## Electrocatalytic Oxygen Evolution Reaction on Iridium Oxide Model Film Catalysts: Influence of Oxide Type and Catalyst Substrate Interactions

Tobias Reier, Inez Weidinger, Peter Hildebrandt, Peter Strasser Electrochemical Catalysis, Energy and Material Science Technische Universität Berlin Straße des 17. Juni 124, Sekr. TC03, 10623 Berlin, Germany

One major roadblock using renewable energy sources is an appropriate storage solution. Long term energy storage can be adequately done by electrocatalytic fuel production processes. Molecular fuels, like hydrogen, methane or hydrocarbons in general consist of atoms in a reduced oxidation state which is raised upon the energy release during the combustion. Any fuel production process, therefore, has to proceed via a catalytic electronconsuming deoxygenation (reduction) and needs an electron supplying counter reaction (oxidation). The oxidation of water to molecular oxygen (oxygen evolution reaction, OER) is the most suitable counter reaction with regard to sustainability, pricing and availability achieved by a closed material cycle.[1]

Although the overall water splitting process was discovered as early as 1789 [1], molecular level knowledge about the anodic part, the oxidation of water to molecular oxygen (OER), is far away from being complete. For instance, several reaction mechanisms were proposed [1,2], however none of them was verified spectroscopically for different catalysts. Furthermore, the relationship between catalyst structure and composition on the one hand and the OER reactivity on the other hand has remained uncertain, even for common ruthenium and iridium catalysts applied in acidic media. Especially amorphous catalysts are often insufficiently characterized with respect to their chemical nature, but offer interesting electrocatalytic properties.

Considering the OER, catalyst substrate interactions are rarely studied. This is remarkable, since the catalyst substrate junction is of great importance for the overall electrocatalytic activity of the system. For common OER catalyst systems, several different catalyst substrate interactions appear plausible, for instance the catalyst can be chemically influenced by the substrate or an interlayer of a new compound can be formed at the junction between catalyst and substrate. This interlayer can have deviating electrocatalytic activity and/or electric conductivity. If the interlayer offers a poor electric conductivity, this can cause an additional voltage drop resulting in the need for higher overpotential. Understanding and identifying materials at the catalyst substrate junction, their properties and their interactions are therefore of great importance for a rational catalyst design. Knowledge about the catalyst substrate interactions can contribute to pave the way to efficient, stable and inexpensive catalysts which are not available until now.

Here, we present a study based on iridium oxide thin film model catalysts demonstrating the formation of different oxide types and their interactions with the substrate. Characterizing the electrocatalytic OER activity of these films demonstrates the impact of the chemical nature of the oxide and the influence of the substrate. The iridium oxide thin film model catalysts (see figure 1) allow excellent control over mass transport, offer a huge surface area-to-bulk ratio and the ability to study catalyst substrate interactions. The thin catalyst films were coated onto different substrates to enable gas phase analytics and electrochemical measurements. Using gas phase analytics (like temperature programmed reduction) we are able to characterize the chemical nature even of amorphous oxides and the interaction with the substrate.



Figure 1: SEM micrographs of iridium oxide model catalyst, left: top view and right: cross section.

Additionally, the films were comprehensively characterized by physicochemical methods to elucidate materials properties like crystal structure, chemical composition and morphology for instance by x-ray diffraction, energy dispersive x-ray scattering, electron microscopy and vibrational spectroscopy. Furthermore, the electrocatalytic activity of iridium oxide films was investigated with controlled mass transport in a rotating disk electrode setup (see figure 2).



Figure 2: Quasi stationary electrocatalytic OER measurement for two different types of iridium oxide.

Combining the results from gas phase and electrocatalytic OER investigations the activity of the different oxide types and the impact of the catalyst substrate interaction can be evaluated. Based on the results, strategies can be developed to ensure maximal noble metal utilization and high catalytic performance not only relevant to the OER in acidic media.

## References

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