

Mechanism of Electrooxidation of Water on Platinum: Quantum Chemical Theory

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The generation of OH(ads) on platinum electrodes is of interest because this is probably the primary oxidant that converts the CO(ads) poison on fuel cell anodes to CO₂. It has been assumed that OH(ads) forms by dissociation of H₂O(ads) to yield OH(ads) + H(ads). At the fuel cell anode working potential, which is > 0.4V(H₂), H(ads) would discharge into solution as H⁺(aq). However, recently estimated OH^{1,2} and H² absorption bond strengths do not appear high enough to support this proposed mechanism and so the most likely alternative, oxidative proton transfer from H₂O(ads) into solution, must be considered. By the same token, as the platinum electrode potential is increased and OH(ads) is oxidized, energetics do not favor its dissociating on the surface, so oxidative deprotonation into solution should be considered for it as well.

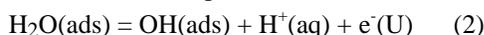
Establishing mechanisms for reactions such as these by either experimental or theoretical means is a difficult proposition. An *ab initio* quantum chemistry approach to calculating redox activation energies and transition state structures and their dependence on electrode potential has been under development recently, with applications to hydrogen evolution⁴ and oxygen reduction⁵. This approach uses a molecular model for the oxidation or reduction centers. In the case of electrooxidation, the reaction center is assumed to become ionized when thermally promoted to a structure where its ionization potential(IP) is related to the electrode potential(U) by

$$U/V = IP(\text{reaction center})/eV - 4.6 \quad (1)$$

where 4.6eV is the thermodynamic workfunction of the hydrogen electrode. For reduction, one substitutes electron affinity(EA) for IP in Eq. 1. In the past reduction work, the reactant H⁺(aq) was modeled by H-OH₂(OH₂)₂⁺.

In the oxidation work reported here the proton solvating species is the available lone-pair orbital of OH₂(OH₂)₂. In this work the effect of the counter anion charge and other ions in solution has been approximated, an advancement over the past studies. Furthermore, O-H bond lengths in the proton accepting H₂O and the hydrogen bond distances have been varied in this work, which is another departure from the previous studies.

In earlier work⁵ a reversible potential of 0.57V was calculated for the first step in H₂O(ads) oxidation:

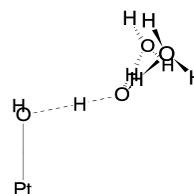


This is close to the approximately 0.6V potential where OH(ads) is thought to form in acid electrolyte. A vibrational band observed first at 0.7V on Pt(111) in 0.1M HClO₄ has been tentatively assigned to OH(ads)⁶.

The calculations include electron correlation energy corrections by means of the Moller-Plesset(MP2) perturbation theory. The 6-31G** basis set is used for H and O atoms and for Pt the Los Alamos pseudopotential

double zeta method is used. Bonds to the platinum electrode surface are modeled with a single Pt atom, which is a satisfactory approximation because the calculated Pt-OH₂, Pt-OH, Pt-H, and Pt-O bond strengths are close to the adsorption bond strengths at low coverages. The same approach was used in Ref. 5.

Using the model discussed above, at the increasing electrode potentials of 0.2V, 0.45V, and 0.7V the calculated activation energy decreases from 0.58eV to 0.26eV to 0.07eV. The value at the predicted reversible potential is 0.18eV. The transition state structure is shown in **1**.

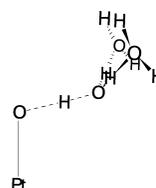


1.

A reversible potential of 1.32V was calculated⁵ for the reaction



A low activation energy is also calculated for it, with the transition state shown in **2**.



2.

From these results it is concluded that on platinum electrodes adsorbed water is oxidized by deprotonation into solution and the activation energies are low enough for OH(ads) and O(ads) formation at low coverage that their formation is under thermodynamic and not kinetic control at the reversible potentials. It is of catalytic significance that the reversible potential for OH(ads) formation will be less on surfaces where OH absorbs more strongly relative to H₂O than in the case of Pt.

Acknowledgment

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1. C. E. Mooney, L. C. Anderson, and J. H. Lunsford, *J. Phys. Chem.* **97**, 2505 (1993).
2. N. M. Markovic, T. J. Schmidt, B. N. Grgur, H. A. Gasteiger, R. J. Behm, and P. N. Ross, *J. Phys. Chem.* **B103**, 8568 (1999).
3. K. Christman, in *Electrocatalysis*, J. Lipkowski and P. N. Ross, Editors, pp. 1-42, Wiley, New York (1998).
4. A. B. Anderson and D. B. Kang, *J. Phys. Chem.* **A102**, 5399(1998).
5. A. B. Anderson and T. V. Albu, *J. Electrochem Soc.* **147**, 4299(2000).
6. T. Iwasita and X. Xia, *J. Electroanal. Chem.* **411**, 95 (1996).

