

# Metal-Free Molecules as Electrocatalysts and Co-electrocatalysts

**Prof. Charles Machan**

Associate Professor  
University of Virginia

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There is continuously expanding interest in developing new electrocatalytic processes as an approach to harness intermittent electricity from renewable sources. Molecular systems are useful to understand and develop fundamental principles of these reactions through mechanistic study, as well as offer the possibility for testing structure-function relationships through iterative synthetic design. Broadly, the fundamental understanding of molecular species as electrocatalysts has relevance to the interconversion of electricity and chemical energy, as well as commodity chemical production. However, in order for homogeneous systems to eventually be scalable, their activity and stability must be improved. In naturally occurring enzymes, redox equivalents (electrons, often in a concerted manner with protons) are delivered to enzyme active sites by small molecules known as redox mediators (RMs). Inspired by this, we have been studying co-electrocatalytic systems which pair chromium-based homogeneous catalysts and metal-free RMs to convert carbon dioxide to carbon monoxide. The distinct advantage of the co-catalytic approach is the ability to independently select the properties of the secondary component without requiring catalyst modification. Based on these lessons from Cr-based co-electrocatalysis, we have more recently begun to examine the possibility of using metal-free molecules as electrocatalysts for the reduction of dioxygen. Interestingly, cationic conjugated organic molecules demonstrate catalytic activity for dioxygen reduction which has mechanistic parallels with well-studied Cu-based systems. Our results suggest that many new opportunities exist for refining reaction design for electrochemical transformations by systemically pairing redox-active small molecules with catalytic active sites, as well as imply that comparable design principles to transition metal-based electrocatalysts can be used develop and optimize organic-based ones.

Biosketch:

Website: <https://machangroup.virginia.edu/>



Charles Machan (muh-hahn) was born in Madison, WI and grew up in Wauwatosa, WI where he attended Marquette University High School before going to Washington University in St. Louis (WashU). While at WashU he played football for four years as a defensive tackle and majored in Chemistry and German (B.A. 2008). Charles attended Northwestern University for graduate school and completed a Ph.D. in Inorganic Chemistry (2012) under the supervision of Chad A. Mirkin. At Northwestern he served as President of the Alpha Gamma Chapter of Phi Lambda Upsilon, a co-ed chemistry honors fraternity, and received the Edmund W. Gelewitz Award for Outstanding

Senior Graduate Student (2012). From 2013-2016 he was a postdoctoral researcher with Clifford P. Kubiak at the University of California, San Diego.

Charles joined the Department of Chemistry at the University of Virginia in 2016 as an Assistant Professor. Since 2022, he has been an Associate Professor in the Department, where his research program currently receives funding from NSF and DOE. He received the Bessel Research Award from the Alexander von Humboldt Stiftung in 2024. His research covers energy-relevant catalysis involving abundant small molecules like carbon dioxide, dioxygen, dihydrogen, and water as reagents at the interface of molecular electrochemistry and materials. The approach focuses on developing new inorganic complexes and materials which incorporate co-catalytic moieties, non-covalent secondary sphere interactions, and substrate relays as catalysts to store electrical energy in chemical bonds.