CO Poisoning of the $H/Pt(111)$ Reaction

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Abstract

The redox reaction of hydrogen on platinum electrodes is important to fuel cell technology. One of the big problems is the CO poisoning of the Pt-Hydrogen oxidation reaction. We have recently proposed a mechanism for this reaction [1] that clearly suggests how the CO blocks this reaction. The central feature of our theory is the formation of a 2 dimensional 'ice' hydrogen bonded phase, from a phase transformation that requires the rotation or flipping of the water molecules adjacent to the Pt electrode. The details of this transformation are discussed in this reference and in previous work cited therein.

For negative potentials the stable structure has one of the hydrogen atoms of the water pointing down, which is the hollow site of the Pt(111) lattice. This is a true two dimensional 'ice'. To satisfy the stoichiometry of the hydrogen bonds, we adsorb 1/3 of the surface sites of H^+ ions, which is the origin of the sharp spike seen in the voltammogram. The charge of the adsorbed moeity is found to be 1.02 ± 0.02 from the concentration dependence of the position of the spike. The reaction, which is perfectly reversible in the absence of CO, is

$$(H_5O_2^+)_3 + 6e^- \rightleftharpoons 6H + (H_3O_2^-)_3$$

The exact position of the flipping potential (the place were 50% of the water molecule have turned[1]) depends work function of the metal surface, the hydrogen bonding, and the bisulfate-ad-water interacion, and of course, all of them in solvated form. This is a very complex problem, and it is impossible to calculate the flipping point from first principles. Besides, that the contribution of the turning of the water dipoles to the current is small. In our previous paper this was used to adjust the small hump seen at around 0.8 V in the voltammogram. A more physically reasonable choice is to take it at the point of zero charge (pzc). And a sensible assignement is to take the flipping point equal to the position of the sharp spike of the voltammogram. The results are shown in figure 1.

Very acurate quantum calculations [1] show that the hydrogen atoms in the hollow positions are neutralized. Since there are 2/3 of the Pt sites in the hollow positions, our model gives a natural explanation to the well known fact that the hydrogen yield is 2/3 on this surface. The new revised turning point renders our theory completely consistent with the CO displacement experiments of Clavilier et al [2]. In our theory we do not have 'unusual' or UPD hydrogen, which is unlikely to exist on the surface of platinum, as shown by a recent calculation [3].

The adsorption of CO on Pt, and the exact structure has been controversial at best (see for example ref [4]). There is no clear concensus if the CO goes to the on top, bridge or hollow positions. Recent ex-situ experiments [5] seem to indicate part bridge and part hollow. Our model clearly indicates that in an active electrode it should be the hollow position.

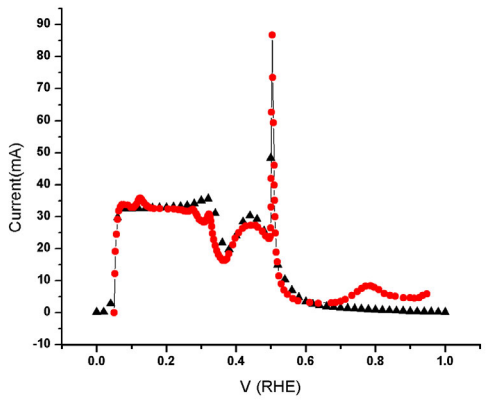

Figure 1

Comparison of the theory with flipping point 0.5 V (=PZC)to experiment for the system $H_2/Pt(111)/H_2SO_4(0.1M)$. Circles are the experiment, and triangles are the theory. Experiment is by V. Climent ([6]). Scanning rate was 50 mV/sec.

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