

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

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## 1 Introduction

The specific problem addressed is how to accurately represent active surfaces of oxides in the oxygen evolution reaction (OER). This problem is relevant because of a recently developed atomistic thermodynamic framework for studying 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  $\ast\text{OOH}$ . Initial studies of these mechanisms were done on ideal surfaces with an arbitrary coverage of intermediates, and water was not assumed to naturally dissociate onto these surfaces.

Recently, two papers from separate research groups have attempted to build on this theory to more accurately mimic actual surfaces of oxides in water. 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>

## 2 Methods

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>. However, Rossmeisl’s goal was to model both the thermodynamics and kinetics of OER and construct a theoretical current-voltage curve, while Carter’s goal was to compare the thermodynamics of pure and doped hematite. 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.

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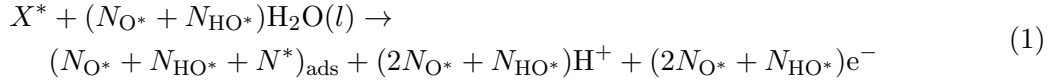
<sup>1</sup>Su, H.; Gorlin, Y.; Man, I. C.; Calle-vallejo, F.; Norskov, J. K.; Jaramillo, F.; Rossmeisl, J. *Physical Chemistry Chemical Physics* 2012, 14, 14010

<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

## 2.1 Rossmeisl Approach: Effects of pH and electrode potential

Rossmeisl et al. (2012) took an approach that involved taking a bulk Pourbaix diagram and ‘upgrading’ it to include surface stability with respect to pH and applied potential. They studied the  $\text{MnO}_x$  system in OER conditions, which include  $\text{Mn}_3\text{O}_4$ ,  $\text{Mn}_2\text{O}_3$ , and  $\text{MnO}_2$ . Their goal was to use DFT to find both thermodynamic and kinetic data and model a fully self-consistent current-voltage curve of a  $\text{MnO}_x$  electrode and compare them to experiments. In order for this curve to be self-consistent, they had to take into account changes of both bulk **and** surface phases with respect to applied potential and pH. Their main equation of modeling dissociation and adsorption of water onto each of the 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  $\text{O}^*$  or  $\text{HO}^*$ . 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.

$$\begin{aligned} G_{\text{surf}} = & E_{(N_{\text{O}^*} + N_{\text{HO}^*} + N^*)_{\text{ads}}} - E_{X^*} - (N_{\text{O}^*} + N_{\text{HO}^*})E_{\text{H}_2\text{O}(\text{g})} \\ & + \frac{2N_{\text{O}^*} + N_{\text{HO}^*}}{2}E_{\text{H}_2(\text{g})} + \Delta\text{ZPE} - T\Delta S \\ & - (2N_{\text{O}^*} + N_{\text{HO}^*})(eU + k_{\text{B}}T\ln 10\text{pH}) \end{aligned} \quad (2)$$

To use this equation, one models the same surface with different coverages of O and OH. Generally, the more adsorbates on the surface, the more free electrons and protons that need to be produced, and the more likely that surface will be present at higher potentials and pH’s.

Note that these surface Pourbaix diagrams are done in the context of a specific bulk Pourbaix diagram. From experiments, the bulk Pourbaix diagrams are assumed to be true, and then in each bulk region of the Pourbaix diagrams, the surface Pourbaix diagrams are constructed. They first did this for  $\text{Mn}_3\text{O}_4$ ,  $\text{Mn}_2\text{O}_3$ , and  $\text{MnO}_2$ , and then made a general  $\text{MnO}_x$  Pourbaix diagram that gave the most stable bulk surface phase.

## 2.2 Carter Approach: A detailed investigation on water dissociation

Carter et al. (2012) studied hematite ( $\text{Fe}_2\text{O}_3$ ) for photocatalytic water splitting. In order to attain a general idea of the surface, they did an extensive literature review of both experimental and computational investigations on the active surface facet and termination of hematite in wet conditions. They found that in water, the most likely surface is an  $\text{H}_3\text{-O}_3\text{-Fe-Fe-R}$  surface.

They opted to not include effects of pH and increasing electrode potential, but did a far more extensive study on possible configurations of possible surface configurations. Starting with an ideal, oxygen terminated surface of hematite, they asked the question, “If we were to make surface with dangling hydroxyl groups, which would be most stable? How many of these oxygens would be hydrated to make hydroxyl’s, and what would the configuration of these bonds be?” To answer this question, they broke up their surface into a 7x7 grid of a total of 49

points. They then placed one hydrogen atom at each of these points at a height of 0.8 Å above the surface, allowed the hydrogen to relax. They would then calculate the adsorption energy as shown below.

$$G_{\text{ads}} = [E(\text{O} - \text{terminated slab} + n\text{H}) - E(\text{O} - \text{terminated slab}) - (n/2)E_{\text{H}_2}]/n + \Delta\text{ZPE} - T\Delta S \quad (3)$$

They then took the structure with the lowest energy and then did the same process again with a second hydrogen atom. By doing this, they could be confident that they are getting the DFT predicted ground state of their system, and they could also systematically analyze increasing coverages of hydroxyl groups. Note that equation (3) is independent of how many hydroxyl groups are on, so it is possible to find the ground state structure.

In addition to finding the most stable  $\text{H}_x\text{-O-Fe-Fe-R}$  surface, they also included affects of a monolayer of water. The orientations of the water molecules were chosen to maximize hydrogen bonding, and similar to the procedure for choosing the most stable hydroxylated surface, the most stable solvated surface, after relaxation, was chosen as well.

### 3 Discussion

When comparing and contrasting both techniques of accurately representing the surface phase in OER conditions, its important note the differing goals of both. Rossmeisl and coworkers were seeking theoretical current-voltage curves that could be directly comparable to experiments. The purpose of this was to use theoretical techniques to probe the fundamental characteristics of active phase as one increased the potential in a typical OER experiment. In contrast, Carter was seeking qualitative agreement between pure and doped hematite surfaces. Therefore, one could easily assume changes in the bulk and surface structures at differing pH's and voltages would not be drastically different across different dopings of cations.

In assessing the reproducibility of the results, the piece of information that is most valuable in these surface calculations is the geometry of the adsorbates. Both articles give specific structural parameters of their surfaces, but only the Carter paper gives a detailed description of how the hydroxylated surfaces were produced. Rossmeisl does not describe the geometry of the  $\text{HO}^*$  and  $\text{HOO}^*$  adsorbates, and from personal experience, these geometries are highly dependent on the initial conditions of the relaxations. Therefore, it is unclear whether Rossmeisl's surfaces are in their ground state, and it is further impossible to reproduce their values. In contrast, Carter's paper gives a clear explanation on how the hydroxylated structures were constructed and geometries and total energies of the most stable structures.