MAR14-2013-020427

Abstract for an Invited Paper
for the MAR14 Meeting of
the American Physical Society

Oxide/Water Interfaces: How the Surface Chemistry Modifies the Electronic Energy Alignment

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The minimum of the *d*-electron conduction band of an aqueous transition metal oxide electrode is typically no more than a few 100 mV away from the standard hydrogen electrode (SHE). Because of this favourable alignment of the electronic energy levels (near) metallic transition metal oxides with partly filled *d* bands can be used as electrocatalysts while the compounds with finite electronic gap can be used as photocatalysts. However, because of their ionic character, transition metal-oxide surfaces also show amphiphilic acid-base activity. At low pH the basic sites are protonated and at high pH the acidic sites deprotonated creating an electrical double layer with corresponding surface potential. The alignment of the electronic energy levels, and by implication their redox activity, is therefore pH dependent. In fact, even in absence of protonic surface charge, the coordination with water molecules is already capable of shifting the electronic energy levels of the oxide by 1 eV or more. Computation of the electronic energies in transition metal oxide electrodes requires therefore a detailed modeling of their aqueous surface chemistry. The solvation energy of the proton is the common energy reference for both redox potentials on the SHE scale and acidity constants (pKa). Computation of the H^+ solvation energy is therefore a key component in a unified treatment of redox and acid-base chemistry. In this talk we outline the Density Functional Theory based Molecular Dynamics (DFTMD) method we have developed for this purpose [1,2]. The central tool of our approach is a method for reversible insertion of protons in the aqueous part of the DFTMD model system. As an illustration we discuss the application to the rutile TiO_2/water and MnO_2/water interface.

[1] Cheng, J.; Sulpizi, M.; VandeVondele, J.; Sprik, M. ChemCatChem 4 (2012) 636.

[2] Cheng, J.; Sprik, M. Phys. Chem. Chem. Phys 14 (2012) 11245.