



WORKSHOP ON NEW MATERIALS FOR RENEWABLE ENERGY
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**ALL ATOM DENSITY FUNCTIONAL THEORY OF THE
LATIMER SERIES OF DIOXYGEN**

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ABSTRACT I:

The Latimer series of electrode potentials for the full reduction of dioxygen by successive addition of four hydrogen atoms in aqueous solution is the reference against which the efficiency of catalysts of this vital process is measured. The same applies to catalysis of the reverse process, the oxidation of water. Computational methods used for the investigation of catalytic mechanisms ought to be able to reproduce the Latimer series of O_2 . An all atom first principle calculation should treat reactive species and the solvent at the same level of theory, which is in practice only feasible using density functional theory (DFT) based molecular dynamics (DFTMD) methods. We have recently carried this calculation using a DFTMD implementation of the normal hydrogen electrode (NHE) developed in the group^[1]. The result is rather discouraging. The generalized gradient approximation (GGA), the workhorse of DFTMD, was found to underestimate the reduction potential for $*OH/H_2O$ couple by 0.6 V and the potential for the $*O_2H/O_2H_2$ couple by 0.5 V. This unacceptable error is a manifestation of the delocalization error in GGA functionals. The failure of the GGA has effectively frustrated our attempts at DFTMD simulation of the electrocatalysis of water oxidation. Progress could be made only very recently thanks to implementation of exact exchange methods in the DFTMD code we use, CP2K (cp2k@berlios.de), by the Zurich group^[2]. We found that application of the HSE06 functional reduces the errors in the reduction potentials for $*OH$ and $*O_2H$ to 0.2V. In this first technical talk the combination of DFTMD and free energy perturbation methods (FEP) used in this calculation will be discussed in some detail. It is also preparation for the application to the study of oxidative dehydrogenation at the titania-water interface presented in the second talk.

[1] Costanzo, F.; Sulpizi, M.; Della Valle, R. G.; Sprik, M., J. Chem. Phys. 134 (2011), 244508

[2] Guidon, M.; Hutter, J.; VandeVondele J. Chem. Theory Comput. 6 (2010), 2348.