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## V.P.10 Theoretical Insights Into Active and Durable Oxygen Reduction Catalysts

Matthew Neurock (Primary Contact),  
Anirbahn Chatterjee and Dr. Michael Paul  
(Students and Postdoctoral Fellows)  
University of Virginia  
Departments of Chemical Engineering and Chemistry  
Charlottesville, VA 22904-4741  
Phone: (434) 924-6248  
E-mail: mn4n@virginia.edu

DOE Program Officers: Dr. Paul H. Maupin,  
Dr. Raul Miranda  
Phone: (301) 903-4355  
E-mail: Paul.Maupin@science.doe.gov  
Phone : (301) 903-8014  
E-mail: Raul.Miranda@science.doe.gov

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### Objectives

The goals of this work are to: 1) determine the controlling elementary reaction pathways and intrinsic kinetics involved in the oxygen reduction reaction over Pt and Pt based alloys and their potential dependent behavior, 2) establish the influence of the extrinsic reaction environment including the surface coverage, alloy composition, solution phase and electrochemical potential and 3) understand the mechanisms that control metal dissolution.

### Technical Barriers

Electrocatalysis is controlled by the complex interplay between the active catalytic sites and the influence of their complex environment at the electrified aqueous/metal interface.[1-3] The most active electrocatalytic materials exquisitely integrate the atomic assembly of the active metal sites responsible for the elementary bond making and breaking steps, together with the carbon support to carry out efficient electron transfer, and polymer electrolyte and water to facilitate proton transfer, thus establishing an optimal three-phase interface. Understanding the elementary catalytic processes along with the atomic scale features that control them, however, is obscured by the complexity of this three phase interface and the dynamic changes that occur to it under operating conditions. We are developing a first-principles framework and simulations tools that can be used to elucidate the elementary molecular catalytic transformations that occur in the

oxygen reduction reaction (ORR) and the distinct role of the surface structure, alloying surface coverage, solution phase and applied potential on ORR and dissolution.

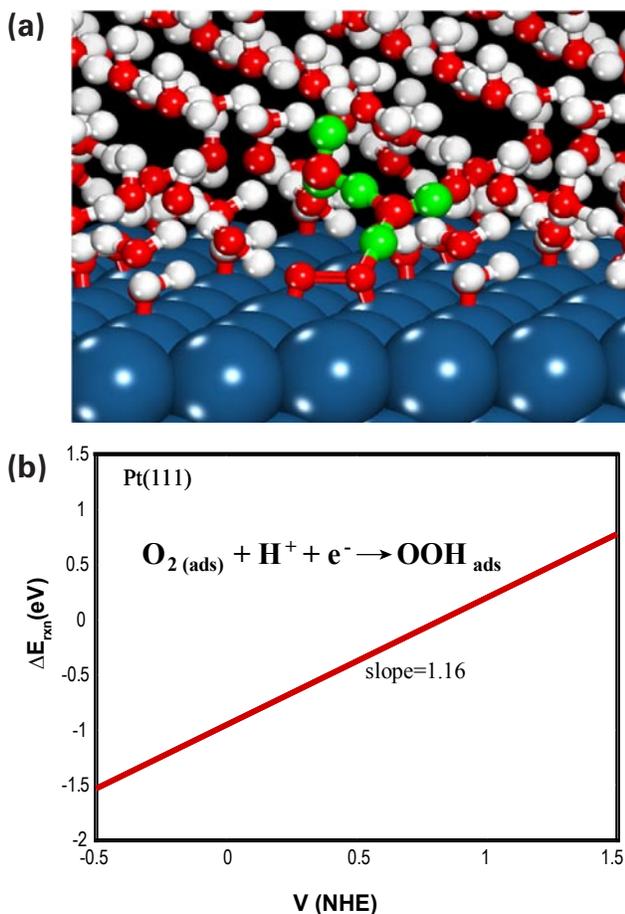
### Abstract and Recent Progress

The ability to follow the molecular level transformations that control electrocatalysis and the mechanisms responsible for metal dissolution are obscured by the complex nature of the water/solution interface.[1-3] In addition to the complexity of the interface, there are a number of challenges in appropriately simulating electrochemical systems which require calculations carried out at constant potentials as they involve grand-canonical ensembles. Current ab initio methods, however, are based on a canonical formalism whereby the number of electrons is held constant. We have recently developed an ab initio approach based upon density functional theory that can be used to simulate different electrochemical and electrocatalytic systems that we describe as the double reference method. [3-6]

The DFT double-reference method is used in this work to simulate the electrochemical double-layer and calculate the elementary reaction energies and activation barriers over a range of potentials applicable to a working PEM cathode. In the first phase of this work, we have focused examined the oxygen reduction reaction (ORR) over different single surfaces Pt and Pt-based alloys and are beginning to transition to Pt nanoparticles in order to explore structure sensitivity.

