to accommodate the surface amorphization during OER. Flexible surface motifs have been reported to promote OER activity by faster formation of active species, as demonstrated by Saveleva et al.17 In attempts to reduce the expensive iridium content, several iridium-based mixed metal oxides have been investigated, with IrNi and IrCo mixed metal oxides being the most prominent ones.18,19 On IrNi oxide thin film catalysts, a dependency of the OH surface ratio to the initial Ni content has been observed.20 The initial Ni leaching is suggested to lead to a surface restructuring that removes oxide surface terminations and reduces the oxidation state of remaining Ir species. A similar restructuring can be expected for the IrNi core—shell particles reported by Nong et al., albeit the shell consists of Ir oxide only after the Ni leaching.21 In contrast to thin films, the particles retain a metallic IrNi core, and their active site was recently suggested to be an electrophilic oxygen species (O(II)−) with reduced Ir−O bond distance.22 Alia et al. recently presented an extensive study on Ir-based mixed metal oxide nanowires (nw) with either Ni or Co content.18 For both types, an increased OH-surface ratio with increasing initial Ni/Co content was observed. In addition, Kuo et al. uncovered an experimental relationship between the oxygen adsorption energy and OER kinetics of IrO₂ (110).23 Besides fundamental mechanistic investigations, the challenges of stabilizing Ir-based catalysts remain, as was recently highlighted by several authors.24–27

Starting from our current understanding of composition, structure, and morphology of a family of highly active IrNi bimetallic OER electrocatalysts, this study unravels general experimental activity predictors for different types of iridium-based OER electrocatalysts. The predictive power of these descriptors advances our understanding of the oxygen evolution electrochemistry and facilitates the design of new, efficient water oxidation electrocatalysts.

2. EXPERIMENTAL PROCEDURES

Sample Preparation. Thin film catalysts were prepared on Ti disc substrates (10 mm diameter, 4 mm thickness, Ti grade 1, Gemmel Metalle, Germany) that were polished to a mirrorlike finish in a three-step process using a half automatic polishing machine (AutoMet 250, Buehler). To remove surface impurities, polished Ti cylinders were treated in hot nitric acid (23%, prepared by dilution of 69% HNO₃, AnalaR Normapur) in a final step.28

Ir(Ni)(O) coatings were deposited by reactive DC magnetron sputtering using Ir and Ni metallic targets on a rotating substrate holder in the presence of argon−oxygen reactive gas mixtures at UTBM. Besides polished Ti cylinders, glass slides, alumina, and Si wafers were used as substrates. The received samples were investigated as prepared or subjected to an additional heat treatment at TU Berlin. Heat treatment was conducted in a rapid temperature rise furnace with a moving heating stage (MTI Corp., U.S.A.) at 450 °C for 20 min in Ar or synthetic air (Air Liquide) for the metallic and oxide samples, respectively. Detailed information on sample preparation and heat treatment can be found in the SI.

Physicochemical Characterization. All samples were subjected to grazing-incidence X-ray diffraction (GI-XRD), scanning electron microscopy (SEM), and energy-dispersive X-ray spectroscopy (EDX) in their as-prepared, heat-treated, and after-OER states.

GI-XRD measurements were run on a D8 Advance lab XRD (BrukerAXS Microanalysis GmbH, Germany) with Cu Kα X-ray tube, Goebel mirror, 0.28° sloller slit, and a scintillation counter point detector. Measurements were conducted at 1° incidence angle, from 20 to 80°2θ with a 0.06° step size. Rietveld refinement was applied with the TOPAS software package (Bruker, Germany).

SEM-EDX was conducted on a JEOL 7401F field emission scanning electron microscope operated at 10 kV. Images were acquired in secondary electron mode. EDX spectra were acquired of at least three separate areas of each sample in the as-prepared, heat-treated (where applicable), and after-OER state with a Quantax 400 detector (BrukerAXS Microanalysis GmbH, Germany) attached to the JEOL 7401F. EDX spectra were evaluated with the Esprit software package (Bruker, Germany).

A scanning transmission electron microscopy (S/TEM) cross-section of IrNi/NiO HT-OER was acquired by preparing a TEM lamella by Focused Ion Beam (FIB). The TEM and STEM measurements were performed at a FEI Tecnai G²30 S-TWIN transmission electron microscope with a LaB₆ cathode operated at an accelerating voltage of 200 kV. Detailed descriptions of (S)TEM-EDX, SAED, and the FIB operation can be found in the Supporting Information. The SAED evaluation was performed with the PASA plugin in Gatan Digital Micrograph. The obtained reciprocal distances were transferred to Cu Kα scale to compare the calculated diffraction patterns to the PDF database. All electron micrographs (SEM, TEM, and STEM) were evaluated with ImageJ (Version 1.48, W.S. Rasband, NIH, U.S.A.).

X-ray photoelectron spectroscopy (XPS) of the as-prepared, heat-treated, and after-OER states of the samples was carried out at room temperature using nonmonochromatized Al Kα (1486.6 eV) excitation and a hemispherical analyzer (Phobos 150, SPECS). The binding energy (BE) scale was calibrated by the standard Au 4f/2 and Cu 2p3/2 procedure. To calculate the elemental composition, theoretical cross sections from Yeh and Lindau11 were used. The XP spectra were analyzed using the CasaXPS software.

