Turning a cheap, poor catalyst into a cheap, excellent catalyst. Optimizing layered metal oxide materials for water oxidation using experiment and theory.

Michael J. Zdilla*

Temple University

Efficient catalytic water oxidation is an important reaction for the development of solar hydrogen as a source of green energy. Extraction of high energy electrons from water for the preparation of fuel leaves O_2 as a byproduct. Nature boasts the only truly effective catalyst for this reaction, the oxygen evolving complex (OEC), a tetramanganese-calcium-oxo cluster. The exploration of solid-state manganese oxides inspired by (or possibly primordial to) this inorganic cluster is of interest for the chemical and electrochemical oxidation of water. While promising catalysts have been discovered, an understanding of their active site structures and mechanisms has been elusive, precluding incremental improvements in design. This lecture is focused on the birnessite phase of MnO_2, a material traditionally seen as a poor water oxidation catalyst. Presented is a combined experimental and theoretical approach where Density Functional Theoretical (DFT), and Molecular Dynamics (MD) computations inform and guide experimental approaches as to understand the functioning of—and thereby identify ways to improve—the catalytic activity of these materials. Modification of birnessite by enrichment with Mn(III) defect sites, intercalated interlayer Co or Ni ions, and alloying of the layers with Co(III), and organizing electronic structure of adjacent layers have turned this relatively poor catalyst into one competitive with excellent IrO- and double-layer-hydroxide-based catalysts. The discoveries have been guided by MD simulations which show enhanced geometric frustration of water enhances electron transfer rates, and DFT calculations which describe geometric features that optimize band structure for beneficial electronic conductivity and charge separation. The findings have led to expansion of studies into nickel- and cobalt oxides, demonstrating generality of the approach for catalytic layered materials.