



WORKSHOP ON NEW MATERIALS FOR RENEWABLE ENERGY
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**THE THERMOCHEMISTRY OF OXIDATIVE DEHYDROGENATION OF A WATER
MOLECULE AT A TiO₂/WATER INTERFACE**

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ABSTRACT I:

The abstraction of an hydrogen atom from a water molecule is enormously costly. The standard potential vs the normal hydrogen electrode (NHE) for oxidative dehydrogenation (ODH) of H₂O is 2.7V, which is more than twice the potential for the full four electron oxidation(1.23V). One might hope that electrocatalysts manage to bring this energy down. We have investigated this question for a surface water molecule at the rutile TiO₂ (111) water interface using the DFTMD/FEP method presented in the previous talk. A crucial property distinguishing transition metal oxide from metal electrodes is that oxides are colloids exchanging protons with the aqueous electrolyte. This creates an electrical double layer shifting the position of conduction and valence band. The pH at which the surface carries no net proton charge(PZC) is therefore special and is the easiest place to start. Our first task was therefore to validate method and model system by estimating the PZC^[1] as well as the energy of the conduction band minimum and valence band maximum at PZC^[2]. We also had to check that the method can reproduce the ODH potential in bulk water with sufficient accuracy. Using an hybrid functional containing a fraction of exact exchange (HSE06) we found 2.5V for the standard potential vs NHE, encouragingly close to the target value of 2.7V as was explained in the first talk. This corresponds to 2.2 V vs NHE at PZC. Adsorption on the TiO₂/water interface reduces the reversible potential to 1.7V. However, resolving the dehydrogenation in an acid dissociation and oxidation of the hydroxide anion, it appears that most of activation by the surface is due to an increase in acidity. The potential for oxidation of the surface hydroxide anion is almost the same as in bulk solution. After outlining how these results were obtained using our DFTMD/FEP method, we will make an attempt to find an explanation for this somewhat counter intuitive observation.

[1] J. Cheng and M. Sprik, J. Chem. Theor. Comp. 6 (2010), 880.

[2] J. Cheng and M. Sprik, Phys. Rev. B 82 (2010), 081406(R).