Electrochemical Characterization and Performance. Electrochemical measurements were performed at room temperature in an RDE setup with a three-compartment electrochemical cell equipped with a Luggin-capsillary, PINE rotator (MSRE, Pine Research Instrumentation, U.S.A.) and an SP-200 or SP-150 potentiostat (BioLogic, France). The electrolyte for all experiments, 0.1 M HClO₄, was diluted from 70% HClO₄ (Sigma-Aldrich, 99.999% purity) with 18 MΩ cm Milli-Q water (Synergy UV, Merck Millipore). A Pt mesh attached to a Pt wire was used as counter electrode, and a saturated mercury/mercury-sulfate electrode was used as reference electrode. The latter was calibrated against a reversible hydrogen electrode (RHE) in the same electrolyte regularly. All potentials in this publication are converted and referred to the RHE scale. A custom-made PEEK-tip was used for the working electrode to incorporate the 10 mm diameter catalyst substrates. The exact electrochemical protocol was published elsewhere20 and can be found in the SI. For each
catalyst, at least three individual measurements were conducted on separately synthesized samples.

3. RESULTS AND DISCUSSION

IrNi/IrNiOx catalysts were chosen alongside Ir/IrOx as a model catalyst system to catalyze the acidic oxygen evolution reaction (OER) or equivalently, water oxidation reaction. The selected Ir-to-Ni ratio of near 80 atomic % initial Ni content matched the Ir-to-Ni ratio for which earlier studies reported an OER activity maximum.20 In order to establish experimental property−activity relationships and eventually derive activity descriptors, sample sets of a metallic IrNi alloy and an IrNi oxide were prepared as thin films on Ti disc substrates by magnetron sputtering (see Experimental Procedures). A variety of well-defined metallic and oxidic Ir and IrNi thin film catalysts was prepared, mimicking the most promising OER catalysts recently published. In particular, these samples resemble the initial state of highly active IrNi nanoparticles (henceforth referred to as IrNi NPs19) and IrNiOx thin film (henceforth referred to as IrNiOx TF20) catalysts. One sample set was investigated in its “as-prepared” state mimicking the IrNi NPs, whereas a second set was heat treated prior to further investigation in order to mimic the IrNiOx TF preparation. Sets of reference Ir and IrOx catalyst were prepared accordingly. Samples are denoted IrNi (HT), IrNiOx (HT), Ir (HT), and IrOx (HT) throughout the manuscript, whereby the suffix HT denotes heat-treated samples. Further suffixes “-ap” and “-OER” indicate whether the samples were investigated in their as-prepared or OER-tested states, respectively. Additionally, an IrNi sample heat treated at reduced partial pressure of oxygen was investigated (IrNi/NiO HT).

Electrochemical Analysis and Performance. Initial catalytic OER activities—measured at 1.53 V_RHE as geometric, specific, and mass-based current density in the beginning of the electrochemical protocol—are presented in Figure S1 and Table S1. Interestingly, the initial specific activities of IrNi and IrNi HT are almost identical and similar to the steady-state activity of IrNi HT (compare Figure S1 and Figure 1a). The latter could indicate that stabilization of the initial state of IrNi could lead to improved performance.
In the steady state, presented in Figure 1a, the monometallic iridium catalysts perform comparably. Except for Ir, which shows improved geometric and specific performance with its specific activity being on a similar level to the bimetallic catalysts. This surprisingly high activity has been observed by other groups as well but could not be fully explained yet.\(^3\) Besides Ir, the mixed metal (oxide) catalysts clearly outperform all monometallic materials. The samples IrNi, IrNi HT, and IrNi/NiO HT, designed to mimic the IrNi core—shell NPs, perform distinctly different from each other. Similar to IrNi NPs,\(^1\) heat treatment led to a strong activity decrease as soon as small amounts of oxygen are present (IrNi/NiO HT shows 1/10th of geometric and mass-based current density of IrNi, specific activity is ∼1/2). In contrast to IrNi NPs, heat treatment of IrNi under oxygen exclusion resulted in increased activities and presented the most active catalyst among the investigated set (IrNi HT).

For the monometallic samples in this study, heat treatment led to declining steady-state OER activities (Figure 1a). However, IrNi HT and IrNiOx HT exhibited higher OER activities than their non heat-treated counterparts did. Though, on IrNiOx HT this is only true for geometric and mass activities as the specific activities of IrNiOx and IrNiOx HT coincided. This could partially be explained by the electrochemical redox behavior of IrNiOx vs IrNiOx HT (see Figure 1b,c), asymmetric behavior in redox peaks, which indicates low conductivity in or slow kinetics on IrNiOx. However, contact problems between Ti and catalyst were not observed in potentiostatic electrochemical impedance spectroscopy (PEIS) measurements at any time. Further sintering during heat treatment could mitigate the disadvantage of low conductivity within the layer and thus lead to the observed activity increase. A similar effect, however, can be expected for catalyst loss that affects geometric and mass-based normalization and not the specific activity. Unlike IrNiOx HT, IrNi HT shows an increase in all three OER activities (geometric, mass-based, and specific) over IrNi, indicating an actual change in the intrinsic activity. Tafel slopes (see Table 1) reflected the observed activity trend. All Tafel slopes were in the usual 30–80 mV dec\(^{-1}\) range for iridium-based catalysts.\(^3\)

