

A First Principles Analysis of the Mechanism for the Electroreduction of Oxygen over Pt

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Introduction

The commercialization of current proton exchange membrane (PEM) fuel cells is challenged by the low activity and durability of the catalysts used. The sluggish rate for the oxygen reduction reaction (ORR) at the cathode limits cell performance. Recent advances, spurred on by theoretical predictions, have illustrated that bimetallic Pt skin electrocatalysts can act to reduce the amount of Pt and improve the performance of the cathode.¹ Alloy design has been guided by Sabatier's principle. A moderate binding energy of the key reaction intermediate is thought to lead to the greatest rate as it balances the increased rate of initial reaction steps with the need to remove the reduction products from the surface. Despite the simplicity of the reactant (O₂) and product (H₂O) molecules, the mechanism for the ORR reaction in the electrocatalytic environment is not fully understood. On the right-hand side of Sabatier's maximum, the strongly bound hydroxyl species that form inhibit the rate of ORR. The rate of the O₂ dissociation is often cited as the step which controls the left hand side of the Sabatier curve. Metals that bind oxygen stronger have lower activation barriers for this step. The first reduction of O₂ to form OOH, however, is thought to be the rate limiting over Pt, whereas the subsequent dissociation of OOH is thought to be very fast.² Despite the success in alloying, the mechanistic factors that control the performance are still openly debated in the literature. Ab initio quantum-chemical methods provide a useful framework for analyzing the reaction energy profiles for complex reaction networks. The complexity of the electrochemical environment, however, has historically limited the application of first principle methods in elucidating the mechanistic pathways that control electrocatalytic systems. Herein, we employ a recently developed, first-principles approach that can explicitly consider the influence of the complex solution phase environment as well as the electrochemical potential on electrocatalytic reaction systems.⁴ The potential-dependent reaction energies and activation barriers for a detailed sequence of elementary steps that comprise different speculated ORR mechanisms are examined here in detail over Pt and Pt₃Co alloy surfaces

Methods

Periodic gradient-corrected density functional theoretical calculations³ were used herein to follow the catalytic reaction pathways and calculate the corresponding energies for the oxygen reduction reaction over Pt(111) and Pt₃Co(111) substrates. The double-reference method, in which charges are added to the unit cell to simulate the electrochemical double-layer, was used to determine the dependence of elementary step reaction energies and activation barriers on the operating cathode potential.⁴

Results and Discussion

The activation barrier for the first reduction step, O_{2, ads} + H⁺_{aqueous} + e⁻ → OOH_{ads}, was determined as a function of electrode potential. Within the confines of the electrolyte structure

and pH considered, this step proceeds through an initial electron transfer followed by the activated transport of the resulting proton through the double-layer region to form the surface OOH intermediate. The calculated transition state is shown below in Fig. 1A. The activation barrier was found to be strongly dependent on potential as is shown in Fig. 1B. At the potentials of interest, however, the barrier is approximately equal to the reaction energy.

At a potential of 1.2 V-NHE, the first reduction barrier (0.7 eV) is close to that calculated for O₂ dissociation (0.77 eV).⁵ However, the reaction energy, and likely the activation barrier, for O₂ dissociation are not strong functions of electrode potential. At 0.8 V-NHE, the barrier to the first reduction step (0.3 eV) was found to be substantially lower than that for O₂ dissociation. Therefore, at operating potentials, the dominate reduction pathway may be expected to proceed through the initial reduction, in agreement with previous calculations on small clusters.² The subsequent dissociation of the OOH* intermediate to O* + OH* occurs with a small activation barrier. 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.

The reaction energy of the initial reduction step is a key factor in dictating catalyst performance, however, consideration of a series of alloy catalysts indicates that this reaction

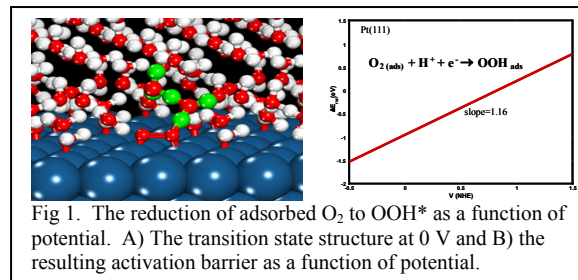


Fig 1. The reduction of adsorbed O₂ to OOH* as a function of potential. A) The transition state structure at 0 V and B) the resulting activation barrier as a function of potential.

does not become more exothermic on surfaces that more strongly bind atomic oxygen. Therefore, this step does not govern the rate or control left-hand side of Sabatier's curve. The results suggest that the initial adsorption of molecular oxygen, in which stronger adsorption correlates directly with binding of oxygen on the surface, may represent the other key factor dictating electrode performance. Stronger O₂ binding should lead to higher reactant coverages and therefore a greater reduction current. Additional analysis of the potential dependence of the reaction energies for the elementary steps of the oxygen reduction reaction provides insight into features that control H₂O₂ formation as well.

Significance

The results presented herein provide the first complete analysis of the potential dependence of the reaction energetics of O₂ electro-reduction over Pt(111). This provides essential insight into the mechanistic factors that dictate the performance of ORR cathodes for use PEM fuel cells.

References

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