

Modeling the Electrocatalytic Oxygen Reduction Reaction using Theoretical and Surface Science Techniques

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Introduction

Although fundamental surface science investigations of catalysis have been extensive, surface-level study of electrocatalysis has lagged behind. The primary reason for the lack of study is the complexity of the electrode | electrolyte interface, which makes many electrode surfaces inaccessible to common spectroscopic methods. Many electrochemical studies rely overwhelmingly on potentiostatic techniques in which the electrochemical cell current is measured under potential control. While limited mechanistic information can be derived from these measurements in some cases, obtaining direct mechanistic data for many electrochemical reactions is not possible. The promise of fuel cells has driven a renewed interest in surface modeling of electrocatalytic reactions. However, because of the complexity of the electrode | electrode interface, most models make simplifying assumptions. Thus, experimental measurements of relevant surface intermediates are needed to confirm model results and establish a basis for future theoretical studies.

We present our work toward the development of a surface level description of the oxygen reduction reaction on Pt(111) using a combination of *ab initio* and surface science techniques. This work involves a so-called “non-situ” approach in which the electrocatalytic chemistry is modeled in ultrahigh vacuum (UHV). While the restriction of UHV conditions imposes important limitations, it does permit detailed characterization (using both experiment and theory) of oxygen reduction chemistry on model surfaces. Reaction pathways and energies computed by *ab initio* calculations can thus potentially be confirmed by direct spectroscopic measurements to better understand the role of the electric double layer environment in controlling reaction mechanisms. We will report results of our studies and address the compatibility of the non-situ techniques with more traditional in-situ potentiostatic techniques.

Materials and Methods

We performed density functional theory calculations (DFT) using VASP. In these calculations, the electrode was modeled as a Pt(111) single crystal, using three frozen Pt layers in a 3x3 unit cell. The solution phase was modeled as H_3O_2^+ .¹ Experiments were performed in an ultrahigh vacuum system (base pressures $< 10^{-10}$ Torr) equipped for high resolution electron energy loss spectroscopy (HREELS). Gases were dosed to a Pt(111) crystal at temperatures < 100 K and then progressively flashed to higher temperatures. Procedures were generally based on the method developed by Wagner et al., who demonstrated that solvated protons could be isolated on Pt(111) by adsorbing water multilayers on H-covered Pt(111).²

Results and Discussion

DFT calculations were used to investigate numerous elementary steps proposed to be important in the oxygen reduction reaction. The DFT calculations support a simultaneous proton and electron transfer step following the initial adsorption of O_2 , as first proposed by Damjanovic et al.³ The activation barrier for this step was calculated to be 0.07 eV,

significantly less than the activation barrier of 0.38 eV calculated for the dissociation of O_2 in solvent-free conditions. Following protonation, dissociation of OOH is the preferred reaction step. The barrier of dissociation is 0.22 eV, which is also less than the barrier of O_2 dissociation. Subsequent proton transfer steps are also low barrier steps, although diffusion steps may play a large role in the reaction.

The DFT calculations indicate that molecular oxygen can proceed through a reaction pathway other than dissociation of O_2 , brought on by the presence of the solvent, despite the lack of control of the electrode potential. We attempted to experimentally verify this in a UHV environment by preparing a condensed “solution phase” on Pt(111) covered by preadsorbed O_2 and H. The computed mechanism suggests that it may be possible to obtain adsorbed O_2 in the presence of solvated protons, and that a new pathway for the reaction of O_2 with hydrogen may be observed under such conditions; this pathway would proceed through an OOH state.

The experimental data clearly indicates that the presence of the water solution inhibits the dissociation of O_2 , which enables proton formation. As shown in Fig. 1, this permits the isolation of protons even for substantial coverages of O_2 on Pt(111). These results suggest that O_2 dissociation does not occur during water formation in the presence of acidic solution. However, the presence of water multilayers complicates identification of key surface intermediates. Promising directions for further UHV characterization of processes relevant for oxygen reduction will be discussed.

Significance

To this point, the limited UHV study of electrochemistry has focused on solvation of simple molecules and the formation of protons. This work begins to examine proton transfer in the oxygen reduction reaction using UHV techniques coupled with *ab initio* calculations. The ability to study electrocatalytic reactions in UHV may significantly advance the understanding of surface processes in electrochemical reactions.

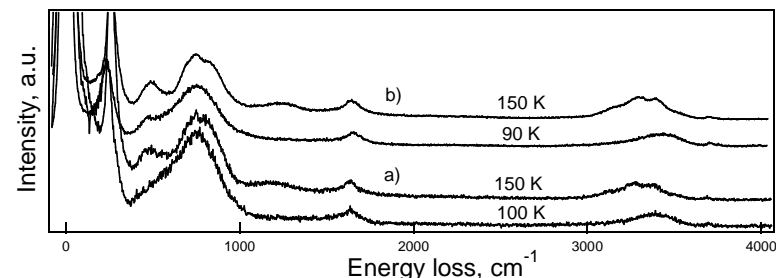


Figure 1. HREELS spectra of proton formation for: a) 0.9 L H_2 , 1 L H_2O b) 0.5 L O_2 , 3.0 L H_2 , 1 L H_2O . The peak at ca. 1200 cm^{-1} indicates that proton formation occurs in the presence of preadsorbed O_2 .

References

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