The Electroreduction of Hydrogen on Pt(111)

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In previous work [1,2]a new theory for the redox of hydrogen in acidic media was discussed. The essential point is that water flips as the potential changes from positive to negative, and that if the water units are all coplanar, the hydrogen bond $O-H-O$ angle is bent from 180°: For positive electrodes the dipole of the water points down, the oxygen binds to the on-top position of the Pt lattice, and a zig-zag chain of hydrogen bonded water is formed which is responsible for the $\sqrt{3} \otimes \sqrt{7}$ phase observed by STM . For negative polarization the water dipole points up. A transition occurs in which a intermediate compound of $(O_2H_5^+)_3$ of honeycomb, $\sqrt{3} \otimes \sqrt{3}$ structure is formed . In the presence of bisulfate, or of bisulfate/perchlorate mixtures, this compound is formed through a first order phase transition. In the absence of bisulfate the same compound is formed, but in a gradual way.As the electrode turns more negative the anions are desorbed and the following reaction takes place

$$(H_3O_5^+) + Pt^-(sol) \Rightarrow H_2(g) + H_2O + HO^- + Pt^+(sol)$$

for the honeycomb sites, which are exactly 2/3 of the available sites of the Pt(111) electrode.

The model is consistent with all known experiments: It reproduces well the experimental voltammogram and the recent radiotracer measurements of bisulfate adsorption. Furthermore it gives a robust explanation of the 2/3 hydrogen yield for this surface. We perform quantum-mechanical simulations on this model, using a recent extension of the Car-Parrinello algorithm developed by two of us (ensemble density-functional theory) [3] that allows the treatment of the same ground metallic systems that do not have a gap in the electronic excitation spectrum. For technical reasons neutral systems are required. For that reason we study the reaction

$$(H_3O_5) + Pt (sol) \Rightarrow H_2(g) + H_2O + HO^- + Pt^+(sol)$$

to mimic the gradual discharge of the honeycomb compound from about 0.3 V to 0.0V(RHE). The fully relaxed structure forms a honeycomb compound $(O_2H_3^-)_3$, which is stable for alkaline solutions, while the H is either sucked up by the Platinum in the hollow positions or released as H_2 gas, depending on the initial conditions of the calc high structural and thermodynamic accuracy with favorable scaling in the system size. We use periodic-boundary conditions, together with a fine sampling of the reciprocal space Brillouin zone, and accurate smearing methods to deal with the discontinuities introduced by the existence of a Fermi surface for the metal. The ions are described via ultrasoft (Vanderbilt) pseudopotentials, allowing for a manageable number of elements in our plane-wave basis set.

References

[1] L. Blum and D. A. Huckaby, Los Alamos preprint chem-ph/0105051/xxx.lanl.gov.(2001), ChemWeb preprint physchem/0106005 (2001).
[2] L. Blum and D. A. Huckaby, Mol. Phys. (in press)(2001)
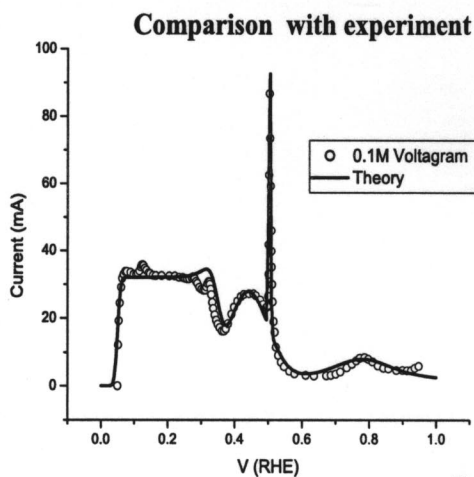[3] N. Marzari and R. Car, to be published

Comparison with experiment

Figure x