Ab initio electrochemistry of water on (111) electrodes

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Recent advances in both experimental surface science techniques and computational simulation suggest that the two approaches to the elucidation of electrochemical interfaces are rapidly converging. *In situ* STM[1], and Raman[2] experiments are revealing increasingly clearer pictures of the adsorption and dissolution processes occurring at the metal-water interface under different electrochemical conditions. The ability to model these same processes using *ab initio* techniques has been hitherto restricted to either cluster models of the surface[3], or periodic calculations performed at the PZC[4].

By utilizing the relationship between the work function of a system and its electrochemical potential, and polarizing the system *via* increments in the total electron density, we have been able to simulate electrochemistry at surfaces using plane-wave density functional theory in a potential-dependent fashion. In this paper we present a series of studies of various (111) metal surfaces in aqueous environments, at not only zero charge potentials, but also at potentials that are arbitrarily anodic or cathodic. We are thus able to calculate both the PZC and the electrochemical response, in addition to the binding energies and vibrational modes, for various polylayer water structures formed above metal (111) surfaces.

This method also lends itself to the description of chemical reactions at varying electrochemical potential. For example, it is known that water activates readily to form dissociation products OH and H on several metal surfaces[5]. By constructing the free energy *versus* potential relationships for reactant and product states we have been able to determine the reaction energies for this process, and the ensuing processes of metal dissolution and hydride absorption. Regions of stability are determined for each particular 'phase,' and the potential of intersection of the free energy *versus* potential curves corresponds to the equilibrium potential for that reaction. These results shall be presented and discussed in the light of the current experimental and theoretical literature.

[1] Strehblow, H.-H.; Maurice, V.; Marcus, P. *Electrochim. Acta* **2001**, *46*, 3755
[2] Niaura, G. *Electrochim. Acta*, **2000**, *45*, 3507
[3] Parito, E. M.; Paredes-Olivera, P. *Surf. Sci.*, **2003**, *527*, 149
[4] Klesing, A.; Labrenz, D.; van Santen, R. A. *J. Chem. Soc., Faraday Trans.*, **1998**, *21*, 3229
[5] Michaelides, A.; Alavi, A.; King, D. A. *Phys. Rev. B*, **2004**, *69*, 113404