

Predicting Tafel Plots for Hydrogen Oxidation on Pt(100) Electrodes

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INTRODUCTION

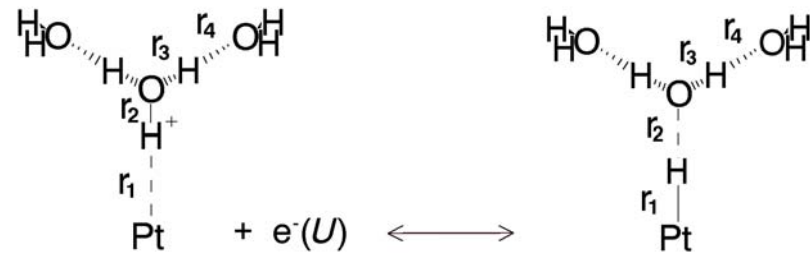
An understanding of hydrogen oxidation platinum electrodes is of interest. Markovic and coworkers have proposed that the Volmer Heyrovsky (V-H) mechanism takes place on Pt(100) electrode surfaces in acid.

We have carried out theoretical modeling using *ab initio* quantum mechanics of the two one-electron steps for this mechanism and obtain electrode potential-dependent electron transfer activation energies that are used to predict the Tafel plot for H₂ oxidation.

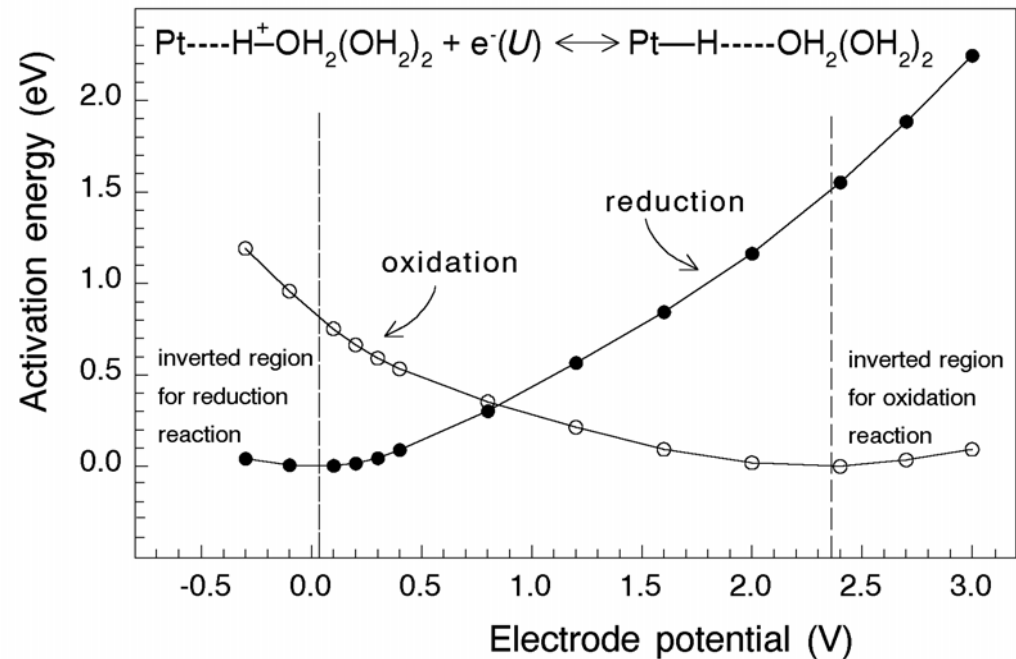
The agreement of the theoretically predicted Tafel plot with the experimental one supports the assignment of the V-H mechanism for the Pt(100) surface.

First step: Pt-H bond formation and breaking.

We have calculated the electrode potential dependence of Pt-H formation in acid. Using the surface Pt-H bond strength for low coverage results in the curves shifting left and a crossing point and onset potential for upd H formation of about 0.4 V. From Anderson *et al.* J. Phys. Chem. B107, 4618-4623 (2003).

