Chemical Engineering Dissertation Defense

Machine-Learning Accelerated Screening of Single Atom Alloys for Electrochemical Nitrate Reduction

School for Engineering of Matter, Transport and Energy

Daniel Rivera

Advisor: Christopher Muhich

Abstract

Nitrate contamination in groundwater and drinking water poses a serious risk to human and environmental health. Electrochemical nitrate reduction (E-NRR) is a promising route for remediating nitrate contamination, though it is hampered by lack of selectivity and parasitic side reactions like hydrogen evolution. Transition metal single atom alloy (SAA) catalysts, a dilute alloy of two metals (the single atom and the host), are a promising technology to improve the activity and selectivity, though they are challenging to systematically investigate due to the huge composition space they inhabit. This dissertation presents innovative methods of screening SAA catalysts for E-NRR using Density Functional Theory (DFT).A data-driven approach was taken towards extracting useful electronic structure descriptors, offering a cost-effective means of generating scaling relationships for predicting their E-NRR performance and yielding useful insights into the controlling factors of activity and selectivity. SAA d-band center (ε_d), d-band filling, d-band width (W_d), and the Fermi level (ε_F) were found to control reaction energetics and site preference of E-NRR intermediates. This technique reduced the required number of DFT calculations to gather surface descriptors by 75% compared to transitional atomic adsorption energy descriptors.

Active Transfer Bagging (ATBagging), a novel transfer learning method was co-developed by the author and used here for the first time. Using ATBagging, a representative subset of SAA catalysts on which to collect activation barriers for vital reaction steps in the E-NRR reaction network was determined. This maximized the value of costly nudged elastic band calculations compared to a randomly selected subset and also eliminated the potential biases of selecting SAA catalysts with chemical intuition. Finally, the models developed herein were used to predict the cost-normalized activity of SAA catalysts for E-NRR, identifying 10 candidate SAAs for further investigation, 9 of which are unreported in the literature. Statistical analysis on the descriptors of this subset compared to the SAA population yielded target properties for further material design: ε_d of -1.24 eV, d-band filling of 0.68, work function (Φ) of 4.97, and single atoms which donate an average of 1 electron to the neighboring host atoms.

March 30, 2026; 2:00pm; DH L1-06

Arizona State University