

Theory for the Electroreduction of Hydrogen on Pt(111)

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The electroreduction of H ions to molecular hydrogen on Pt(111) electrode surfaces in the presence of acids is an interesting process because of its potential applications (to fuel cells) and because of the increasing amount of experimental information that is available for this system. It is known that for positive polarization of the electrode surface in the presence of sulfuric acid an ordered phase with $1/5$ coverage and a $\sqrt{3} \cdot \sqrt{7}$ structure (elongated hexagons, seen by STM) is formed. When the polarization changes to positive the electrochemistry (the voltammogram, which is a derivative of the charge adsorption isotherm) clearly indicates that a $\sqrt{3} \cdot \sqrt{3}$ structure must exist, since the yield of molecular hydrogen is almost exactly $2/3$, which corresponds to regular hexagons.

We discuss a model that explains both phases and the transition between them using the well known hypothesis of N.F.Mott and J. Watts-Tobin [1] that because of its large dipole moment the water is oriented with the oxygen down for positive electrodes and with the hydrogen down for negative polarizations. In our model water forms hydrogen bonded networks in both cases.

We propose a new structure for the HER intermediate. The requirements on the potential model for the water model are:

- 1) It must be of tetrahedral coordination.
- 2) It must be analytical to be able to include the double layer effects, ions and external fields, in the calculations.
- 3) The angular part of the potential must be relatively soft, since the angle O-H-O of the hydrogen bond is not necessarily π in our case[2].

The analytical tetrahedral Yukagawa model of water [3] satisfies all of these requirements

References

[1] N.F. Mott and J. Watts-Tobin, *Electrochim. Acta* **4** 79 (1961).

[2] R. Chidambaram, *Acta Cryst.* **14** 467 (1961).

[3] L. Blum, F. Vericat and L. Degreve, *Physica A* **265**,396 (1999)