The Electroreduction of Hydrogen on Pt(111)

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ABSTRACT

The electroreduction of hydrogen on Pt(111) in acidic media is the primary fuel cell reaction. The explicit mechanism for this process involves a first order phase transition, which is due to the rotation of the water dipole as the electric field is changed. For positive electrodes the water forms linear 'polywater' chains that run between the adsorbed bisulfate ions. This phase is seen by STM experiments. When the electrode turns negative, then a honeycomb structure is formed by the reaction

$$H_3 O^+ + H_2 O = H_5 O_2^+ \tag{1}$$

The structure of this intermediate compound is studied using high accuracy generalized gradient PW91 calculations for a 5 layer Pt slab

Keywords: fuel cells, generalized gradient PW91, Density Funtional, electrode processes, surface reactions.

1   INTRODUCTION

The reduction of hydrogen in the presence of bisulfate on platinum electrodes is of interest because its close relation to fuel cells technology. It was first studied by Clavilier[1,2], and the current-voltage curve (the voltammogram), shown in fig.1, comprises three distinct regions. In previous work we developed a structural theory to explain this reaction [3,4].

1. The H-UPD region, which except for small features is relatively flat and featureless. Our model is that as the electrode becomes more negative the HER compound, $(H_5O_2^+)$ discharges

$$(H_5O_2^+) + 2\ e = H_2 + H_2O + HO^- \tag{2}$$
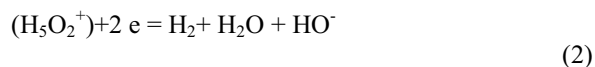
We will discuss below the results of detailed first principles electronic structure calculations

2. The CP('Clavillier papillon') butterfly region: Here there are two distinct features, a sharp spike and a bulge. The spike corresponds to a first order phase transition due to the co-adsorption of bisulfate and water, forming a honeycomb structure of three units of the HER compound, formed by the reaction

$$H_3O^+ + H_2O = H_5O_2^+ \tag{3}$$

The bulge corresponds to the desorption of the sulfate by a simple Langmuir process.
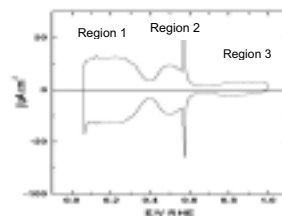
Electroreduction of hydrogen on Pt(111)
in the presence of 0.1M sulfuric acid.

Figure 1 Voltammogram Courtesy of V. Climent.

3.The positive region: In this region the $\sqrt{3} \times \sqrt{7}$ structure is observed by STM [5-8]. We explain this structure by a one dimensional water chain, which sits between adsorbed bisulfate ions. For positive electrodes, its lone pair to the on top position of the platinum adsorbs the water. As the electrode becomes more negative the water molecule has to flip, and therefore it will be adsorbed at the hollow position of the (111) surface.
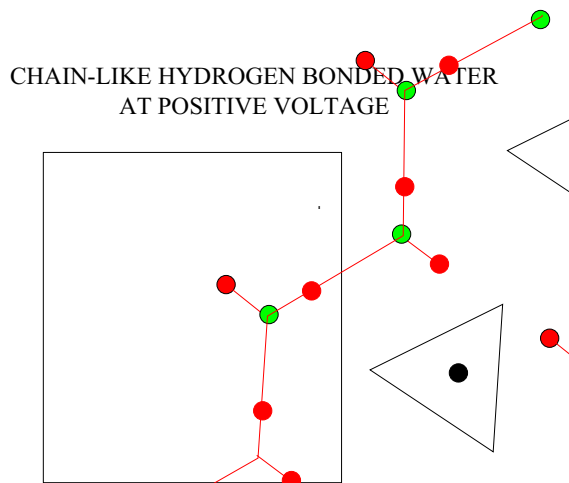
CHAIN-LIKE HYDROGEN BONDED WATER
AT POSITIVE VOLTAGE

Figure 2 Model of the $\sqrt{3} \times \sqrt{7}$-bisulfate water co adsorption compound. The triangles represent the bisulfate ion.

In our theory the hydrogen evolution reaction intermediate (HER) ($H_5O_2^+$) ion, which is formed at the electrode surface. For the (111) face of platinum this compound is very closely commensurate with the platinum lattice distance of 2.77 Å and forms, for negative electrode polarization, a commensurate honeycomb structure. For positive electrodes only water is adsorbed, but because of its polarization no ordered two-dimensional adlayers can be formed, only one-dimensional chains are allowed. In the presence of (bi) sulfate ions these chains are stretched and result in the $\sqrt{3} \times \sqrt{7}$ structures observed by STM.

