

Synthesis and *in-situ* characterization of metastable metal oxide polymorphs for oxygen evolution catalysis

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Abstract

Many technologically relevant materials are metastable, in that they exist above their thermodynamic minimum and must be kinetically stabilized. Within the realm of metastable materials, many polymorphic metal oxides show improved functionality over their thermodynamically stable form. Of particular interest is manganese oxide, highly desirable as a viable acid-stable oxygen evolution catalyst. In order to understand the energetics and transformation pathways to synthesize specific polymorphs, my research investigates the mechanisms of kinetically trapping transition metal oxides in metastable, catalytically active states. Our studies reveal that Mn^{3+} may be introduced into the $\delta\text{-MnO}_2$ polymorph by an electrochemically induced comproportionation reaction, significantly enhancing the catalytic activity of the film. We further show that Mn^{3+} is kinetically trapped in tetrahedral sites, inducing a local strain on the oxide sublattice and a reduced HOMO-LUMO gap. These factors contribute to enhanced activity for the oxygen evolution reaction by facilitating oxyl radical formation for reductive coupling to produce oxygen, providing crucial design principles for the improvement of oxygen evolution activity in metal oxidic catalysts.