Unifying the 2e– and 4e– Reduction of Oxygen on Metal Surfaces

Understanding trends in selectivity is of paramount importance for multi-electron electrochemical reactions. The goal of this work is to address the issue of 2e– versus 4e– reduction of oxygen on metal surfaces. Using a detailed thermodynamic analysis based on density functional theory calculations, we show that to a first approximation an activity descriptor, \( \Delta G_{\text{OH}^*} \), the free energy of adsorbed OH*, can be used to describe trends for the 2e– and 4e– reduction of oxygen. While the weak binding of OOH* on Au(111) makes it an unsuitable catalyst for the 4e– reduction, this weak binding is optimal for the 2e– reduction to H2O2. We find quite a remarkable agreement between the predictions of the model and experimental results spanning nearly 30 years.