Sulfate +Water+Hydronium Co-adsorption
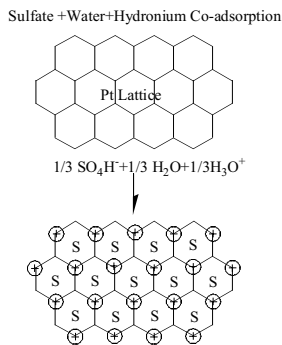
Pt Lattice

$1/3\ SO_4H+1/3\ H_2O+1/3H_3O^+$

Figure 3 Model of the HER honeycomb compound as it is formed by co-adsorbed bisulfate ions.

The water molecule is reoriented as the potential is changed. At negative potentials water turns so that its dipole points towards the Pt. Then the hydrogen will point towards the platinum and the preferred adsorption should be on the hollow site. It will form a regular honeycomb network of hydrogen-bonded molecules, with the sulfate at the center of the hexagons, as shown in figure 3. As the bisulfate is desorbed it will leave leaving the honeycomb HER structure behind. Our model thus provides an

explanation of the well known fact that only 2/3 of the platinum atoms are active in the reduction of the hydrogen.
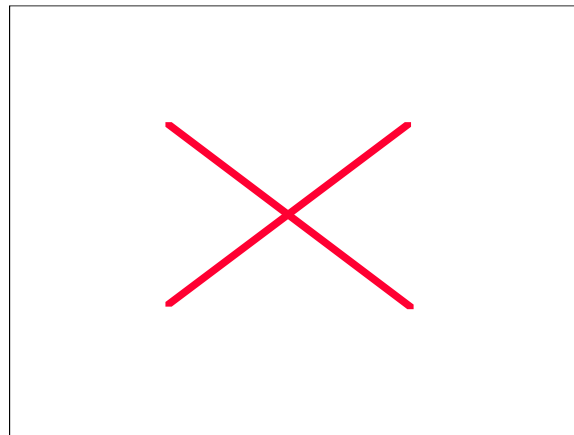

Figure 4 Theoretical explanation of the voltammogram in terms of the HER complex formation

The agreement of this simple model with the experimental voltammogram of V. Climent [9] is excellent, considering that there are very few adjustable parameters. Details of the theory can be found in the paper by Blum and Huckaby [3,4]. This model also has the correct proton concentration dependence and predicts also the correct patterns of rows with 120 degrees kinks for low sulfate concentration.

2 QUANTUM CALCULATIONS

. We perform quantum-mechanical simulations on this model, using the generalized gradient approximation PW91 [10], as implemented in the PWSCF package of Baroni et. Al [11], as well a recent extension of the Car-Parrinello algorithm to ensemble density-functional theory developed by two of us [12]. For technical reasons neutral systems are required. For that reason we study the reaction
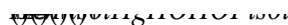
$$\tag{4}$$

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 , which is stable for alkaline solutions, while the H is either sucked up by the Platinum in the hollow positions or released as (gas), depending on the initial conditions of the calculation. The resulting structure is shown in the figures 5-7. In our simulations, the electronic ground state is calculated using density functional-theory together with the generalized-gradient approximation to the exchange-correlation energy functional: this combines the merit of 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)[13] pseudopotentials, allowing for a manageable number of elements in our plane-wave basis set.

In spite of the fact that the calculation is done in the absence of electric field and electrolytes, it is clear that the final state of the model corresponds to 0.0 Volts in either Fig. 1 or 4. It is also clear that in an acidic solution the OH⁻ produced in reaction (4) will be neutralized. Keeping these facts in mind we can analyze the results of the calculations.

In figures 5 and 6 we show the results for a calculation in which the initial configuration was that of the HER, in which the hydrogen of the water is placed in the hollow position of the Pt (111) surface, and consequently the oxygen is also in that position. As the system relaxes the platinum leaving behind a quite planar hexagonal honeycomb structure, which is displayed in Fig 5, basically sucks up the hydrogens. What is very interesting is that while the hydrogen is detached from the oxygen, the most favorable adsorption position for the oxygen is on top of the platinum. As we can see it in figure 6, the hydrogens are well separated from the oxygens but are not exactly below the oxygens.

Another interesting fact is that the HER complex is nearly perfectly planar, which confirms our initial assumptions on the formation of an ordered lattice.

When the initial configuration has the hydrogen pointing upwards (Figure 7), then the final state consists of the same HER ring as in our previous case, but then the hydrogen forms molecular H2 which is what is seen experimentally at 0.0 volts.

