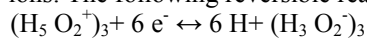


Oxidation of H<sub>2</sub> on Pt(111) and the reaction with CO

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Single crystal electrodes exhibit a rich variety of phase transitions, which are experimentally seen as sharp peaks in voltammograms. These features give invaluable information about the structure and reactions occurring at the interface. A robust theory that provides quantitative understanding of these 'discreteness of charge' effects is the Sticky Site Model (SSM) {1,2,3}. In this theory the full 3-dimensional electrode problem is transformed to a 1-dimensional flat electrode problem coupled to a 2-dimensional lattice problem. The parameters that control the electrode transitions are the adsorbate's effective density (fugacity) and the mean field pair interaction. The water fugacity is a function of its orientation. In this theory the shift in the transition potential and the charge of the adsorbate {4} are directly related. Recent experiments by Climent et al {5} (figure 1) show very clearly that the shift of the sharp spike corresponds to a charge of  $1.0 \pm 0.02$  units.

The bisulfate ion has a large dipole moment and is strongly adsorbed on the positive electrode. Due to the large field gradients at the electrode interface, the oxygen atoms of the adsorbed water molecules point down and bind to the on-top positions of the platinum substrate. As the electrode becomes more negative the field gradient changes direction and the water dipoles gradually reverse their orientation. The calculation of the orientation of water was done using new analytical results for liquid water/ionic solutions {6,7}. We assume now that the point in which half of the waters are oriented each way is the point of zero charge. This means that we neglect the influence of the bisulfate on the orientation of the adsorbed water. For negative potentials the stable structure has one of the hydrogen atoms of the water pointing down, and the hydrogen is in the hollow site of the Pt lattice. In order to satisfy the stoichiometry of the hydrogen bonds, we need to adsorb 1/3 of the surface sites of H<sup>+</sup> ions. The following reversible reaction occurs



For the (111) surface of Platinum, and because of the geometrical match-up (the Pt-Pt distance is 2.77 Å, and the water diameter is 2.76 Å) this reaction occurs as a first order transition, visible in the voltammogram as a sharp peak. High accuracy quantum calculations on a 5 layer platinum metal slab show that this compound is stable in the absence of bisulfate ions {5}.

Figures 2 and 3 show the reaction which occurs at the hollow site of the platinum surface. When this position is blocked by CO no reaction can occur. With the turning point of water at the point of zero charge our theory agrees well with the experiments of Clavilier et al {8}.

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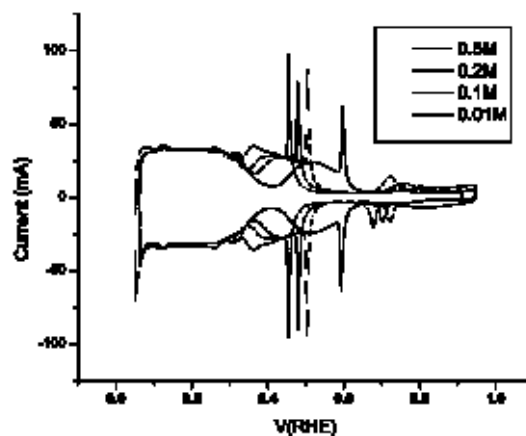


Figure 1 Concentration dependence of transition {5}.

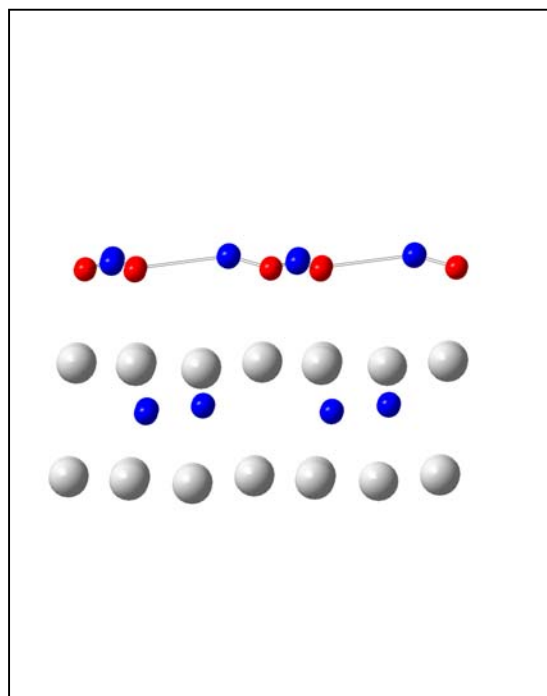


Figure 2 Side view of hydrogen electroreduction compound.

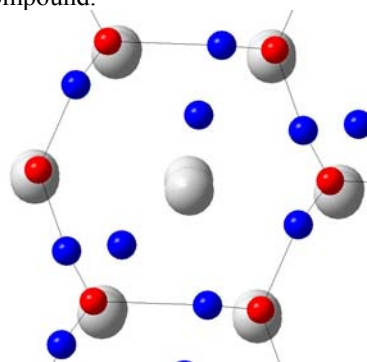


Figure 3 Top view of hydrogen electroreduction compound.

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