

The mechanism of the H/Pt(111) fuel cell
 L. Blum,¹ D.A. Huckaby,² N. Marzari³ and R. Car⁴
¹University of Puerto Rico
 Physics Dept. POB 23343, Rio Piedras, PR, 00931
²Texas Christian University
 Chemistry Dept., Fort Worth, TX 76129
³MIT
 Dept. of Materials Science, MIT, Cambridge MA 02138
⁴Princeton University
 Dept. of Chemistry, Princeton University, Princeton N.J.
 08544

We propose a new mechanism for the electroreduction of hydrogen in acidic media. The specific model and theoretical calculations are designed for the Pt(111) surface [1,2], because this is the only face that exhibits a clear first order phase transition. The basic mechanism however, applies to the other faces of Pt as well. The principal ingredient of our theory is the assumption that the water molecules in the inner Helmholtz layer are strongly oriented by the field. This means that hydrogen bonds have to be bent considerably. An appropriate water model has to be tetrahedral and flexible. Then, as the polarity of the electrode is changed:

- (a) For positive electrodes most of water the dipoles point down, and a zig-zag chain of hydrogen bonded water is formed which is responsible for the elongated hexagon structure of the sulfate observed by STM. This structure is either $\sqrt{3} \times \sqrt{7}R$ or more likely $\sqrt{3} \times \frac{5}{2}R$.
- (b) For negative polarization most of the water dipoles point up. The (bi)sulfate, and the water form a periodic structure by incorporating 1/3 of hydronium, which then is adsorbed with a hydrogen down in the hollow sites of the Pt(111) electrode. This compound is neutral and forms a two dimensional honeycomb arrangement of water with bisulfate ions.
- (c) When the electrode turns more negative, then the bisulfate is desorbed, but the honeycomb structure remains because of the reaction



This reaction is studied by a high accuracy generalized gradient PW91 calculation for a 5 layer Pt slab. The HER or intermediate reaction compound $(H_3O_2^-)_3$ is stable on the Pt(111) face. The model is consistent with all known experiments: It reproduces well the experimental voltammogram [3] and the recent radiotracer measurements of bisulfate adsorption [4]. Furthermore it gives a robust explanation of the 2/3 hydrogen yield for this surface. The implications of this model to the kinetics and the use of alkaline cells is also discussed.

References

1. L. Blum and D. A. Huckaby, 2002, Mol. Phys., 100, 2911.
2. L. Blum, D. A. Huckaby, N. Marzari, and R. Car, 2003, J. Electroanal. Chem. In Press.
3. Climent, V., E. Herrero, Orts, J.M., Feliu, J.M., and Aldaz, A., unpublished
4. Kolics, A. and Wieckowsky, A., 2001, J. Phys. Chem., 103B, 3556.