Reactive oxygen species in iridium-based OER catalysts†

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Tremendous effort has been devoted towards elucidating the fundamental reasons for the higher activity of hydrated amorphous IrII/IV oxyhydroxides (IrOx) in the oxygen evolution reaction (OER) in comparison with their crystalline counterpart, rutile-type IrO2, 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 IrOx 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 IrOx. We propose that the dynamic nature of the Ir framework in amorphous IrOx imparts the flexibility in Ir oxidation state required for the formation of this active electrophilic oxygen.

Ir-based materials are promising candidates to catalyze the oxygen evolution reaction (OER) in acidic media. Iridium oxides, both anhydrous rutile-type IrO2 and hydrated X-ray amorphous forms, have been widely considered as possible OER catalysts.1–8 Of these, the amorphous and nano-structured Ir-based catalysts have been shown to exhibit higher OER activities than rutile-type IrO2.9,10 Although numerous studies exist on such amorphous structures, and activity descriptors like mixed iridium oxidation states

WOC–O+ + H2O(ads) → WOC–O–O–H + H+ + e−. (1)

In this mechanism water acts as the nucleophile, donating electrons to the reactive oxygen, which can alternatively be formulated WOC=O+ to emphasize its susceptibility to nucleophilic attack.13 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:

IrOxO(ads) + H2O → IrOx–O–O–H + H+ + e−, (2)

with [IrOxO(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 (IrIII) and anionic frameworks (O2−) that are nearly absent in less active rutile-type IrO2.18 The holes in the O 2p states of IrO2 may make the O2− an electrophile that, in analogy to the biological cycle, may lead to the enhanced OER activity of amorphous IrO2. To test this hypothesis, we need to understand the chemistry of these O2− species.

A powerful means of uncovering the chemistry of the O2− is through CO oxidation, a reaction that has proven essential in developing a fundamental understanding of heterogeneous processes.29 Herein we use this probe to test if the O2− in X-ray amorphous IrO2 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 CO2.30,31

The sample investigated is a commercially available, hydrated, X-ray amorphous IrIIIIV oxyhydroxide (IrOx, Premion, AlfaAesar). In a control experiment, a less active, crystalline rutile-type IrO2 (Sigma Aldrich) was examined. The properties of both materials are described in ref. 10. Therein, we showed that O2− is identifiable by an excitation energy resonance at 529 eV in the near-edge X-ray absorption fine structure (NEXAFS) of the O K-edge that is not present in pristine rutile-type IrO2. Herein, the spectroscopic features corresponding to these O2− species were monitored by quasi in situ X-ray photoemission spectroscopy (XPS) and NEXAFS before and after CO exposure to observe whether O2− reacts with CO during titration of the IrOx 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.

In a preliminary experiment, we tested the general activity of the two iridium oxide powders towards a stoichiometric oxidation of CO to CO2 at room temperature and atmospheric pressure in a standard flow-through reactor (details in ESI†). To ensure reaction of CO was exclusively with active oxygen from the iridium oxide samples, we did not add O2 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 IrO2 leads to no change in the CO2 signal (Fig. 1). In contrast, when introducing CO into the reactor loaded with IrOx, the CO2 signal shows a sharp increase followed by a decline towards the baseline (Fig. 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 gold catalysts,22 and reveals the high reactivity of the IrOx. As there is no external oxygen source available in the present experiment, the effluent CO2 must be due to the stoichiometric reaction of CO with an oxygen species present in IrO2 and nearly absent from the rutile-type powder. Because only IrO2 has an abundance of O2−, 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 O2− ($\approx$ 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 IrO2 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 Fig. 1). Finally, we evacuated the chamber and without air contact measured the sample after CO (details see ESI†).