![Figure 1a](https://example.com/figure1a.png)

**Figure 1a.** State of the art Ir-based catalysts for OER. IrOx (black), IrNiOx (gray), and IrNi (green) are compared with the commercial Ir/C catalyst (white). The insets show the nanoscale architecture of IrNiOx (left) and IrNi (right). \(Q_{\text{OER}}\) is the total anodic charge normalized to the corresponding geometric current density (OER害応するIr(Ox)表面積, \(10^{-26}\)) and was used to calculate the specific current density here, allowing a more precise comparison of the CVs (see experimental section). Remarkably, all highly active catalysts were characterized by large \(Q_{\text{OER}}\) a more negative peak position for redox transition a\(2/3\) and low Tafel slopes. Positions and the corresponding anodic charge are presented in Table 1.

**Table 1.** Redox Peak Positions, Total Anodic Charge Measured between 0.4–1.4 V\(_{\text{RHE}}\) and Tafel Slopes of the Sample Set

<table>
<thead>
<tr>
<th>sample</th>
<th>(a)-OER peak position/V(_{\text{RHE}})</th>
<th>(b)-OER peak position/V(_{\text{RHE}})</th>
<th>(Q_{\text{OER}})/mcC</th>
<th>Tafel slope/mV dec(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ir</td>
<td>0.83 ± 0.01</td>
<td>0.87 ± 0.01</td>
<td>8.4 ± 1.0</td>
<td>45 ± 48</td>
</tr>
<tr>
<td>IrOx</td>
<td>0.84 ± 0.02</td>
<td>0.92 ± 0.02</td>
<td>1.9 ± 0.4</td>
<td>71 ± 46</td>
</tr>
<tr>
<td>IrNi</td>
<td>0.81 ± 0.02</td>
<td>0.80 ± 0.02</td>
<td>18.2 ± 0.5</td>
<td>35 ± 37</td>
</tr>
<tr>
<td>IrNi/NiO</td>
<td>-</td>
<td>0.86 ± 0.02</td>
<td>-</td>
<td>64 ± 7</td>
</tr>
<tr>
<td>IrNiOx</td>
<td>0.87 ± 0.02</td>
<td>0.79 ± 0.02</td>
<td>4.2 ± 0.6</td>
<td>50 ± 33</td>
</tr>
</tbody>
</table>

**Physicochemical Characterization.** GI-XRD patterns are given in Figure S2 for all samples in their -ap (Figure S2a) and -OER states (Figure S2b). -ap and IrNi-ap could be attributed to the corresponding metallic Ir phase with the reflex positions being shifted corresponding to the Ni insertion for IrNi-ap, while IrOx-ap revealed a single, broad reflection around 34°20 only. Heat treatment led to an increase in crystallinity for IrOx HT-ap and IrNi HT-ap. In the -ap stage, IrNi HT-ap was well in line with the IrO\(_x\) pattern of similarly calcined thin films presented elsewhere.\(^14,20\) On IrNi/NiO HT-ap, the heat treatment in the presence of oxygen residues produced an additional phase that could be identified as NiO (bunsenite) by comparison to reference patterns from the PDF database and by Rietveld refinement (see Figure S3). Rietveld refinement of IrOx-ap and -HT presented in Figure S4 exemplarily shows a substoichiometric TiO\(_x\) phase (hongkongite) that was visible on all nonheat-treated samples. IrNiOx-ap and IrNiOx HT-ap were completely X-ray amorphous, comparable to the template IrNiOx TP catalyst of similar composition.\(^20\) After OER (Figure S2b), the nonheat-treated samples showed decreasing (metallic samples) to no (oxidic samples) XRD reflexes. No additional phases emerged on any of the samples. Surprisingly, the observed NiO phase remained on IrNi/NiO HT-OER.

Table 2 gives the average crystallite size of the main phase in each catalyst in the -ap, HT-ap, and (HT)-OER states. Heat treatment leads to increased crystallinity and crystallite size, respectively. Crystallite sizes for IrNiOx (HT) and IrOx-ap could not be obtained due to the X-ray amorphous structure of the catalyst layers.

