# Adlayer Structure on Pt(111): A First-Principles Study of the Water Discharge Mechanism

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A combination of Density Functional Theory (DFT) calculations and Dynamic Monte Carlo (DMC) simulations was employed to study the process of O-containing adsorbates formed from the electrochemical discharge of water on Pt(111) in acidic environment. Potential-dependent activation energy and rate-coefficients, as input for DMC simulations, were obtained for the electrochemical reactions $H_2O_{ads} \Leftrightarrow OH_{ads} + H^+_{aq} + e^-$ and $OH_{ads} \Leftrightarrow O_{ads} + H^+_{aq} + e^-$ using DFT calculations. From DMC simulations, we find that OH is the dominant adsorbate between 0.5 and 0.8 V, but above 0.8 V OH and O co-exist (Figure 1). Ordered structures are found for OH at 0.8 V, and for O at 0.9 V [1].
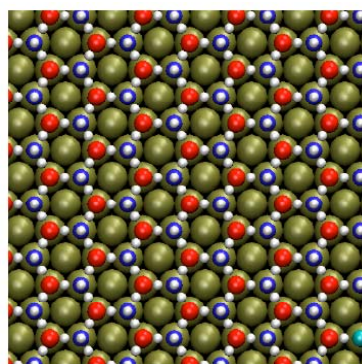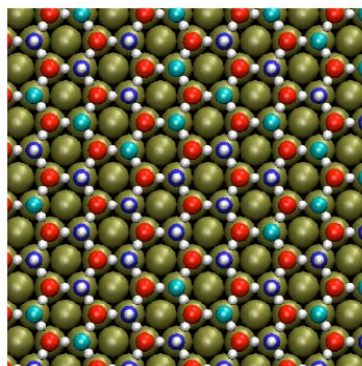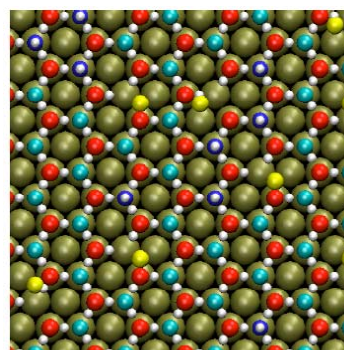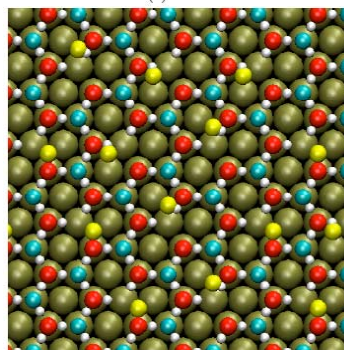

(c) 0.8 V

(d) 0.9 V

Figure 1: Snapshots of the adsorbate layer at different electrode potentials obtained from a combination of DFT and DMC simulations. Atoms: Pt (Gold), H (White), O in H_2O(parallel) (Red), O in H_2O(vertical) (Blue), O in OH (Cyan), and atomic O at the fcc site (Yellow). High coverage by O and OH at higher potentials (snapshots c and d) significantly reduces the performance of PEM fuel cells by rendering catalyst sites inaccessible to oxygen (O_2).

References:

[1] V. Rai, M. Aryanpour, and H. Pitsch, Accepted for publication in *J. Phys. Chem. C*, April 2008

(a) 0.5 V

(b) 0.7 V