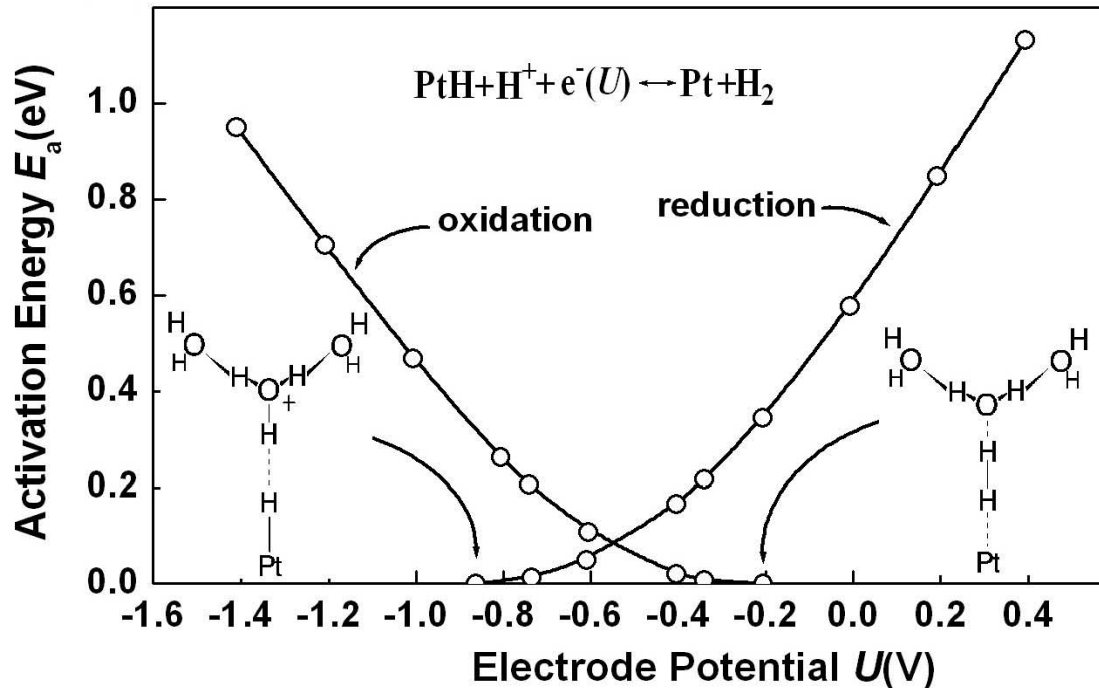


Reaction model



Results

Second step in the V-H mechanism.

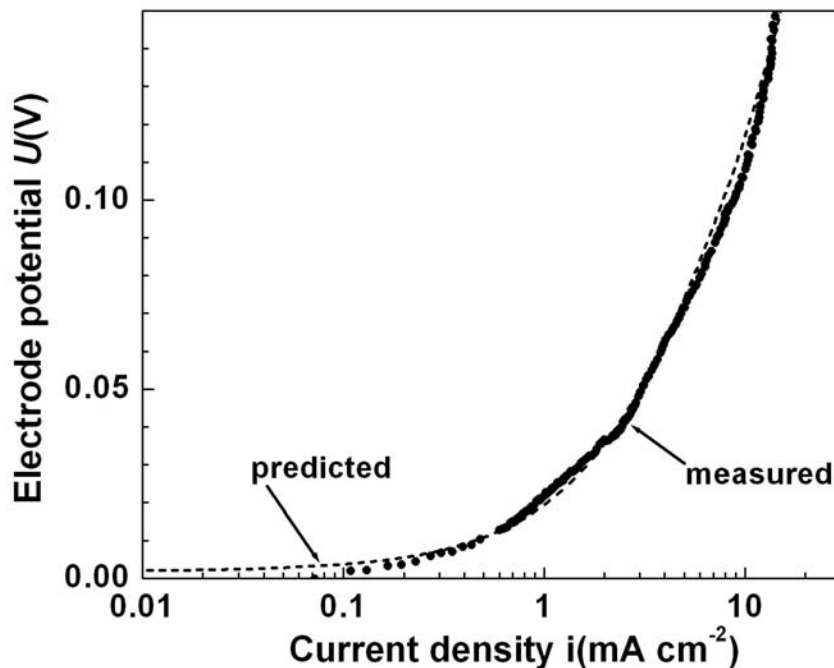


This models H_3O^+ reduction on a saturated surface. Use of experimental high coverage Pt-H bond strengths will shift the curves right with the crossing point i.e. reversible potential at about 0 V.

We have used the calculated activation energies for the second (V-H) step in the Butler-Volmer formula:

$$i = |i_{\text{ox}} - i_{\text{red}}| = A|\exp(-E_a^{\text{ox}}(U)/RT - \exp(-E_a^{\text{red}}(U)/RT)|$$

With the pre-exponential A set to 33, the following Tafel plot for H₂ oxidation is predicted with this formula.



The measured values of Markovic *et al.*, J. Phys. Chem. B101, 5405-5413 (1997) are for the Pt(100) surface.

CONCLUSIONS

1. The Volmer-Heyrovsky mechanism is supported by quantum theory for Pt(100) electrodes.
2. Tafel plots for Pt(111) and (110) are different (Markovic *et al.*) and the Tafel-Volmer mechanism ($2\text{H(ads)} \leftrightarrow \text{H}_2$) may apply to them.
3. The Tafel plot for H_2 oxidation up to 150 mV on the Pt(100) surface is mainly dependent on the applied potential dependencies of the activation energies and not on variations in coverage of H(ads), which evidently are small up to 150 mV.
4. Experimentally observed deviations from theoretical predictions from this model (such we have found for O_2 reduction on Pt) can be attributed to coverage-dependent activation energies and pre-exponential factors.

ACKNOWLEDGMENTS

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