When comparing the XPS core lines recorded before and after CO exposure, the Ir 4f spectra show no obvious changes (Fig. S3†). In contrast, the intensity at low binding energies (529–530 eV) in the O 1s spectrum is slightly reduced after CO exposure (Fig. S3†), indicating the potential loss of O2−. The corresponding O K-edge NEXAFS 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 (Fig. 2). A comparison of the difference spectrum of the O K-edges before and after CO exposure with that calculated for O2− (see Fig. 2) supports this conclusion, suggesting O2− is consumed from IrO2 by oxidizing CO to CO2 at room temperature.

Interestingly, more bulk sensitive total electron yield (TEY) measurements of the O K-edge also show reduced 529 eV intensity after CO exposure (see Fig. S5†). Hence, subsurface O2− species migrating to the surface also appear to be involved in the reaction with CO. This observation alludes to the dynamic mobility of O2− in the porous structure30 of IrO2. Nevertheless, since the CO2 signal in the standard reactor and the NAP-XPS chamber declines immediately after the initial increase, the reservoir of mobile O2− species seems to be rapidly exhausted. However, since the 529 eV component does not vanish completely in either AEY and TEY, part of the O2− seem unavailable for reaction with CO over the time scale of our experiment.
Though comparison of our theoretical and experimental O K-edge spectra supports the conclusion that $O^{\text{II}}$ 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$_x$O$^{n^-}$):

$$\text{IrO}_xO^{n^-} + \text{CO(g)} \rightarrow \text{IrO}_x + \text{CO}_2(g) + ne^{-}. \quad (3)$$

The liberated $ne^{-}$ 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 ESIF for details), and 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 microralorimetry). 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$_3$ (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 ESIF for full details). Both types of surface have under coordinated O atoms whose simulated O K-edge spectra agree with that measured for O$^{\text{II}}$ (see ESIF). The reduced surfaces also have under coordinated Ir atoms that can adsorb CO with adsorption energies of $\approx$180–210 kJ mol$^{-1}$ (see ESIF).

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$^{\text{II}}$ like species, an O$^{\text{I}}$ like species, and oxygen on the coordinatively unsaturated site (CUS), the last of which was not observed experimentally (Fig. S14†). The O$^{\text{I}}$ has a barrier for reaction (3), $\approx$10 kJ mol$^{-1}$, that is slightly larger than $k_B T$ at room temperature, and the reaction is $\approx$90 kJ mol$^{-1}$ exothermic. In contrast, the activation energy associated with the reaction of CO$_{(g)}$ directly with O$^{\text{II}}$ is significantly larger than the energy available at room temperature, 170 kJ mol$^{-1}$, and is exothermic by $\approx$50 kJ mol$^{-1}$.

To test the reaction of adsorbed CO with an O$^{\text{I}}$ like species, we computed minimum energy paths on the partially reduced (113) surface (see ESIF for details). In this case, CO oxidation by an O$^{\text{I}}$ 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 CO$_2$, not CO$_2(g)$. Overall reaction (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$^{\text{I}}$ on a partially reduced (110) surface with an Ir vacancy.

These results suggest that, if present, surface O$^{\text{I}}$ 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 their apparent absence in rutile-type IrO$_2$ loaded from air$^{18}$ and the lack of CO$_2$ formation when rutile-type IrO$_2$ is exposed to CO (see Fig. 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$^{\text{I}}$ in the subsurface/bulk region. These subsurface species are depleted during CO oxidation (see Fig. S5†). If we assume that once on the surface any O$^{\text{I}}$ 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$^{\text{II}}$ of rutile-type IrO$_2$, is thermoneutral, whereas reaction with bulk O$^{\text{I}}$ species$^{29}$ is 110–120 kJ mol$^{-1}$ exothermic, depending on the atomic structure around the anionic defect. As with the surfaces, we see that bulk O$^{\text{I}}$ species are more weakly bound, hence more electrophilic, than the bulk O$^{\text{II}}$. These results are summarized schematically in Fig. 3.

When the heats of reaction for all the oxygen species studied in this work are considered, we find that the O$^{\text{II}}$ type generally gives rise to higher heats of reaction than the formally O$^{\text{I}}$.

