

Electrocatalysis: Mechanistic Insight and Electrode Design using Quantum-Chemical Methods

Michael J. Janik

Department of Chemical Engineering, Pennsylvania State University
104 Fenske Lab, University Park, PA 16802, mjanik@psu.edu

The ability to link the function of catalytic materials to their atomic level structure guides the rational design of new catalysts. Quantum-chemical methods, such as density functional theory (DFT), can be used to determine atomic structures, reaction energies and activation barriers directly from first-principles, thus enabling the creation of structure-function relationships. However, the influence of the electrochemical environment and electric fields that develop at the metal-water interface on the kinetics has proved challenging for electronic structure modeling, thereby limiting the application of these methods to electrocatalytic mechanisms occurring at fuel cell electrodes. This poster will discuss the application of a novel DFT based method to examine the effects of the solution phase and electric field on elementary energetics. Results from completed studies of methanol and carbon monoxide oxidation as well as oxygen reduction reactions will be reported. Future directions of Dr. Janik's new research group at Penn State will be discussed.

The activity and selectivity of the anode of the direct methanol fuel cell is a function of the electrode potential. Platinum-ruthenium bimetallic catalysts show greater oxidation rates at lower potentials than pure platinum due to improved tolerance to carbon monoxide poisoning, reducing the anode overpotential and thereby improving the cell fuel efficiency and power generation. In order to explain these effects, the dependence of elementary reaction energetics on the electrode potential must be determined. Density functional theory was applied, employing the double-reference formalism to include the metal-water interfacial potential drop within the simulation cell, to determine the elementary pathways of methanol and CO oxidation. The inclusion of subsurface ruthenium decreases the barrier to CO and OH coupling as compared to the pure Pt surface, while inclusion of surface ruthenium reduces the equilibrium potential of water activation, thereby increasing the rate of CO oxidation through both ligand and bifunctional effects. This fundamental understanding of the role of alloy structure in improving the rate of methanol oxidation is utilized to design ternary alloys for improved performance.

The sluggish rate for the oxygen reduction reaction (ORR) at the cathode limits the performance of proton exchange membrane fuel cells. Despite the multitude of theoretical studies evaluating the reactivity of O₂ on transition metal catalysts, few have considered the mechanism of the proposed rate limiting step, reduction of adsorbed molecular oxygen, due to its electrochemical nature. Results illustrate that initial reduction occurs with electron transfer to a delocalized state encompassing both adsorbed O₂ and an approaching solvated proton prior to forming the O-H bond. These results motivate future studies assessing how the electrolyte-electrode structure affects the energetics of this important reduction step. Additional future research directions include extending the application of these methods to anode development for direct hydrocarbon utilization solid oxide fuel cells and for direct borohydride fuel cells.