**Table 2.** Crystalline Sizes Obtained by Rietveld Refinement of GI-XRD Patterns

<table>
<thead>
<tr>
<th>sample</th>
<th>-ap crystallite size/nm</th>
<th>-ap OER HT-ap</th>
<th>HT-ap OER HTOER</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ir</td>
<td>7.2 ± 1.2</td>
<td>5.5 ± 0.4</td>
<td>17.2 ± 1.3</td>
</tr>
<tr>
<td>IrNi</td>
<td>3.3 ± 1.3</td>
<td>3.2 ± 0.7</td>
<td>6.6 ± 0.4</td>
</tr>
<tr>
<td>IrNi/NiO</td>
<td>-</td>
<td>-</td>
<td>41.0 ± 0.6</td>
</tr>
<tr>
<td>-IrNi</td>
<td>-</td>
<td>-</td>
<td>10.4 ± 1.8</td>
</tr>
<tr>
<td>-NiO</td>
<td>-</td>
<td>-</td>
<td>7.4 ± 1.3</td>
</tr>
</tbody>
</table>

\(^*\)For IrNi/NiO HT, crystallite sizes are given for the NiO as well as the IrNi phase as indicated by bold letters for the respective phase in the sample column.
A recent study found that the electrochemical oxidation of the metallic substrate can also play a role in catalyst adhesion. The bonding between a sputtered metal versus an oxide and non-heat-treated oxides were heavily damaged during OER, therefore, decreased interconnection, the catalyst layers of the former only. Possibly owing to their smaller crystallite size and, versus the metals, catalyst layer degradation (e.g., corrosion, fissures, Figure S5b) would explain the reduced corrosion no change in the structure of the metal (oxide) sample taken after OER. SEM micrographs revealed a very similar, flat and smooth surface structure for Ir-ap (Figure 2a) and IrNi-ap (Figure 2b) as well as IrOx-ap and IrNiOx-ap (Figure 2cd, respectively). The metallic samples showed microcracks in the low nanometer range (up to 1 μm length, 3–6 nm width), whereas the oxide samples seemed almost crack-free (10–40 nm length, ≤2 nm width). After heat treatment, some surface cracks were induced in the oxide samples (Figure 2k, l) and IrNi HT-ap (Figure 2j). No further change was observed, except for IrNi/NiO HT-ap, which changed from a flat, smooth surface to wrinkled platelets (see Figure S5a) that resemble NiO catalysts presented in the literature but on a much smaller length scale here. The emergence of NiO is in line with the corresponding XRD pattern, indicating the formation of a rather thick NiO layer. In fact, it seemed that this structure had formed on top of the initial morphology.

After electrocatalytic operation, IrOx-OER and IrNiOx-OER lost most of the catalyst layer due to dissolution or delamination (see Figure S6 for photos of the electrodes after OER). On the Ir-OER and IrNi-OER catalyst, loss occurred to a much lower extent while minimal to no damage was observed on the HT-OER samples visually (see Figure S6). Where there was a catalyst layer left, SEM micrographs revealed no change in the structure of the -OER samples (Figure 2e–h). On the HT-OER samples, increased surface cracking (Figure 2m–p) was observed. On IrNi/NiO HT-OER, the platelets formed a denser NiO surface layer that was disrupted by small holes (Figure S5b).

Interestingly, despite the less-cracked structure of the oxides versus the metals, catalyst layer degradation (e.g., corrosion, delamination, etc.) turned out to be a major problem on the former only. Possibly owing to their smaller crystallite size and, therefore, decreased interconnection, the catalyst layers of the non-heat-treated oxides were heavily damaged during OER. The bonding between a sputtered metal versus an oxide and the metallic substrate can also play a role in catalyst adhesion. A recent study found that the electrochemical oxidation of sputtered Ir films took place at the grain boundaries, possibly leading to an increase in film stability by improved grain interconnection. This would explain the reduced corrosion on the metallic versus the non-heat-treated oxide samples. Minimal catalyst loss on all HT-OER samples suggested a stronger catalyst adhesion and improved integrity of the layers to be a major influence of heat treatment.

To elucidate the structure of the emerging NiO layer and its stability, (scanning) transmission electron microscopy (S/TEM), selected area electron diffraction (SAED), as well as STEM-EDX line scans were performed on a cross-section sample of IrNi/NiO HT-OER (see Figures S7–S11) revealing a roughly 25 nm thick NiO layer on top of an extended IrNi layer (∼134 nm vs ~87 nm on Ir-ap, see Figures S12 and S13). Most likely, the catalyst layer expanded during the Ni oxidation due to the distinct diffusivities of Ir and Ni, especially in NiO as well as due to the NiO formation inside the formed pores and holes. The IrNi bulk layer was characterized by pores and holes filled with NiO. STEM-EDX line scans (see Figure S8) revealed a clear distinction between the IrNi bulk and NiO surface layers, whereas a mixed interlayer existed between support and catalyst layer. Inside the NiO layer, indications for Ir-containing crystallites were found by analysis of lattice fringes. A detailed description of the cross-sectional analysis can be found in the SI.

SEM cross sections (see Figure S12 and S13) of all -ap and HT-ap samples revealed a layer thickness of about 80 nm for all -ap catalysts. Here, heat treatment led to a slight layer shrinkage possibly due to sintering.

