Recent results on the H/Pt(111) fuel cell

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We have recently proposed a [1,2] theory for the hydrogen/Pt(111)fuel cell reaction. In this theory water flips as the potential changes. When the electrode is positive then the lone pair points towards the platinum: the oxygen binds to the on-top position of the Pt lattice, and a one dimensional chain of hydrogen bonded water is formed. This chain intercalates between rows of adsorbed bisulfate ions, which are responsible for the elongated hexagon structures seen by STM[3,4]. Our first observation is that for the same bisulfate coverage of 1/5 two structures are possible: 1) either$\sqrt{3} \times \sqrt{7}R71^o$ or more likely $\sqrt{3} \times \frac{5}{2}R90^o$ While the coverage is exactly the same for both alternatives (1/5),the spacing of the bisulfates is 2.64 Å. for structure 1 while it is 2.5 Å. for structure 2.

The sharp peak of the Climent [5]voltammogram corresponds to the electro-sorption of the hydronium: This fact is confirmed by comparing the concentration dependences [6]of the peak position for pure bisulfate[5] and a bisulfate/per-chlorate mixture[7]. The analysis [6] of two experiments involving sulfate and per- chlorate shows a strikingly linear transition voltage/concentration graph, that depends not on the anions, but on the hydrogen concentration. The 'experimental' electrovalence of the adsorbed moiety is $\nu = 1.0 \pm 0.1$. A detailed discussion of the expertiments for bisulfate and perchlorate will be given.

As the electrode turns more negative the anions are desorbed and the following reaction takes place

$$(H_5O_2^+)_3 + 6e^- \rightarrow 3H_2 + (H_3O_2^-)_3 \tag{1}$$

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.

More recent calculations for the positive branch involving bisulfate will be analyzed.

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