

# The Combination of In Situ X-Ray Resonant Photoelectron Spectroscopy and Density Functional Theory Calculations: A Useful Tool for the Understanding of Electrochemical Reactions

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In this contribution the application of resonant photoelectron spectroscopy under reaction condition to Copper electrodes in CO<sub>2</sub>RR and Iridium oxides in OER will be discussed. The results will be combined with DFT calculations.

In case of Iridium electrodes in OER the intrinsic activity of Iridium oxide scales with the formation of  $\mu$ 1-O (terminal oxygen) is found. It is shown that the peroxy species do not accumulate under reaction conditions. Rather, the formation of  $\mu$ 1-O species, which are active in O-O bond formation during the OER, is the most oxidized oxygen species observed, which is consistent with an O-O rate-limiting step. Thus, the oxygen species taking part in the electrochemical oxidation of water on Iridium electrodes are more involved and complex than previously stated. This result highlights the importance of employing theory together with true and complementary operando measurements capable of probing different aspects of catalysts surfaces during operation.

In case of Copper electrodes in CO<sub>2</sub>RR it is found that the pseudocapacitive charging of copper, produced by the incorporation of protons and electrons into the subsurface, facilitates the activation of CO<sub>2</sub>, while simultaneously increasing the barrier for H-H coupling. The net result is that cathodic pseudocapacitive charge suppresses the hydrogen evolution reaction and promotes the production of hydrocarbon and oxygenated products on Copper[2].

[1] J.-J. Velasco-Velez, D. Bernsmeier, Rik V. Mom, P. Zeller, Y. Shao-Horn, B. Roldan Cuenya, A. Knop-Gericke, R. Schlögl, T.E. Jones; Adv. Energy Mater. 2024, 14, 2303407. [2] J.-J. Velasco-Vélez, A. Knop-Gericke, B. Roldan, R. Schlögl, T.E. Jones; Adv. Energy Mater. 2024, 240005.