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 *O, *OH, and *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 oxide surfaces 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.[1,2]

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 [3]. Both articles took the basic framework established and used it to look at two different systems (MnO_x and Fe_2O_3) with two different goals. 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 only the thermodynamics of pure and doped hematite for photovoltaic applications. In accomplishing goals, both articles opted to include the effects of water dissociation on an idealized surface, and I will only focus on this aspect of both articles for the literature review.
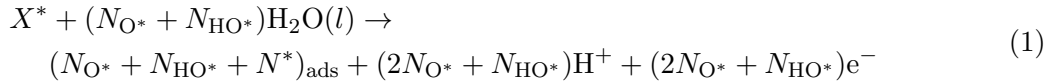
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[1] Su, H.; Gorlin, Y.; Man, I. C.; Calle-vallejo, F.; Norskov, J. K.; Jaramillo, F.; Rossmeisl, J. Physical Chemistry Chemical Physics 2012, 14, 14010

[2] Liao, P.; Keith, J. A; Carter, E. A Journal of the American Chemical Society 2012, 134, 13296

[3] Man, I.; Su, H.; Calle-Vallejo, F. ChemCatChem 2011, 3, 1159

2.1 Rossmeisl Approach: Effects of pH and electrode potential

Rossmeisl's goal was to construct a current-voltage curve of the performance of the MnO_x system in both oxygen evolution and reduction and compare this to experiments to help elucidate possible mechanims and surfaces. Therefore, they had to add in effects of pH and varying electrode potential. They did this by taking a bulk Pourbaix diagram and 'upgrading' it to include surface coverages with respect to pH and applied potential. They studied the MnO_x system in OER conditions, which included Mn_3O_4, Mn_2O_3, and 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 MnO_x electrode and compare them qualitatively 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.

$$
\begin{aligned}
X^* + (N_{O^*} + N_{HO^*})H_2O(l) \rightarrow \\
(N_{O^*} + N_{HO^*} + N^*)_{ads} + (2N_{O^*} + N_{HO^*})H^+ + (2N_{O^*} + N_{HO^*})e^-
\end{aligned}
\tag{1}
$$

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 preferentially stabilize coverages with more of these intermediates. The Gibbs free energy of a surface under these conditions is shown below.

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

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.

To implement this in predicting active surface phaes, they would first graph the relationship between applied voltage and Gibbs free surface energy of the surfaces they were investigating. For each of their close packed surfaces, they computed total energies with numerous different adsorbates on, including mixtures of OH and O groups. Figure 1 shows a sample.
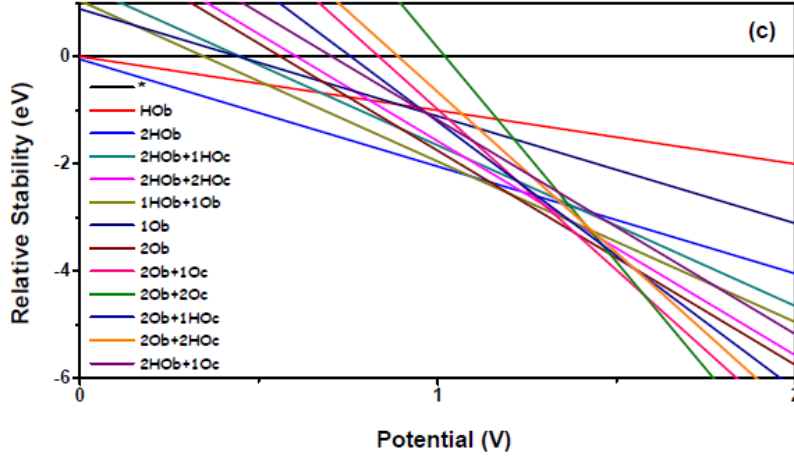
Figure 1: The phase diagram of $MnO_2(110)$ surface calculated as function of the potential at pH=0. The notations b and c indicate bridge sites and coordinated unsaturated sites

This is done at pH=0, and at higher pHs, surfaces with more OH and O adsorbed would become lower because of the proton released in the adsorption. Graphs like this were also done for $Mn_3O_4(001)$ and Mn_2O_3 (110), which can be found in the supplementary data.

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. For example, the above graph does not this show this, but at a high enough potential, the manganese oxide will naturally be converted into $MnO_4{}^-$. Therefore, above a certain potential, the predictes coverages above would be meaningless. The above graph can then be 'mapped onto' a region on the experimentally attained bulk Pourbaix diagram to give more information on active surface phases. The example for MnO_2 is shown in figure 2.
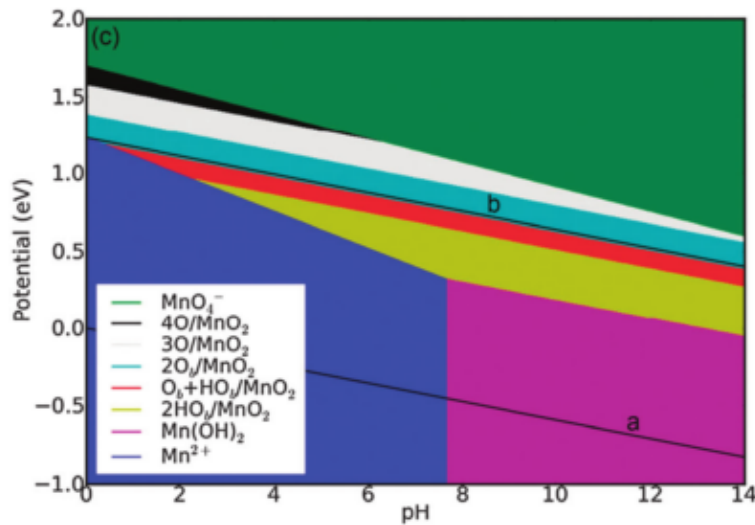

Figure 2: The bulk and surface Pourbaix diagram of $MnO_2(110)$ surface

3

Their final step was combining the Pourbaix diagrams of Mn_3O_4, Mn_2O_3, and MnO_2 to make a general MnO_x diagram that would predict both the active bulk **and** surface phase at varying potentials and pH. Details of this procedure can be found in the attached supplementary information. I chose not to go over the details of this procedure out of time and space constraints.

