

A First-Principles Approach for Quantification of Potential-Dependent Adsorbate Interactions: Application to Water Discharge Mechanism on Platinum(111)

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Slow electrochemical reactions (ECR) at the cathode of PEM fuel cells are known to cause substantial potential losses. These ECR are typically catalyzed by nanometer-size platinum particles, and involve a number of surface species possibly involving adspecies interactions [1-2]. The inability of the mean-field approach to describe such systems accurately has been discussed widely in the literature, and dynamic Monte Carlo (DMC) simulations have been the favored choice instead [3-7].

One of the main bottlenecks in the application of the DMC method to PEM fuel cell electrochemistry has been the unavailability of rate parameters, especially for ECR. Recent applications of *ab-initio* and DFT calculations combined with efficient optimization algorithms have led to a remarkable headway, and reasonable estimates for chemical kinetics rate parameters are becoming increasingly available [8-9].

In this work we present DMC simulations of a linear sweep voltammetry experiment for an oxygen-free rotating disc Pt(111) electrode in 0.1 HClO₄ solution. We use activation and interaction energies obtained from quantum simulations to elucidate the coverage of Pt(111) surface by adsorbates, especially OH. At first, data for reaction kinetics for chemical and electrochemical reactions are obtained using quantum simulations. Subsequently, the competitive reaction dynamics are simulated using DMC simulations. This attempt of a first-principles based simulation of the water discharge reaction on platinum is a necessary step in the validation of a detailed reaction mechanism of the oxygen reduction reaction on platinum. It will also shed some light on the importance of the individual elementary reaction steps and the details of interactions of the individual adspecies.

The results of the simulations are in excellent agreement with the measured data of Wang *et al.* [2]. In agreement with the findings of Wang *et al.* [2], we find that interactions among adsorbates are of paramount importance in correctly describing the catalyst surface coverage. In the low overpotential region of about 0.9 V w.r.t. standard hydrogen electrode, the surface coverage by OH is approximately 0.4 monolayer and that by O is about 0.05 monolayer. The coverage with adsorbates decreases with decreasing potential. At about 0.7 V, the OH coverage is reduced to 0.1 monolayer, while O coverage is negligible. OH coverage becomes very small at approximately 0.6 V, below which the surface is clean. These results are consistent with previous experimental findings [2].

Our simulations also suggest that even though OH predominantly covers the surface, adsorbate interaction contributions from both O and OH are crucial for describing the complete picture. Specifically, OH-OH interactions are significant above 0.7 V, and O-OH interactions become important above 0.8 V.

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