STEM-EDX results shown in Figure 3a,b (bulk, open triangles and dashed lines) confirmed the composition of all -ap mixed metal (oxide) samples to be Ir:Ni 17:83, well in line with XRD results. No change was observed for the HT-ap samples. After electrocatalysis the samples retain various reduced Ni contents. Only, IrNi/NiO HT-OER showed no Ni loss (Ir:Ni 18:82). XPS analysis confirmed the Ir:Ni surface ratio (full triangles and lines in Figure 3ab) of the -ap catalysts to be in line with EDX results, except for IrNi/NiO HT-ap where the rather thick NiO surface layer formation prevented any Ir to be detectable. Ir:Ni surface ratios after electrocatalysis suggested the formation of a nickel-depleted near-surface IrOx overlayer on IrNi-OER and IrNi HT-OER with about 6.4% and 0% Ni, respectively. In line with EDX observations, IrNi/NiO HT-OER retained most of its Ni with a small Ir signal emerging in the near-surface region. The surface concentration of Ni in IrNiOx HT-OER (20.6%) was slightly lower than in the bulk (25%, Figure 3B), whereas IrNiOx-OER (similar bulk Ni concentrations) had no Ni left in the surface, which fits very well to IrNiOx TF catalysts with the same starting composition.

The oxygen content of these samples (both EDX and XPS) is depicted in Figure S14. On the metallic catalysts, the (bulk)
oxygen content increased to a lower extent in the −HT and −OER states than on the oxides, indicating the formation of a thin oxide layer with unchanged metallic parts of the bulk catalyst underneath.

XPS probed the surface layers of the -ap and -OER catalysts. In the measurements presented here, the inelastic mean free paths (IMFP) are 1.9, 1.4, and 1.0 nm for Ir 4f, O 1s, and Ni 2p, respectively. The fitted XPS spectra can be found in the Supporting Information (see Figures S15–S20). The Ir 4f/2 peak consisted of three contributions (Ir⁰, Ir⁴⁺, and Ir⁵⁺), ~60.8, ~61.7, and ~62.3 eV, respectively, see Figure 4a, b and Figure S17 for the fitted Ir 4f spectra.

**Figure 4.** XPS results for Ir 4f contributions in the (a) -ap and (b) -OER states as well as O 1s contributions in the (c) -ap and (d) -OER states of the investigated bimetallic catalysts. As no Ir 4f signal could be detected on IrNi/NiO HT-ap, no statement about the distribution of Ir species can be made.

SI). Despite ongoing debate about the true origin (Ir⁵⁺ or Ir⁴⁺) of the last feature at ~62.3 eV under in operando conditions, it is denoted as Ir⁵⁺ in this work as it seems highly unlikely that Ir⁴⁺ could exist ex situ.67,38 Nevertheless, it should be noted that we cannot completely rule out an Ir⁴⁺ contribution at similar binding energies and we would not necessarily draw the same conclusions on in operando XPS data. See Figure S15 for Ir 4f and O 1s spectra of IrNi/NiO HT-OER, Figure S16 for Ir 4f species of all -OER samples and Figure S17 for the fitted Ir 4f spectra.

IrOx HT-ap and -OER consist of Ir⁵⁺ only, proving the formation of a pure rutile oxide phase (Figure S16). Interestingly, IrOx-ap showed an Ir⁰ contribution, which was decreasing (~23% to ~6.5%) but still present after electrochemical testing. Since the samples were prepared by sputtering of metallic targets in oxygen atmosphere, it seems possible that the -ap oxide contained metallic states which were not fully oxidized electrochemically. An unexpected reemergence of Ir⁰ was observed on IrNi/NiO HT-OER, indicating metallic Ir contributions in the vicinity of the electrochemically active surface (cf. Figure 4a, b). Similarly, small Ir⁰ contributions remained on IrNi-OER and IrNi HT-OER. The latter showed a surprisingly high Ir⁵⁺ contribution (~68%) fitting those of IrNiOx-OER and IrNiOx HT-OER.

The Ni 2p peak was not fitted but compared to reference spectra of NiO and Ni(OH)₂, as well as to the position of metallic Ni (852.6 eV) in Figure S18. IrNi-ap and IrNi HT-ap showed a strong metallic Ni component, corresponding well to the metallic character in the Ir 4f spectra further proving the IrNi alloy formation and stability during heat treatment. The Ni 2p peak of IrNi/NiO HT (-ap and -OER) closely resembled NiO, whereas the oxidic samples and all other bimetallic -OER samples were more similar to Ni⁴⁺ hydroxide.

The distribution of oxygen species detected in the O 1s spectra (see Figure 4c, d) supports the findings from Ir 4f and Ni 2p spectra. Two contributions could be assigned to lattice oxygen (1: Ni-bound lattice O, “Ni−O”, 2: Ir-bound lattice O, “Ir−O”, at ~529.5 eV and ~530.0 eV, respectively), one contribution was assigned to a surface hydroxyl “OH” species (~531.3 eV) and finally H₂O/organic O-species (~533.0 eV). Where applicable, contributions of Ni−OH were fitted in the XPS analysis as well (see SI). On catalysts with a significant amount of TiOx present in the spectra, these contributions were fitted and excluded corresponding to a reference TiOx-OER sample (see SI for further information). See Figure S19 for the distribution of O 1s species and Figure S20 for the individual O 1s fits. On all samples, the O 1s peak was dominated by surface OH contributions, except for IrNi/NiO HT-ap where the major contribution was Ni-bound lattice oxygen fitting well to the Ni 2p peak shape similar to NiO. IrNi-ap, IrNi HT-ap, IrNiOx-ap, and IrNiOx HT-ap show small contributions of lattice oxygen bound by Ni as well.