Finally, the charge density profile for the final state is shown in Figure 8. A preliminary calculation of the potential profile shows that in the final state the surface Platinum layer is negative with respect of the water layer, which is in general agreement with experiment
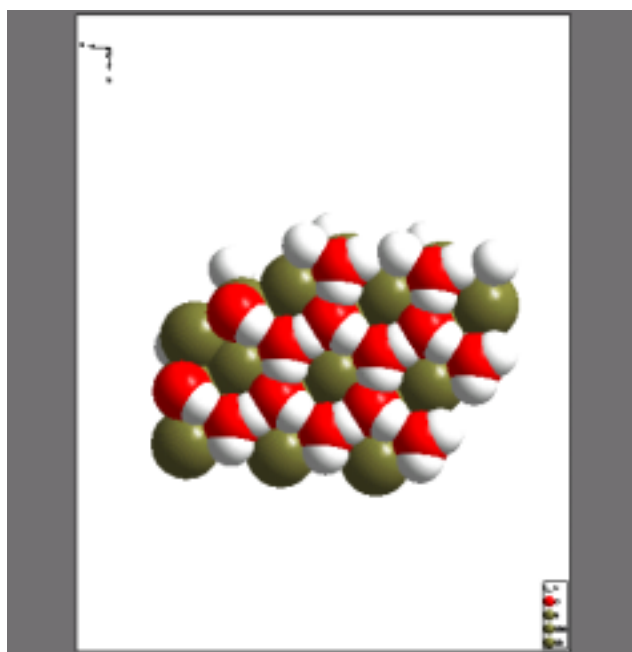

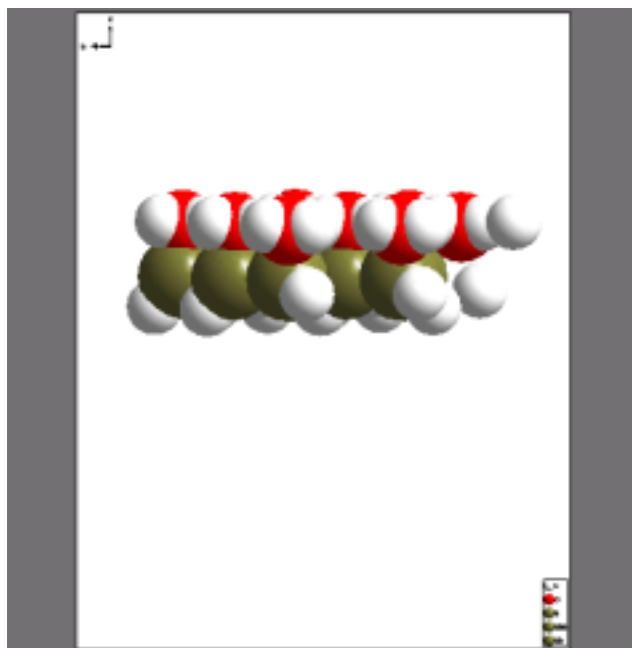Figure 5 HER honeycomb compound viewed from above

