

# Exploiting multi-metal interactions of water oxidation catalysts using *in situ* soft x-ray absorption

Xueli Zheng<sup>1, 2</sup>, Edward Sargent<sup>2</sup>, Yi Cui<sup>1, 3</sup>

<sup>1</sup>Department of Material Science and Engineering, Stanford University, Stanford, CA 94305, USA.

<sup>2</sup>Department of Electrical and Computer Engineering, University of Toronto, 35 St George Street, Toronto, Ontario M5S 1A4, Canada.

<sup>3</sup>Stanford Institute for Materials and Energy Sciences, SLAC National Accelerator Laboratory, 2575 Sand Hill Road, Menlo Park, California 94025, USA.

Earth-abundant first-row (3d) transition-metal-based catalysts have been developed for the oxygen-evolution reaction (OER); however, they operate at overpotentials significantly above thermodynamic requirements. Density functional theory suggested that non-3d high-valency metals such as tungsten and phosphate can modulate 3d metal oxides, providing near-optimal adsorption energies for OER intermediates. We developed a room-temperature synthesis to produce gelled oxy-hydroxide materials with an atomically homogeneous metal distribution. These gelled FeCoW oxy-hydroxide exhibits the lowest overpotential (191 mV) reported at 10 mA/cm<sup>2</sup> in alkaline electrolyte. The catalyst shows no evidence of degradation following more than 500 hours of operation. X-ray absorption and computational studies reveal a synergistic interplay between W, Fe and Co in producing a favorable local coordination environment and electronic structure that enhance the energetics for OER.

We took the view that generating transition metal sites with high valence at low applied bias should improve the activity of neutral OER catalysts. We therefore explored, using density functional theory, novel strategies to minimize the formation energy of prospective active sites, such as Ni<sup>4+</sup> formed from Ni<sup>2+</sup>, under neutral OER conditions. Using density functional theory, we find that the formation energy of desired Ni<sup>4+</sup> sites is systematically modulated by incorporating judicious combinations of Co, Fe and non-metal phosphorus. We synthesized NiCoFeP oxyhydroxides and probed their oxidation kinetics employing *in situ* soft X-ray absorption (sXAS). These *in situ* sXAS studies of neutral-pH OER catalysts indicate ready promotion of Ni<sup>4+</sup> under low overpotential conditions. The new catalysts exhibit exceptional OER performance, with a 330 mV overpotential at 10 mA/cm<sup>2</sup> in CO<sub>2</sub>-saturated 0.5 M KHCO<sub>3</sub> electrolyte. The new catalyst outperforms the leading precious metal oxide IrO<sub>2</sub> and retains its performance following 100 hours of operation. We showcase the new catalyst in a membrane-free CO<sub>2</sub> electroreduction system that achieves a 1.99 V cell voltage at 10 mA/cm<sup>2</sup>, reducing CO<sub>2</sub> into CO and oxidizing H<sub>2</sub>O to O<sub>2</sub> with a 64% electricity-to-chemical-fuel efficiency.