

Slurry of Transition Metal Chalcogenides for Multifaceted Electrochemical Applications: Energy Conversion, Storage, Sensing & Catalysis

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Transition metal chalcogenides has been at the center of attraction for materials chemistry for decades owing to their novel and interesting optoelectronic properties that can be tuned with anion composition, coordination and doping. Recently these transition metal chalcogenides have also been explored for several electrochemical energy-related applications with primary focus on sustainable energy conversion. In the Nath group we have explored electrocatalytic properties of these transition metal chalcogenides focusing more on elucidating the surface evolution under operational conditions and correlating solid state chemistry with electrochemical properties. Specifically, several transition metal chalcogenides have been identified as highly efficient electrocatalysts for clean hydrogen and oxygen generation through water splitting which surpasses state-of-the-art precious metal oxides by several orders of magnitude. Our main design principle is based on the idea that chalcogenides, specifically, selenides and tellurides will show much better oxygen evolution reaction (OER) catalytic activity due to increasing covalency around the catalytically active transition metal site, compared to the oxides caused by decreasing electronegativity of the anion, which in turn leads to variation of chemical potential around the transition metal center, [e.g. lowering the $\text{Ni}^{2+} \rightarrow \text{Ni}^{3+}$ oxidation potential in Ni-based catalysts where Ni^{3+} is the actually catalytically active species]. More importantly, it has been proposed that the chalcogenide surface evolves into a mixed anionic (hydroxy)chalcogenide active phase. We are investigating this interface evolution hypothesis further through experimental studies by creating structural analogues of the mixed anionic surface and integrating with DFT calculations to estimate variation of activation energy as function of surface composition. The electrochemical tunability of these transition metal chalcogenide surfaces along with their increased lattice covalency has also led to development of the concept that some of these compositions can enhance CO_2 reduction (CO_2RR). Specifically, we have focused on Cu and Ni-based chalcogenides based on the hypothesis that higher *d*-electron occupancy of the transition metal within a covalent lattice will lead to better adsorption of intermediate $\ast\text{CO}$ on the surface through enhanced metal-to-ligand back-bonding, which in turn leads to longer dwell time and subsequent reduction of the *CO* intermediate to higher carbon content reduction products. The Nath group has recently discovered Cu- and Ni-chalcogenides as highly active electrocatalysts for CO_2 reduction to C2 and C3 products with high selectivity. The functionality of transition metal chalcogenides has been expanded even further by identifying their electrochemical activity towards small molecule oxidation that makes them applicable as biosensors. In the Nath group we are trying to understand the intricacies of transition metal chalcogenides with respect to their electronic, bonding, and transport properties in an attempt to understand their electrochemical tunability and facile intermediate adsorption on the surface.