Figure 6 HER honeycomb compound with the hydrogen below viewed from the side.
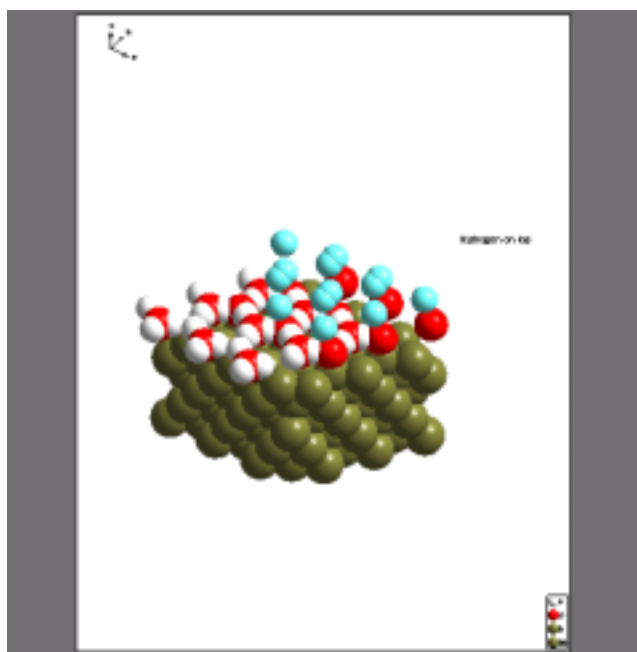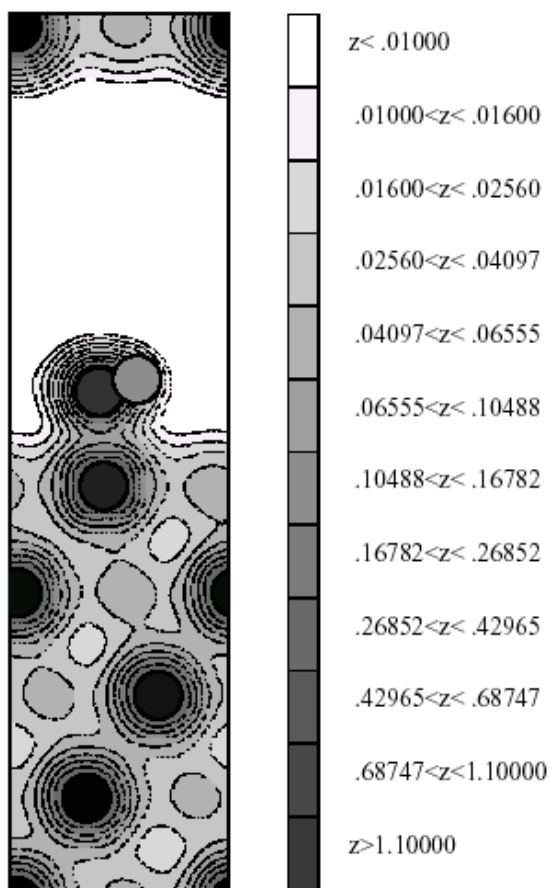
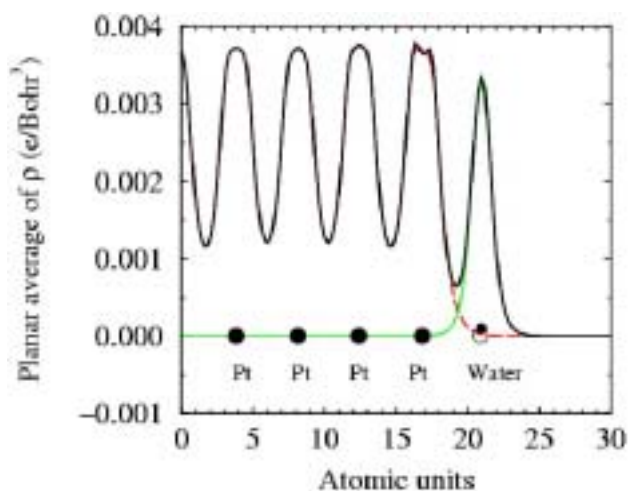Figure 7 HER honeycomb with hydrogen evolution

Figure 9: Average electron density profile

REFERENCES

[1] Clavilier, J., Faure, R., Guinet,G., and Durand,R. , J. Electroanal. Chem. 107, 205,1908.
[2] Clavilier, J, 1980, J. Electroanal. Chem., 107, 211, 1980.
[3] L. Blum and D. A. Huckaby, Los Alamos preprint chem-ph/0105051/xxx.lanl.gov.,2001, ChemWeb preprint physchem/0106005, 2001.
[4] L. Blum and D. A. Huckaby, Mol. Phys. (in press) ,2001.
[5] Futnikov, A.M., Linke, U., Stimming, U., and Vogel, R., Surf. Sci. , , 324, , L343,1995.
[6] Wan, L.J., Yau, S. L., and Itaya, K, J. Phys. Chem., 99, 9507., 1995.
[7] Wan, L.J., Suzuki, T., Sashikata, K., Okada, J., Inukai, J., and Itaya, K., J. Electroanal. Chem., , 461, 26,2000.
[8] Kim,J. G., Soriaga, J. B., Vigh, G. and Soriaga, M. P., J. Coll. Interf. Sci., , 15, 26, 2000,
[9] V. Climent, personal communication.
[10] Perdew, J. P. In Electronic Structures of Solids '91; Ziesche, P., Eschrig, H., Eds.; Akademie Verlag: Berlin, 1991, p 11].).
[11] PWSCF package, S. Baroni, A. Dal Corso, S. de Gironcoli, and P. Giannozzi, http://www.pwscf.org.
[12] N. Marzari and R. Car, in preparation.
[13] D. Vanderbilt,Phys. Revs. B, 32, 8412,(1985).

Figure 8 Charge density in atomic units