![Image](https://example.com/image.png)
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 O K-edge spectrum of an oxygen species and its corresponding heat of reaction with CO (see Fig. S15†). Thus, the O K-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 OI species present in our experiments (O K = 529 eV) is 100 kJ mol⁻¹.

To validate the calculated heats of reaction for room temperature CO oxidation on IrO₂, we titrated IrO₂ with CO at 313 K using in situ microcalorimetry.²³ A gas phase analysis after the experiment confirmed the predominant presence of CO₂(g), supporting our assumption in eqn (3) and allowing to complete oxidation of the dosed CO (see Fig. S11†). 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 kJ mol⁻¹ ± 40 kJ mol⁻¹ for the 2 mmol g⁻¹ of reacted CO (see Fig. 4). These measured differential heats of reaction agree with those calculated for CO₂(g) oxidation by OI species (see Fig. 4), whereas they are much larger than the thermoneutral reaction of CO₂(g) with OII. In fact, the mean measured value (125 kJ mol⁻¹) is similar to the heats calculated for reaction with bulk OI, while the upper and lower ends of the standard deviation window agree with the calculated reaction enthalpies for CO₂(g) with OI on the partially reduced (113) and fully oxidized (110) surfaces, respectively. In addition, we observe a broadening of the thermosignal time profiles with increasing amount of reacted CO (see Fig. S8–S10†), which could be an indication for the involvement of subsurface OI liberated by the reaction heat evolved in the surface region.

Hence, the calculations corroborate our assumption that during the exposure of IrO₂ to CO, OI reacts with CO at room temperature. Combining our NEXAFS and microcalorimetric measurements with our theoretical calculations therefore suggests that the OI is a stoichiometric oxidant of CO to CO₂, and therefore strongly electrophilic.

Now that we have demonstrated the reactivity of the OI species, it seems appropriate to consider their regeneration since for the OER cycle to be catalytic, reactive oxygen must be replenished. To test whether OI can be replenished on IrO₂ 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 O₂, 25 Pa H₂O, and 25 Pa O₂ : O₃ (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 O K-edge only after the exposure of the sample to the ozone-containing gas mixture. A comparison of the O K-edges after CO and after subsequent ozone exposure indicates a replenishment of OI by a more intense 529 eV feature after ozone exposure, see Fig. S6.† However, we found that the formally OI 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 OI 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 OI 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 OI species considered in our work can be characterized as a μ₃-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 μ₁-oxo into μ₂-oxo bridges. This process gives rise to holes in the O 2p states, due to the removal of IrIV and 4e⁻, making the μ₂-oxo bridges charge deficient. Such μ₂-oxo bridged atomic structures have been identified as key motifs in amorphous IrOₓ thin films and as active centers in liquid-phase iridium oxidation catalysts 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 OI species seen in XPS and NEXAFS need not exclusively be due to such μ₂-oxo bridges. Instead, they may also emerge when substituting an IrIV with a lower-valent element, such as NiII, as the holes formed by replacing IrIV and 4e⁻ with NiII and 2e⁻ 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 O K-edge spectra of the rutile-type IrO₂ or amorphous IrO₂ samples, see Fig. S14.†

In conclusion, we showed that the OI species adsorbed on the surface and in the subsurface of OER-active IrO₂ 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.
temperature, with a portion of the reacting oxygen coming from the subsurface region of the amorphous catalyst. The exceptional reactivity of the formally O\textsuperscript{2-} species is suspected to play a critical role in the OER by reacting with OH/H\textsubscript{2}O to form the OOH intermediate, which, when considering that weakly electrophilic oxygen formation in iridium, which is apparently during the O–O bond formation. The creation of electrophilic oxygen in Ir\textsuperscript{III/IV} oxyhydroxides is an optimal precursor site for the nucleophilic attack of (pre)adsorbed water during the O–O bond formation. Likewise flexibility in the oxidation state for iridium is needed for electrophilic oxygen formation in iridium, which is apparently found in the Ir\textsuperscript{III/IV} oxyhydroxides.

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