Upon oxidation and Ni leaching during OER, the Ni−O lattice contribution vanished on all samples except for IrNi/NiO HT-OER where it was still a major component, but now being surpassed by surface OH (Figure 4d). A minor contribution of Ir−O appeared on the metallic -OER samples, while it slightly decreased on the oxidic -OER samples. Furthermore, conducting OER increased the OH-surface contribution for all catalysts, with IrNi-OER and IrNi HT-OER exhibiting the smallest change. Interestingly, the surface OH contribution of Ir-OER reached similar levels as the IrNi (HT)-OER and IrNiOx (HT)-OER samples (85–90%), while the remaining monometallic iridium (oxide) catalysts only exhibited about 65–70% OH. With below 60% IrNi/NiO, HT-OER developed the lowest amount of OH contribution. The H₂O/organic species contribution to the O 1s spectra was comparably low on all samples and remained essentially unchanged after OER.

**Physicochemical and Morphological Changes by Heat Treatment and OER.** As discussed extensively in the past,12,14,39 heat treatment has a strong influence on the mechanical catalyst stability, which is reflected by the catalyst loss observed on the nonheat-treated -OER samples. The second impact of heat treatment is chemical change. As shown by Reier et al., Ti substrates used for the preparation of Ir oxide films start to oxidize at 450 °C in air.15 Despite the detrimental effect on activity, this might help to “anchor” the catalyst layer on the substrate. Indeed, a mixed Ti–Ir–Ni interlayer existed between substrate and catalyst layer of IrNi/NiO HT-OER (see Figure S7c) fitting well to the observed stability and the study by Reier et al.14 In addition, heat treatment with increasing temperature produced more crystalline and less-hydrated iridium (oxide) that is reported to have lower OER activity.28 Consequently, on almost all samples in this study, heat treatment led to reduced OH and H₂O species in the surface layer (Figure 4c) as well as decreased catalyst degradation. A suggested oxide formation scheme on IrNi bimetallic catalysts can be found in the Supporting Information (Figure S21).

**Elucidation of Experimental OER Activity Predictors.** In the following, we derive general, experimental OER activity
predictors from the presented data. We want to emphasize the importance of in operando measurements to elucidate the actual active site(s) and OER mechanism. However, this study focuses on finding easily accessible ex situ descriptors, to facilitate reasonable OER catalyst development tools available to every lab. Such descriptors can help in identifying and narrowing the catalyst range suitable for in operando investigation, too.

The observed effect of heat treatment on the OER activity can in large part be attributed to catalyst corrosion or rather its mitigation. In the steady state, presented in Figure 1 and Table 3, the monometallic samples followed the same trend of heat-treated catalysts performing worse than non heat-treated catalysts, which was already observed in initial activities. However, the performance of the bimetallic -HT samples improved over the non heat-treated samples. In the case of IrNiO\textsubscript{x}, this might have been an effect of the before mentioned poor catalyst adhesion in the non heat-treated samples and the resulting catalyst loss. Both geometric and mass-based activity normalization are based on initial values (area and loading), since their change cannot easily be monitored in situ. Thus, smaller geometric area (e.g., temporarily by bubble blockage or permanently by catalyst loss) or reduced loading (e.g., by delamination or dissolution) were not taken into account. However, this would only underestimate the activity, and while being imperfect, it would not falsify the measurements.

Table 3. Summary of Figures of Merit at the Three Most Common Potentials vs RHE\textsuperscript{a}

