

# Literature Review: Using DFT to study active surfaces in the oxygen evolution reaction (OER)

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## Problem

The specific problem addressed is how to accurately model surface coverages of oxides in water with an applied potential and varying pH. This problem is relevant because of a recently developed atomistic thermodynamic framework for studying the oxygen evolution reaction (OER). This framework allows us to calculate theoretical activities of oxides in OER off of the adsorption energies of  $\ast\text{O}$ ,  $\ast\text{OH}$ , and  $\ast\text{OOH}$ . However, initial studies of these mechanisms were done on ideal surfaces, and coverages were not made to be consistent with actual OER conditions.

Recently, two papers from separate research groups have attempted to build on this theory to more accurately mimic actual surfaces of oxides in water with an applied potential and varying pH. The two papers are titled “Identifying active surface phases for metal oxide electrocatalysts: a study of manganese oxide bi-functional catalysts for oxygen reduction and water oxidation catalysis” and “Water Oxidation on Pure and Doped Hematite (0001) Surfaces: Prediction of Co and Ni as Effective Dopants for Electrocatalysis”, and their corresponding authors are Jan Rossmeisl and Emily A. Carter, respectively. Detailed references can be seen in the footnotes and the full article can be found in the folder with this assignment.<sup>1, 2</sup>

## Use of DFT

Both article’s overall goal was to evaluate catalyst’s performance in the oxygen evolution reaction (OER) using the same atomistic framework constructed in a previous article<sup>3</sup>. By using density functional theory (DFT) as a tool to model oxide surfaces and calculate adsorption energies of water electrolysis intermediates, one could then use these adsorption energies to calculate reactivities of oxide surfaces that were in qualitative agreement with experiments. This work helped validate the approach with idealized surfaces, so the next question is what the actual surfaces were in OER conditions, which includes effects of water solvation, applied potential, and pH effects.

Rossmeisl and coworkers took an approach that involved taking a bulk Pourbaix diagram and ‘upgrading’ it to include surface stability with respect to pH and applied potential. Their

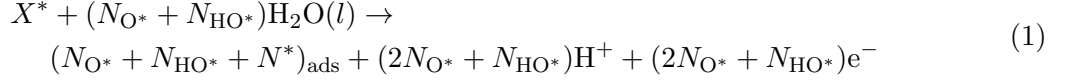
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<sup>1</sup>Su, H.; Gorlin, Y.; Man, I. C.; Calle-vallejo, F.; Norskov, J. K.; Jaramillo, F.; Rossmeisl, J. *Physical Chemistry Chemical Physics* 2012, 14, 14010

<sup>2</sup>Liao, P.; Keith, J. A.; Carter, E. A *Journal of the American Chemical Society* 2012, 134, 13296

<sup>3</sup>Man, I.; Su, H.; Calle-Vallejo, F. *ChemCatChem* 2011, 3, 1159

main equation of modeling dissociation and adsorption of water onto idealized surfaces is shown below.



This reaction describes the interaction of water with surfaces. Starting with a clean surface with a total of  $X^*$  sites, water will adsorb and produce protons, electrons, and adsorbed species of either  $O^*$  or  $HO^*$ . In producing these intermediates, there will be a release of an electron and proton, and higher pHs and higher applied potentials will stabilize these intermediates. The Gibbs free energy of a surface under these conditions is shown below.

$$\begin{aligned} G_{\text{surf}} = & E_{(N_{O^*} + N_{HO^*} + N^*)_{\text{ads}}} - E_{X^*} - (N_{O^*} + N_{HO^*})E_{H_2O(g)} \\ & + \frac{2N_{O^*} + N_{HO^*}}{2}E_{H_2(g)} + \Delta ZPE - T\Delta S \\ & - (2N_{O^*} + N_{HO^*})(eU + k_B T \ln 10 \text{pH}) \end{aligned} \quad (2)$$