Theoretical Model for Predicting Potentials for upd H and OH(ads) Formation on Platinum in Base

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We have devised and tested quantum mechanically an interfacial model for calculating reversible potentials of surface reactions in base. Conceptually, the model parallels out previous work for surface reactions in acid.[1,2] Whereas the reactant hydronium ion in acid was satisfactorily modeled with two hydrogen-bonded "solvating" water molecules, in the present modeling in base the OH^- reactant has three water molecules hydrogen bonded to it and for satisfactory results each of these had to have a water molecule in a second "solvation shell" hydrogen bonded to it as in figure 1. This figure shows
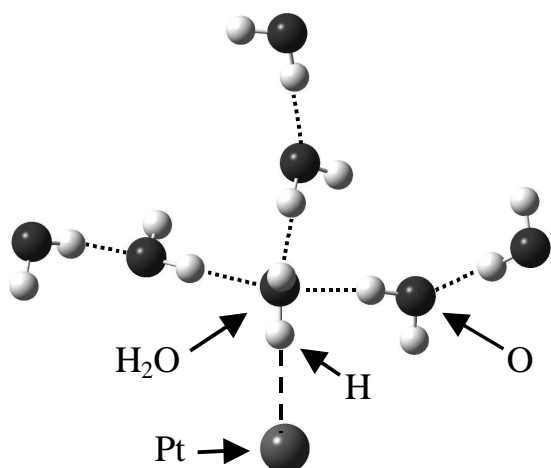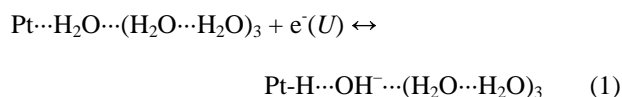

Figure 1. Precursor to upd hydrogen formation on Pt. Broken lines indicate hydrogen-bonding.

the precursor to upd H, which is a water molecule hydrogen-bonded to Pt. We have calculated the onset potential for upd H deposition using the reaction

$$Pt\cdots H_2O\cdots(H_2O\cdots H_2O)_3 + e^-(U) \leftrightarrow$$

$$Pt\text{-}H\cdots OH^-\cdots(H_2O\cdots H_2O)_3 \quad (1)$$

by finding the energy of the electron on the vacuum scale that makes Eq. 1 an equality, and subtracting this energy from the 4.6 eV thermodynamic workfunction of the standard hydrogen electrode.[3] This yields the reversible potential, U, on the standard hydrogen scale. The model also includes a Madelung term in the ab initio hamiltonian that corresponds to a sum over the ion charges in the electrolyte, assuming that they are distributed in a regular array on average. It is assumed that, since *on the standard hydrogen scale* the potential of zero charge (pzc) in 0.1 M base is about 0.15 V and the reversible potential for hydrogen evolution is -0.77 V, the formation of upd H will take place over negatively charged Pt sites to which water molecules can be only weakly hydrogen bonded. A value of 0.15 eV is calculated with the above model. We note that the calculated Pt-H bond strength overestimates the experimental value at the low-coverage corresponding to the onset of upd H, by 0.78 eV, and so when the reaction energy calculated for Eq. (1) is corrected for this

overestimate, the predicted reversible potential is -0.66 V. For Pt (111) and (110) electrodes the measured value is ~ -0.45 V,[4] which we consider to be in good agreement.

The measured onset potential for OH(ads) formation on Pt(111) and (110) electrodes is ~ -0.15 V. We calculated

$$Pt\cdots OH_2\cdots OH^-\cdots(H_2O\cdots H_2O)_3 \leftrightarrow$$

$$Pt\text{-}OH\cdots OH_2\cdots(H_2O\cdots H_2O)_3 + e^-(U^o) \quad (2)$$
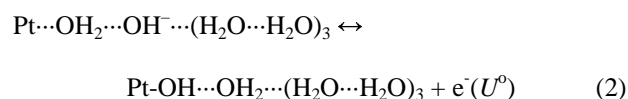
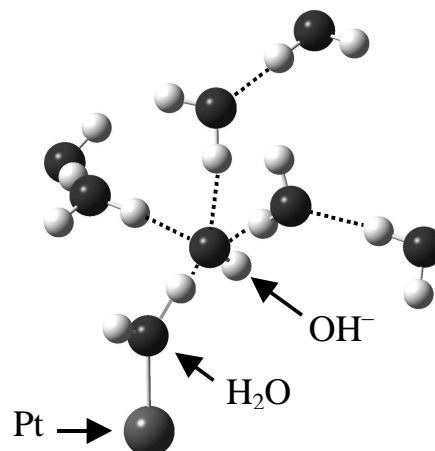as modeled in Fig. 2 and predicted $U = 0.00$ V for this

Figure 2. Precursor to OH^- oxidation and OH(ads) formation on Pt. Broken lines indicate hydrogen bonding.

reaction. This result agrees well with measurement.

A second method for predicting reversible potentials makes use of a linear relationship between reaction energies in the bulk electrolyte and the reversible potential.[5] Incorporating measured H and OH adsorption energies into the reaction energies in this approach also gives accurate predictions for forming Pt-H and Pt-OH in base. The following table summarizes all the results:

Species	onset U(V) of formation		
	interface model	bulk model	experimental[4]
Pt-H	-0.66	-0.48	-0.45
Pt-OH	0.00	-0.09	-0.15

Footnotes and references:

1. A. B. Anderson, N. M. Neshev, R. A. Sidik, and P. Shiller, Electrochim. Acta, **47**, 2999 (2002).
2. A. B. Anderson, R. A. Sidik, J. Narayanasamy, and P. Shiller, J. Phys. Chem. B, 107, 4618 (2003).
3. We used the B3LYP hybrid density functional theory in the Gaussian 03 package with the 6-31+G** basis set for H and O and an effective core potential the LANL2DZ basis set for Pt.
4. T. J. Schmidt, P. N. Ross, and N. M. Markovic, J. Electroanal. Chem. **524-525**, 252 (2002).
5. J. Narayanasamy and A. B. Anderson, J. Phys. Chem. B, 107, 6898 (2003).