

Charles W. Machan
Associate Professor
Department of Chemistry
University of Website: machangroup.virginia.edu

Title: “Enabling Catalytic Dioxygen Reduction with Early Transition Metal Complexes and Organic Molecules”

Abstract:

The electrocatalytic reduction of dioxygen (O_2) has relevance to the development of more efficient fuel cells and chemical oxidations, as well as our understanding of how bioinorganic systems convert energy-rich molecules during respiration. Thanks to decades of research inspired by the study of active sites of biological systems, Fe- and Cu-based systems dominate synthetic catalyst development for the oxygen reduction reaction (ORR). Although O_2 -dependent Mn-based biological systems are well-known and Mn centers generally exhibit a greater affinity for binding O_2 (and other reactive oxygen species) than Fe in analogous mononuclear complexes, few reports exist on the ORR mediated by Mn complexes.

The challenge of developing Mn-based ORR catalysts arises from the formation of stable intermediates, resulting in slow reaction rates. Strategies for improving the catalytic properties of Mn complexes which rely on modifying the ligand environment and use of small-molecule redox mediators to transfer electrons and protons to the active site will be described. Given that these redox mediators must tolerate an O_2 -rich environment, their stability and reactivity under aerobic conditions is also of interest for study. Based on these desired properties, we have developed strategies for making stable catalytic systems based on purely organic redox-active organic that parallel the reaction pathways and stabilities known for transition metal-based systems, despite lacking *d* orbital manifolds.