The initial reduction of molecular oxygen ( $O_{2,ads} + H^+_{aqueous} + e^- \rightarrow OOH_{ads}$ ) was found to proceed through a proton-coupled electron transfer step followed by the addition of hydrogen to the bound  $O_2^*$  to form the surface  $OOH^*$  intermediate. The transition state for this step is shown below in Fig. 1A. The calculated activation barrier was found to be strongly dependent on potential as is shown in Fig. 1B. The resulting barriers were found to be in good agreement with measured activation barriers over a range of potentials reported in the literature.[7-9]

Over the potentials of interest, the barrier was found to be nearly equal to the overall reaction free energy for this step. At a potential of 1.2 V-NHE, the first reduction barrier (0.7 eV) is close to that calculated for  $O_2$  dissociation (0.77 eV). However, the reaction energy, and likely the activation barrier, for  $O_2$  dissociation is not a strong function of electrode potential. At 0.8 V-NHE, the barrier to the first reduction step (0.3 eV) was calculated to be substantially



**FIGURE 1.** The reduction of adsorbed  $O_2$  to  $OOH^*$  as a function of potential. A) The transition state structure at 0 V and B) the resulting activation barrier as a function of potential.

lower than that for  $O_2$  dissociation. Therefore, at operating potentials, the dominate reduction pathway is expected to proceed through the initial reduction, in agreement with previous experimental and theoretical suggestions. [10-11] The subsequent dissociation of the  $OOH^*$  intermediate that forms to  $O^* + OH^*$  occurs with an activation barrier of less than 0.1 eV. A detailed reaction path analysis indicates that the ability of the catalyst to break the O-O bond should not directly relate to the ORR performance.

At potentials above 0.8 V, the reaction is limited by reduction of the  $OH^*$  intermediates that form on the surface. Below 0.8 V, the reaction was calculated to be limited by the initial reduction of  $O_2$  to form the peroxy intermediate. Through a series of calculations carried out over different pseudomorphic Pt overlayers, we defined the optimal oxygen binding energies to carry out both the initial  $O_2^*$  and subsequent  $OH^*$  and  $O^*$  reductions. This defined a series of different Pt-alloys which can meet the optimal binding energies. The results are consistent with previous reported work for  $O_2$  reduction.[12-13]

Our more recent efforts have focused on the effects of  $OH^*$  coverage on each of the elementary steps in the ORR mechanism and analyzing Pt dissolution for different Pt and Pt alloy surface structures.

### Coverage Effects

The presence of surface hydroxyl intermediates were found to significantly alter the adsorption energies for all intermediates and their reaction energies and activation barriers. We examined the influence of coverage on:  $O_2^*$  dissociation and  $O_2^*$ ,  $O^*$ ,  $OH^*$  and  $OOH^*$  reduction. The results for all of these reactions clearly show a linear relationship between the changes in the strength the initial adsorbed intermediate and the changes in their barriers for reaction. The adsorption energies for these intermediates are guided by the complex interplay between both attractive and repulsive interactions with  $OH^*$  surface intermediates which result from hydrogen bonding and lateral repulsive interactions. These interactions are functions not only of their relative distances to one another but also in their specific orientation with respect to one another as hydrogen-bonding is directional. While the activation barrier for the reduction of  $O^*$  is found to have the highest activation barrier especially at higher potentials, the coverage of  $OH^*$  can considerably reduced the barrier as a result of stabilizing the calculated transition states.

### Activation of Water and Dissolution of Pt

We have used the double reference approach to map out the surface phase diagrams for water, hydride, hydroxide, oxygen-covered surfaces, as well as solvated Pt ions and their corresponding passivated oxide over Pt(111), Pt(100), and Pt(110) and PtCo alloy surfaces in order to establish the lowest energy surface structures and the energies required to transition between one another phase to another over a range of potentials. The results have been used to show that the more coordinatively unsaturated surfaces more favorably activate water and subsequently undergo dissolution than surfaces comprised of more coordinatively saturated metal atoms. The introduction of Co appears to enhance the reactivity of Pt when Co is in the surface layer but decreases its activity when it's located below the surface.

### Simulating Electrocatalytic Kinetics

We have constructed a 3D kinetic Monte Carlo simulation algorithm that can begin to simulate the kinetics of the oxygen reduction over different sized cuboctahedral Pt particles as function of potential, temperature and reaction conditions. The simulations track the elementary molecular transformation that occur and as such can follow the changes surface coverages, the rate of water and hydrogen peroxide

production as well as the potentials at which reactions proceed. The initial simulations reveal that at potentials about 0.8 V the surface is predominantly covered with surface hydroxyl intermediates. We are beginning to extend these initial efforts to provide relevant information on particle size effects on the kinetics for ORR.

### Future Work

We are currently extending the work to other Pt-based alloys (Pt-Ni, Pt-Fe), and Pt nanoparticles. More specifically we have focused on the activation of water and its dissolution over large 201 atom Pt nanoparticles in a box of over 450 water molecules. These have been very difficult calculations as there are tremendous challenges in converging the lowest energy water structure at a given potential at the surface of the nanoparticle. An appropriate water surface structure is critical in establishing the appropriate electrochemical and electrocatalytic behavior. We will complete these studies and examine the O<sub>2</sub> reduction mechanism as a function of potential.

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