ABSTRACT

A major goal of applied electrocatalysis research has been the development of electrode materials that are active, selective, stable, and cost effective in producing electricity or desired products. In recent years, developments in *ab initio* methods for the simulation of catalyst surfaces, and electrochemical reactions occurring over them, have enabled the development of a fundamental understanding of the processes occurring at the solid-liquid interface at an atomistic scale. In combination with experiments, they are helpful in elucidating design principles that can then inform electrocatalyst design. In this work, we describe the application of density functional theory, *ab initio* molecular dynamics, and high throughput materials informatics approaches to understand oxygen and carbon based electrochemistries, with relevance to electricity conversion and environmental protection. We also discuss an approach based on the Born Haber cycle used to quantify adsorbate stabilization from solvent molecules that are ubiquitous for any electrochemical reaction occurring at the solid-liquid interface.

The oxygen reduction reaction (ORR) occurs at the cathode in hydrogen fuel cells and, in conjunction with the hydrogen oxidation reaction (HOR) at the anode, produces electricity and water. While platinum group metals are the current state-of-the-art catalysts for ORR, their high cost has necessitated the search for alternatives. We investigated iron-nitrogen-carbon (Fe-N-C) catalysts, which are platinum group metal-free and show reasonable activity compared to platinum. Despite their potential as cost effective materials, they are not durable over long-term operation of fuel cells, impeding their commercial adoption. The mechanisms of deactivation of the iron-nitrogen-carbon catalysts under aqueous acidic electrochemical reaction conditions remain debated, and deciphering them is complicated due to the complex structure of the catalyst. We attempt to address these challenges by first examining the structural aspects of the catalyst, sampling numerous potential active site configurations, determining their in-situ structure, and linking them to intrinsic activity and intrinsic stability descriptors. Our findings reveal an activity-stability tradeoff, with the most active sites being most prone to stability issues. Additionally, we explored the role of hydrogen peroxide, a side product of ORR, in degrading Fe-N-C catalysts, where we found that it oxidizes the catalyst surface thereby causing a loss in its activity. Based on these insights, we propose design principles to enhance the activity and stability of Fe-N-C catalysts.

We extended similar strategies to study the ORR on platinum catalysts, the oxygen evolution reaction (OER) on iridium oxides, and the carbon dioxide reduction reaction (CO_2R) on copper catalysts in water electrolyzers. For the ORR on platinum, we identified the formation of hydroxyl and water adsorbate rings on stepped surfaces, akin to hexagonal rings found on terraces. The ORR follows an associative mechanism involving proton coupled electron transfer to these ring structures. Furthermore, we provided activity descriptors that aligned with experimental observations, showing a higher activity on stepped surfaces compared to terraces. For the OER on iridium oxides, we examined transformations of IrO_2 (110) surfaces, and pinpointed oxidation of bridge and coordinatively unsaturated top sites as key charge transfer steps that correlate with peaks in cyclic voltammograms. Finally, for the CO_2R on copper, we investigated the role of water as a proton source under neutral or alkaline conditions, and shed light into the effect of coverages of surface species on the kinetics of water dissociation that provide protons for the CO_2 reduction while competing with proton combination steps leading to the hydrogen evolution reaction.

Through this work, we have gained a deeper understanding of various materials under conditions relevant to each type of electrochemistry. We elucidated the relationships between the in-situ structure, activity, and stability for the electrocatalysts, and identified key factors influencing catalyst performance. Integrating such insights from a computational perspective with experimental approaches holds great potential in making significant advancements in developing sustainable energy technologies and ultimately contribute to the progress towards a greener and more energy-efficient future.