2.2 Carter Approach: A detailed investigation on water dissociation

Carter et al. (2012) studied hematite (Fe_2O_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 H_3-O_3-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 groups be?" To answer this question, they first 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.

$$
\begin{aligned}
G_{\text{ads}} = [&E(O-\text{terminated slab} + n\text{H}) \\
&E(O-\text{terminated slab}) - (n/2)E_{H_2}]/n \\
&+ \Delta\text{ZPE} - T\Delta S
\end{aligned}
\tag{3}
$$

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 over different coverages of hydroxyl groups. Figure 3 shows the ground state surfaces at multiple covergaes of HO groups.
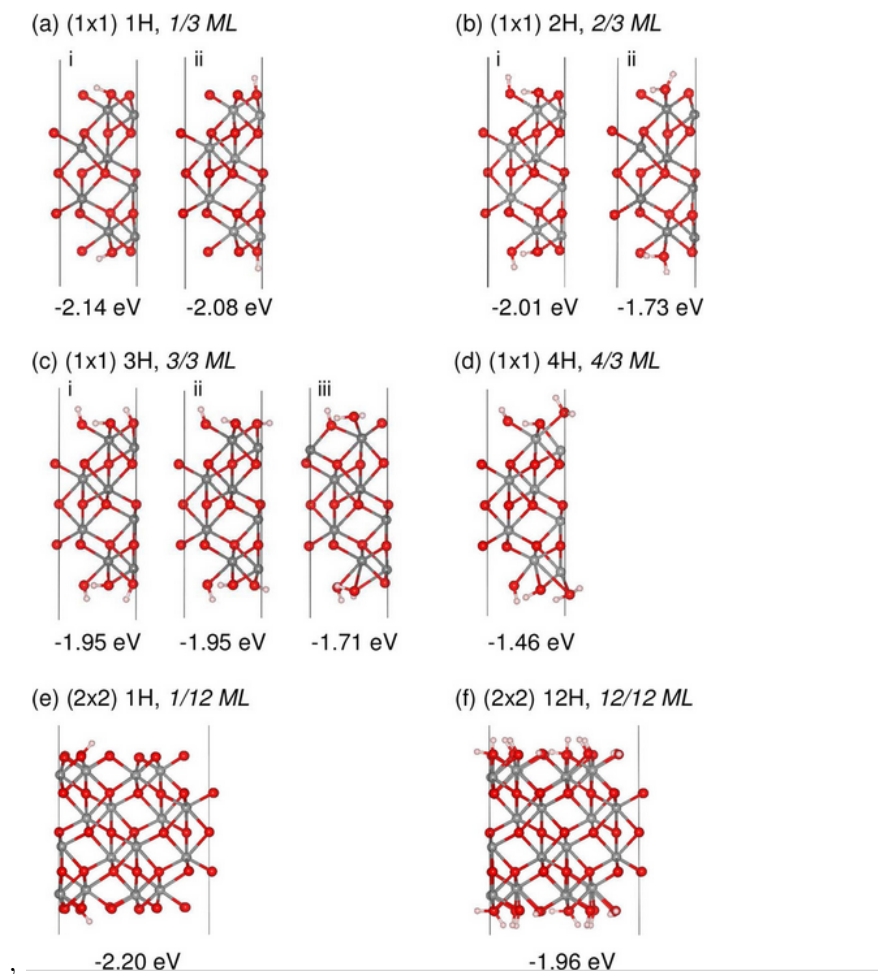
Figure 3: Lowest energy configurations of HO surfaces at multiple coverages and hydrogen adsorption energies.

In addition to finding the most stable H_x-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.

Finally, in calculating adsorption energies of O*, HO* and HOO*, they images on which adsorbates would be involved in the reaction. This image can be found in the attached article.

3   Discussion

When assessing both techniques of accurately representing the surface phase in OER conditions, its important note the different 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. Hence, Rossmeisl would need to take into account the relationship between bulk/surface stability with potential and pH. 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.

To reproduce these results, the most difficult calculation to reproduce geometries of adsorbed intermediates (HO* and HOO*). From personal experience, these geometries are highly dependent on their initial, pre-relaxed states. Rossmeisl does not describe the geometry of the HO* and HOO* adsorbates, furthermore, it is evident from the supplementary data of Rossmeisl's paper that he and coworkers performed adsorption energy calculations of O*, HO*, and HOO* on at least 50 different surfaces, and it is unclear how these adsorption energies were calculated in lieu of different coverages.

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. Furthermore, Carter went a step further to clearly show how OER was taking place in midst of these coverages. Granted, Carter was investigating only one surface and one source of varying coverage (H atoms), but she documented the process to achieving these ground states well.