<table>
<thead>
<tr>
<th>sample</th>
<th>1.50 V</th>
<th>1.53 V</th>
<th>1.55 V</th>
<th>1.50 V</th>
<th>1.53 V</th>
<th>1.55 V</th>
<th>Tafel slope/mV dec(^{-1})</th>
<th>(\eta/\text{mV (10mA cm}^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ir</td>
<td>9</td>
<td>39</td>
<td>80</td>
<td>0.14</td>
<td>0.59</td>
<td>1.55</td>
<td>45</td>
<td>293</td>
</tr>
<tr>
<td>Ir HT</td>
<td>2</td>
<td>5</td>
<td>10</td>
<td>0.12</td>
<td>0.25</td>
<td>0.46</td>
<td>48</td>
<td>336</td>
</tr>
<tr>
<td>IrNi</td>
<td>123</td>
<td>410</td>
<td>653</td>
<td>0.22</td>
<td>0.73</td>
<td>1.42</td>
<td>35</td>
<td>271</td>
</tr>
<tr>
<td>IrNi HT</td>
<td>199</td>
<td>632</td>
<td>1012</td>
<td>0.33</td>
<td>0.91</td>
<td>1.39</td>
<td>37</td>
<td>276</td>
</tr>
<tr>
<td>IrNi/NiO\textsubscript{HT}</td>
<td>13</td>
<td>44</td>
<td>95</td>
<td>0.09</td>
<td>0.32</td>
<td>0.89</td>
<td>64</td>
<td>329</td>
</tr>
<tr>
<td>IrO\textsubscript{x}</td>
<td>4</td>
<td>11</td>
<td>18</td>
<td>0.11</td>
<td>0.30</td>
<td>0.66</td>
<td>71</td>
<td>509</td>
</tr>
<tr>
<td>IrO\textsubscript{HT}</td>
<td>4</td>
<td>21</td>
<td>55</td>
<td>0.04</td>
<td>0.23</td>
<td>0.81</td>
<td>46</td>
<td>349</td>
</tr>
<tr>
<td>IrNiO\textsubscript{x}</td>
<td>44</td>
<td>135</td>
<td>263</td>
<td>0.15</td>
<td>0.48</td>
<td>1.45</td>
<td>33</td>
<td>277</td>
</tr>
<tr>
<td>IrNiO\textsubscript{x} HT</td>
<td>126</td>
<td>540</td>
<td>1335</td>
<td>0.15</td>
<td>0.48</td>
<td>1.45</td>
<td>33</td>
<td>277</td>
</tr>
<tr>
<td>IrO\textsubscript{x} TF\textsuperscript{20}</td>
<td>91</td>
<td>370</td>
<td>759</td>
<td>0.21</td>
<td>0.86</td>
<td>1.77</td>
<td>41</td>
<td>315</td>
</tr>
<tr>
<td>IrNi NPs\textsuperscript{19}</td>
<td>68</td>
<td>311</td>
<td>700</td>
<td>0.18</td>
<td>0.80</td>
<td>1.79</td>
<td>-</td>
<td>329</td>
</tr>
<tr>
<td>Elyst Ir\textsuperscript{75}</td>
<td>5</td>
<td>14</td>
<td>35</td>
<td>0.17</td>
<td>0.52</td>
<td>1.30</td>
<td>57</td>
<td>460</td>
</tr>
<tr>
<td>IrNi nw\textsuperscript{18}</td>
<td>-</td>
<td>1650</td>
<td>3353</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

\(j_{\text{mass}}/A g^{-1}\text{Ir}\) \(j_{\text{spec}}/m A m C^{-1}\)

\(a\) Data from the corresponding references has been extracted by Origin’s “digitize” function where necessary and should be treated with caution. In the case of IrNi NPs, \(j_{\text{spec}}\) is normalized to \(Q_\text{anodic}\). Data in bold: this study.

Figure 5. Property–activity relationships found in this study. (a) Ir\textsuperscript{III+}-surface concentration vs OH-surface concentration, derived from Ir 4f and O 1s XP spectra. (b) Specific activity vs OH-surface concentration reveals a volcano-type relationship. Specific activity in 0.05 M H\textsubscript{2}SO\textsubscript{4} was obtained from steady-state SPV measurements at the end of 5 min potentiostatic holds and normalized to \(Q_\text{anodic}\). IrNiO\textsubscript{x} TF data taken from Reier et al.\textsuperscript{20} Dashed lines are inserted to guide the reader’s eye.
thermochromically and could have occurred at high potentials during OER and simultaneous catalyst delamination, too. Possibly, a very mild heat treatment could improve catalyst adhesion; however, this is out of the scope of this paper.

Despite the remarkable stability of its surface layers, IrNi/ NiO HT proved to be the least active bimetallic catalyst in this study. However, it still outperformed the monometallic iridium (oxide) catalysts. While the higher conductivity of the remaining metallic layer underneath the surface oxide of Ir (HT)-OER and IrNi (HT)-OER could be a positive influence on activity of the other metallic samples, this advantage would be inhibited by the semiconducting NiO layer on IrNi/NiO HT-OER (see Figure S7 and S21d). Nevertheless, the formation of a stable, Ir-doped NiO layer could be an interesting catalyst choice for acidic water oxidation.

Independent of its true origin, the Ir$^{2+}$ species observed at $\sim$62.3 eV in situ by several research groups is discussed as a possible active species of iridium-based electrocatalysts for OER. Findings in the literature correlate the improved activity of IrNiOx TF catalysts to an increase in and stabilization of surface OH-sites where Ni-vacancies are formed during the electrochemical leaching. More recent publications assign an electrophilic oxygen $\text{O}^{2-}$ species as the active site. For both interpretations, $\text{Ir}^{III}$ detected ex situ could serve as a precursor for the active species that is mostly observed in situ only. Additionally, Nong et al. and Massue et al. recently suggested the combination of both Ir$^{2+}$ and electrophilic oxygen denoted $\text{O}^{(II)-}$ into a hole-doped shared active site. Thus, even though the ex situ state differs from the in situ or in operando state, it appeared plausible to correlate the $\text{Ir}^{III}$-surface concentration ($\text{Ir}^{III}$ vs $\text{Ir}^{IV}$, calculation see S1) with the observed OH-surface concentration (OH vs lattice O, not to be confused with the surface OH contribution of the O 1s peak; calculation see S1). A linear trend of increasing OH-surface concentration with rising $\text{Ir}^{III}$-surface concentration (see Figure 5a, dashed red line) was found regardless of composition and pretreatment. This correlation is only slightly broken by IrNi HT, which, interestingly, is also the catalyst with the highest observed activity. Hence, ex situ $\text{Ir}^{III}$ content appears to play an important role in the investigated sample set but additional activity promoters may exist on IrNi HT.

