Nanoscale Electrochemical Processes on Cu(111) Surface using Periodic DFT and Quantum/Classical Simulations

Aslihan Sumer, Martin Losada, Santanu Chaudhuri

ISP/Applied Sciences Laboratory, Washington State University
Spokane Technology Center
120 N. Pine St. Spokane, WA 99202

Oxygen reduction reaction (ORR) is a topic of interest in electrocatalysis due to its application in fuel cell cathodes, as well as its relevance to the design of corrosion resistant materials. The electrochemical process occurs at the interface between the electrode surface and electrolyte solution in the presence of an external electric field. The composition of the solution, the chemical and physical properties of the electrode surface, the solution-surface interaction and the electrostatic potential can all impact the behavior of the reactants and thus influence the overall rate. An accurate and efficient computational model that can incorporate the various aspects of the process in a collective way and ultimately describe the overall rate can be obtained by coupling of different levels of theoretical techniques and thus, eliminating the intrinsic limitations that would be encountered when each of these methods would be applied on such a complex system alone.

In this talk, we summarize a multi-scale modeling approach that was applied to explore ORR at the Cu(111) surface. The structure and stability of various forms of oxygen species at the surface was analyzed with respect to the surface electronic structures using Density Functional Theory (DFT). The mechanism and energetics of possible chemical reactions between these oxygen species and other surface adsorbates, e.g. H_2O, H_2, etc. were explored. The computations were performed in vacuum and then repeated with water layers on top of the metal surface to incorporate and analyze the consequences of electrolyte ordering and other double layer effects. An external electric field was also incorporated to evaluate the relation between the electrode potential and the structure and stability of adsorbates on the surface and the mechanism and energetics of the reactions. The theoretical challenges of a polarized metal-electrolyte interface have not been fully resolved yet. We will compare the relative merits of two approaches here. First, a DFT analysis of charge and dipolar corrections of the surface was analyzed with respect to adsorption energy and reaction energetics. The periodic DFT calculations were compared with quantum chemical calculations of the polarized O_2 molecule on the surface (Figure 1). Second, the transport through a polarized double layer was used at the core of writing a full rate equation. DFT methods cannot fully identify the kinetics at higher potentials when the rate of ORR is diffusion controlled.

To model the transport of O_2 through the double layer at the electrolyte/Cu(111) interface, molecular dynamics (MD) computations with classical potentials were used. Structure of the solution, formation of the double layer over the Cu surface, and diffusion rate of oxygen in the solution were evaluated at various electrode potentials. TIP4P model for water (four-cite model) with NaCl as electrolyte was proven to give trends for the diffusion constants of O_2 that are comparable to the experimental values. Finally, to further explore ORR at the Cu surface under the influence of the electrolyte layer and electrode potential, hybrid quantum mechanics/molecular mechanics (QM/MM) computations were being explored for the interface (Figure 1). The QM part abstracted from the MD simulations can be treated at DFT and other correlation-consistent levels of theory. The complexity of the electrode/electrolyte interface and limitations of current approaches will be discussed. However, even with imperfections in our understanding of solvated electrons and polarization of the double layer, the multi-scale approach of modeling can provide valuable guidance for investigating the fundamental aspects of electrochemical ORR and lead to the development of an insightful microkinetic model that can combine experiments and theory under a unified framework. We will discuss how we can further develop such methods to provide a fuller picture of the dynamics at the electrode interface that no single atomistic modeling technique is capable of addressing at the present moment.
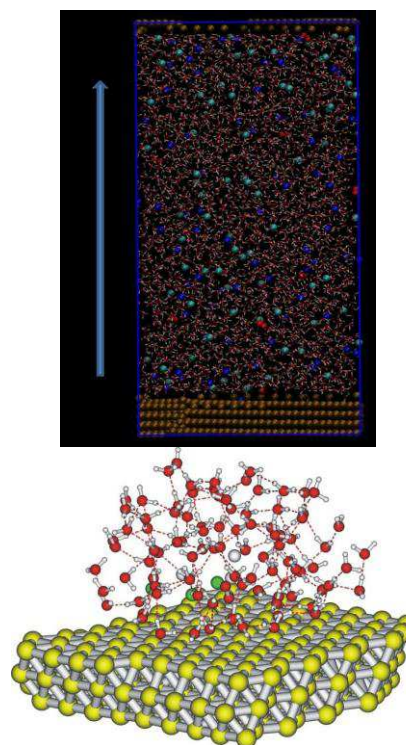
Figure 1: MD simulation of O_2 transport and QM region at the Cu(111) surface with solvated intermediates were compared with periodic DFT calculations of the same ORR pathways at different electrode potentials.