FIRST PRINCIPLES AND MACHINE LEARNING-BASED ANALYSES OF STABILITY AND REACTIVITY TRENDS FOR HIGH-ENTROPY ALLOY CATALYSTS

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Since its inception, the field of heterogeneous catalysis has evolved to address the needs of the ever-growing human population. Necessity, after all, fosters innovation. Today, the world faces numerous challenges related to anthropogenic climate change, and that has necessitated, among other things, a search for new catalysts that can enable renewable energy conversion and storage, sustainable food and chemicals production, and a reduction in carbon emissions. This search has led to the emergence of many promising classes of materials, each having a unique set of catalytic properties. Among such candidate materials, high-entropy alloys (HEAs) have very recently shown the potential to be a new catalyst design paradigm. HEAs are multimetallic, disordered alloys containing more than four elements and, as a result, possess a higher configurational entropy, which gives them considerable stability. They have many conceivable benefits over conventional bimetallic alloy catalysts—greater site heterogeneity, larger design space, and higher stability, among others. Consequently, there is a need to explore their application in a wide range of thermal and electrocatalytic reaction systems so that their potential can be realized.

In the past few decades, first principles-based approaches involving Density Functional Theory (DFT) calculations have proven to be effective in probing catalytic mechanisms at the atomic scale. Fundamental insights from first principles studies have also led to a detailed understanding of reactivity and stability trends for bimetallic alloy catalysts. However, the express application of first principles approaches to study HEA catalysts remains a challenge, due to the large computational cost incurred in performing DFT calculations for disordered alloys, which can be represented by millions of different configurations. A combination of first principles approaches and computationally efficient machine learning (ML) approaches can, however, potentially overcome this limitation.

In this thesis, combined workflows involving first principles and machine learning-based approaches are developed. To map catalyst structure to properties graph convolutional network (GCN) models are developed and trained on DFT-predicted target properties such as formation energies, surface energies, and adsorption energies. Further, the Monte Carlo dropout method is integrated into GCN models to provide uncertainty quantification, and these models are in turn used in active learning workflows that involve iterative model retraining to both improve model predictions and optimize the target property value. Dimensionality reduction methods, such as principal components analysis (PCA) and Diffusion Maps (DMaps), are used to glean physicochemical insights from the parameterization of the GCN.

These workflows are applied to the analysis of binary, ternary, and quaternary alloy catalysts, and a series of fundamental insights regarding their stability are elucidated. In particular, the origin and stability of “Pt skins” that form on Pt-based bimetallic alloys such as Pt_3Ni in the context of the oxygen reduction reaction (ORR) are investigated using a rigorous surface thermodynamic framework. The active learning workflow enables the study of Pt skin

formation on stepped facets of Pt_3Ni (with a complex, low-symmetry geometry), and this analysis reveals a hitherto undiscovered relationship between surface coordination and surface segregation. In another study, an active learning workflow is used to identify the most stable bulk composition in the Pd-Pt-Sn ternary alloy system using a combination of exhaustively sampled binary alloy data and prudently sampled ternary alloy data. Lastly, a new GCN model architecture, called SlabGCN, is introduced to predict the sulfur poisoning characteristics of quaternary alloy catalysts, and to find an optimal sulfur tolerant composition.

On another front, the electrocatalytic activity of quinary HEAs towards the ORR is investigated by performing DFT calculations on HEA structures generated using the High-Entropy Alloy Toolbox (HEAT), an in-house code developed for the high-throughput generation and analysis of disordered alloy structures with stability constraints (such as Pt skin formation). DFT-predicted adsorption energies of key ORR intermediates are further deconvoluted into ligand, strain, and surface relaxation effects, and the influence of the number of Pt skins on these effects is expounded. A Sabatier volcano analysis is performed to calculate the ORR activities of selected HEA compositions, and correspondence between theoretical predictions and experimental results is established, to pave the way for rational design of HEA catalysts for oxygen reduction.

In summary, this thesis examines stability and reactivity trends of a multitude of alloy catalysts, from conventional bimetallic alloys to high-entropy alloys, using a combination of first principles approaches (involving Density Functional Theory calculations) and machine learning approaches comprising graph convolutional network models.