Furthermore, in Figure 5b the specific activity was plotted against the OH-surface concentration. Well in line with the observations of Reier et al., a high OH-surface concentration correlated with increased OER activity. Based on the present comparison, the former correlation of Reier et al. could be extended to other types of Ir-based OER catalysts leading to a general unprecedented volcano plot presented in Figure 5b. This volcano plot identified an optimal OH-surface concentration of $\sim$95–97%, indicating a small contribution of lattice oxygen to be important as well. This is in excellent agreement with recent findings in literature that propose OH surface oxygen to be important as well. This is in excellent agreement with recent findings in literature that propose OH surface oxygen to be important as well. This is in excellent agreement with recent findings in literature that propose OH surface oxygen to be important as well. This is in excellent agreement with recent findings in literature that propose OH surface oxygen to be important as well. This is in excellent agreement with recent findings in literature that propose OH surface oxygen to be important as well.

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Unfortunately, no specific activity based on $Q_{\text{adonic}}$ was published, and as a result, it is unclear whether the specific activities would compare as it is the case for the three highest-performing IrNi(Ox) catalysts in this study. The roughly similar specific activities of IrNi-OER, IrNiOx (HT)-OER, and IrNiOx TF$^{20}$ (as IrNi NPs$^{19}$ were normalized to $Q_{\text{adonic}}$).
comparison was not directly possible) seemed to indicate that for these kind of IrNi-based catalysts the maximum intrinsic activity has been found. However, IrNi HT-OER exhibited increased specific activity, indicating that the structural similarity to IrNi NPs could act as an additional activity promoter. With a more application focused view, improvements are possible by catalyst design and engineering as demonstrated in the IrNi NW mass activity.

4. CONCLUSIONS

This study presents a detailed investigation of the relations between chemical state and OER catalytic activity of a set of sputtered, well-defined iridium-based thin film catalysts in their monometallic and oxide forms as well as bimetallic (oxide) films. The range of their chemical molar Ir: Ni ratios was chosen to straddle that of the most active IrNi-based OER catalysts described in the literature. Physico-chemical analysis confirmed that all catalyst films were of comparable uniformity and physicochemical homogeneity, despite the wide range of different types and compositions. Based on the extensive analysis, a model on the surface oxide layer formation of bimetallic IrNi catalysts is suggested.

A few remarkable observations were made in regard to the OER catalytic activity in acidic conditions: To the best of our knowledge, IrNi HT and IrNiOx HT exhibited unprecedented activities among iridium-based thin film catalysts, outperforming the reference catalyst with a 31% and 4.6% increase in mass and specific activity, respectively. When compared among all IrNi(Ox) catalyst types in the literature, IrNi HT exhibited the second-highest mass activity reported. Beyond their nominal OER activity, the present study also suggested interesting catalyst-support interactions for heat-treated catalyst samples based on Ti-Ir-Ni-interlayers, in particular for the IrNi/NiO HT-OER catalyst. The presented data further suggests that for mechanistic investigation, activity normalization by electrochemical surface area can be beneficial. Unfortunately, no ideal measure of ECSA has been found and agreed upon yet, making data comparison difficult.

More importantly, the present study first uncovered an important close correlation between the ex situ ratio of Ir[III]-concentration in the catalyst surface and the ex situ surface OH concentration. Either one may serve as a reliable experimental catalytic OER activity predictor for a general volcano relationship, applicable to Ir-based OER electrocatalysts with or without a secondary sacrificial metal ion. The detailed experimental volcano relationship uncovered here suggests as high as possible Ir[III] surface ratios combined with ~95–97% surface OH concentration as design targets for active OER catalysts. Both ex situ activity descriptors are in full agreement with insights from extensive in situ/in operando studies. However, unlike operando techniques, the ex situ predictors are much more facile to evaluate, while providing similar indicative power as to the OER catalyst performance. While we acknowledge the importance of in operando measurements, the presented ex situ descriptors can help in developing active materials for large-scale applications and facilitate catalyst design alongside of fundamental research. Because of the surface sensitivity of XPS analysis, the presented descriptors can be applied to nanoparticle catalysts without further adaption as long as strong influences of support materials can be ruled out.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.9b00648.

Detailed experimental description, calculations, Rietveld refinement data, SEM and TEM cross-section micrographs, STEM-EDX line scans, photographs of the catalyst delamination, XPS spectra, additional EDX results, a suggested oxide formation scheme, and activity data (PDF).

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#### Notes

The authors declare no competing financial interest.

### ACKNOWLEDGMENTS

The authors deeply thank Dr. Arno Bergmann and Benjamin Paul for insightful discussion and advice with Rietveld refinement and SEM-EDX analysis, respectively. Technical support for the (S)TEM measurements by TUB’s center for electron microscopy (ZELMI) is gratefully acknowledged. The authors thank Dr. Dirk Berger for preparation of the FIB lamella for the cross-sectional analysis of IrNi/NiO HT-OER.

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