

High-valent states in cobalt and nickel oxygen-evolving catalysts and their role in O–O bond formation

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The solar-to-fuels conversion is a promising alternative to traditional energy sources such as fossil fuels, and the overall efficiency relies heavily on catalysts of the oxygen evolution half-reaction (i.e., $2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$). This four-electron, four-proton coupled reaction ultimately provides the reducing equivalents for solar fuels synthesis. Earth-abundant first-row transition metal oxides of cobalt, nickel, and their mixed-metal forms can drive this half-reaction at relatively low overpotentials. This presentation will discuss recent studies utilizing a combination of *in situ* and *ex situ* optical and X-ray spectroscopies, including resonant inelastic X-ray scattering, on oxygen-evolving thin films and their molecular and heterogeneous inorganic analogs. Experiment coupled with density functional theory calculations has provided insights into the electronic structures of the high-valent states involved in the mechanism of O–O bond formation.