356e Insights into the Electrochemical Oxygen Reduction Reaction through Density Functional Theory

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Rational design of metal catalysts for fuel cell electrodes has eluded researchers due to the limited understanding of the mechanisms of the surface reactions. While surface reactions taking place at gas-metal interfaces can be studied using an array of techniques, electrochemical reactions are more difficult to probe due to the complex nature of the interface of the metal electrode and the electrolyte solution. This interface is known as the electric double layer (EDL) owing to the charge accumulated on the metal surface resulting from adsorption and counter charge in the solution at the interface. While several factors influence the molecular level picture of the EDL, the interface always consists of large electric fields and solvating water molecules. Any attempt to understand the mechanisms of electrochemical reactions must consider how those factors affect the surface chemistry.

We have studied the reduction of oxygen on Pt(111) using model EDL physics with density functional theory (DFT). To model the solvent effects, we used protonated water clusters that adsorb on the surface very weakly. The electrostatic effects were modeled using homogeneous electric fields. The results show that two new pathways emerge in the presence of the solvent. In one pathway, molecular oxygen simultaneously dissociates and accepts a proton from the water cluster. In the other pathway, molecular oxygen accepts the proton without dissociating. Additionally, the reactions of solvated oxygen are more significantly affected by electric fields than unsolvated oxygen with the restructuring of the solvent during the surface reaction. We will explain these results and demonstrate their consistency with experiments. Finally, we will discuss how these fit into the understanding of fuel cell chemistry.