

# Unifying concepts for electrochemical water splitting on various iridium (hydr-)oxides

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Global warming provides an urgent reason to store renewable energies chemically. A promising molecule to that end is hydrogen. It could serve as a central node of a new energy and chemistry network. Electrochemical water splitting is one of the most promising ways to produce hydrogen. Electrolyzers with proton exchange membranes (PEM) are compatible with intermittent renewable energy sources and produce hydrogen at large current densities. However, they suffer from large overpotentials and insufficient long-term stability at the anode. To address these issues, we need to understand the processes at the anode surface, at which the oxygen evolution reaction (OER) takes place.

Iridium oxides take a unique place among OER catalysts in PEM electrolyzers, since they are both active and stable under acidic conditions. To understand what makes iridium oxides special, we studied a range of different materials, including metallic iridium, iridium oxides, hydroxides, and alloys with other transition metals, and looked for unifying concepts for their activity.

To that end, we employ X-ray spectroscopy. This method is well suited for such a study, since it is element-specific and reflects the electronic structure of the catalyst. However, the actual measurements can be challenging<sup>1</sup> and depending on whether a study of the bulk material or of the surface is required, different experimental approaches are needed.

We developed many different in situ cells within our group specifically for each research question<sup>1-3</sup>. With the different approaches, we can also strike the balance between how realistic the conditions are and how easy data acquisition is. In close contact with advanced computational spectroscopy, we test predictions from computation under operando conditions.

We find the following: the strong hybridization between iridium and oxygen leads to holes shared between the two; the further the material is charged, the more charge transfer from iridium to the oxygen ligand is expected<sup>2</sup>. Depending on its coordination, oxygen can ultimately end up as a radical oxyl species,  $\mu_1\text{-O}$ . Such a species was proposed to be highly active in O-O bond formation<sup>4</sup>. We were able to find that species under wet conditions via its O K-edge absorption signal. A small amount appeared at the onset of the OER. Calculations and experiments are in good agreement about the deprotonation potentials and the O K-edge absorption energies of the considered surface oxygen species.

The steady state concentration of the different oxygen species also provided insight into the kinetics of the OER. The currently proposed mechanism of the OER proceeds from adsorbed water over two deprotonation steps to an active  $\mu_1\text{-O}$  species, which then forms the O-O bond in a nucleophilic attack by water<sup>4</sup>. The computed phase diagram predicts a fully deprotonated surface at OER conditions. In our in situ studies, however, we find far more  $\mu_1\text{-OH}$  than  $\mu_1\text{-O}$  or  $\mu_1\text{-OO}$  species at the surface during the OER. Such a distribution suggests that  $\mu_1\text{-OH}$  is the resting state of the active site.

We also find that the rate of oxygen evolution is controlled by the amount of charge that is stored in the catalyst during its oxidation. The large quantities of charge the investigated materials can store indicate that surface deprotonation is the main route of storing charge in iridium (hydr-)oxides.

- (1) Knop-Gericke, A.; Pfeifer, V.; Velasco-Velez, J.-J.; Jones, T.; Arrigo, R.; Hävecker, M.; Schlögl, R. In Situ X-Ray Photoelectron Spectroscopy of Electrochemically Active Solid-Gas and Solid-Liquid Interfaces. *J. Electron Spectrosc. Relat. Phenom.* 2017, 221, 10–17.
- (2) Velasco-Vélez, J. J.; Jones, T. E.; Streibel, V.; Hävecker, M.; Chuang, C.-H.; Frevel, L.; Plodinec, M.; Centeno, A.; Zurutuza, A.; Wang, R.; et al. Electrochemically Active Ir NPs on Graphene for OER in Acidic Aqueous Electrolyte Investigated by in Situ and Ex Situ Spectroscopies. *Surf. Sci.* 2019, 681.
- (3) Frevel, L. J.; Mom, R.; Velasco-Vélez, J. J.; Plodinec, M.; Knop-Gericke, A.; Schlögl, R.; Jones, T. E. In Situ X-Ray Spectroscopy of the Electrochemical Development of Iridium Nanoparticles in Confined Electrolyte. *J. Phys. Chem. C* 2019, 123 (14), 9146–9152.
- (4) Ping, Y.; Nielsen, R. J.; Goddard, W. A. The Reaction Mechanism with Free Energy Barriers at Constant Potentials for the Oxygen Evolution Reaction at the IrO<sub>2</sub> (110) Surface. *J. Am. Chem. Soc.* 2017, 139, 149–155.