Dependence of Surface Orientation of Nickel-based Catalyst for Water Oxidation Reaction: A Computational Study

Author: Justin J. Choi[1]

Seoul International School, Sujeong-gu, Seongnam-si, Kyeonggi-do, Republic Korea [1];

E-mail: justinchoi7746@gmail.com [1]

ABSTRACT

In this investigation, I simulated the bonding of hydroxide (OH) to nickel oxide (NiO) surface to understand the role of surface orientation in the oxygen evolution reaction (OER). Density functional theory (DFT) calculations indicate that OH creates single-coordination to the (100) surface, whereas triple-coordination to the (111) surface, explaining weaker bond with the (100) surface. The (100) surface is likely to be more effective in functioning as catalytically active sites because weaker binding with reactants is more preferred in proceeding the reaction. This study shows that the atomic simulation is useful in understating the role of a catalyst in the OER at the atomic level.

Keywords: computational study; nickel catalyst; surface orientation; water oxidation

1. INTRODUCTION

The global energy consumption has recently risen very sharply. As a result, the level of greenhouse gases has soared to harm the environment and accelerate global warming to its highest stakes. Global warming has already been a serious concern worldwide in the past decade by exacerbating the climate situation; for instance, the increased temperature fluctuations between seasons, unpredicted flood and drought, and abnormal temperature rise or drop. Under these circumstances, other than limiting one's capability to use energy, the focus of the scientific community today has tilted towards finding a replacement of these harmful sources of energy in such a way that the energy sources are easily accessible, cheap, and renewable. Numerous trials and searches for sources that meet these requirements have long been undertaken until it was clarified that the most competent source of energy has been nearby under the plain sight: hydrogen separated from the water [1].

Along this direction, electrochemical devices were developed to produce oxygen and hydrogen gas by splitting water. The water splitting consists of the oxygen evolution reaction (OER) and hydrogen evolution reaction (HER), which are paired with each other. Between these two reactions, OER is energetically more demanding compared to HER [2]. Therefore, developing efficient OER catalysts is of utmost priority in advancing the water splitting and thus producing hydrogen from water. In my previous paper [3], I improved the catalytic activity of a nickel(Ni)-based OER catalyst [4] by increasing the surface area. For this purpose, surfactants of sodium dodecyl sulfate (SDS) and P123 were included during electrodeposition involving the nickel precursor, nickel nitrate ($Ni(NO_3)_2$), to turn the electrode porous and hold a high surface area. The increased surface area by optimizing the surfactant conditions resulted in enhanced catalytic activity. Thus, it was concluded that morphological control of a catalytic electrode could play a critical role in activating the OER and thus the water splitting. In spite of the useful lesson obtained, fundamental understanding on how the catalyst operates at the atomic level in interacting with the reactant is lacking.

To address this point, the overall OER was split into series of elemental reactions according to the literature [5] as below. In setting up these series of reactions, my previous water splitting condition of pH 14 was taken into consideration in a way that the main reactant that interacts with the catalyst is hydroxide (OH).

$$H_2O(l) + * \rightleftharpoons H^+ + HO* + e^- \quad \Delta G_1 \quad (1)$$

$$HO* \rightleftharpoons H^+ + O* + e^- \quad \Delta G_2 \quad (2)$$

$$O* + H_2O(l) \rightleftharpoons H^+ + HOO* + e^- \quad \Delta G_3 \quad (3)$$

$$HOO* \rightleftharpoons H^+ + O_2(g) + e^- + * \quad \Delta G_4 \quad (4)$$

, where * represents the active site on the catalyst. In step (1), water molecule reaches the active site on the catalyst to produce proton (H^+) and OH*. In step (2), the OH* splits to produce proton and O*. In step (3), this oxygen atom reacts with another water molecule to produce proton and HOO*. In step (4), finally, this HOO* leaves the active site by producing proton and oxygen molecule (O_2). Obviously, simulating these entire series of steps are nontrivial. Instead, it is preferred to identify the most critical (or slowest) step that represents the overall reaction. In this line, according to the literature [6], how strongly OH binds with the active site determines the efficiency of the entire reaction.

2. RESULTS

Based on this background, I simulated the binding of OH on the surface of NiO using computational chemistry. I first created the slab of NiO with two different surface orientations, (001) and (111), in the crystal information file (CIF). A CIF file contains the coordinate information of all atoms in the lattice. My files contain OH bound to NiO as well to simulate the binding of OH. The CIF files were then fed into VASP program to configure the most stable structures. As shown in figure below, the oxygen in OH binds with the Ni in NiO due to electrostatic interaction related to their partial positive and negative charge character. Surprisingly, the oxygen in OH binds with a single Ni atom in NiO in the case of (100) surface, whereas the oxygen in OH with three Ni atoms simultaneously in the case of (111) surface: single vs. triple coordination.
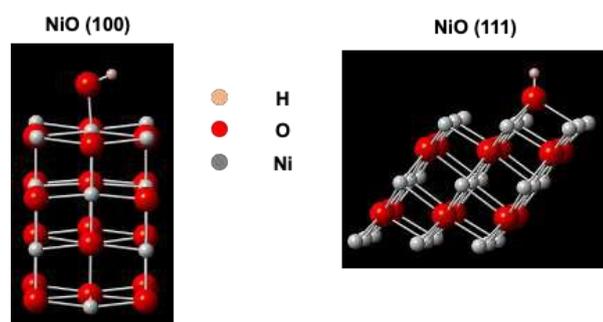

Figure 1. Lattice structures of NiO with (100) and (111) surface orientations. OH is bound onto these surface.

Next, the binding energy (Gibbs free energy) was calculated according to the following equation to see the binding strength of OH:

$$\Delta G = G \ (product) - G \ (reactant)$$

Reactant: NiO, OH

Product: NiO−OH

The calculations yielded the following energy values for both cases.

Table 1. Gibbs free energy values for (100) and (111) surface orientations

(100) orientation		(111) orientation	
	Energy (eV)		Energy (eV)
Blank NiO	−90.0114	Blank NiO	−103.121
OH	−7.1264	OH	−7.1264
NiO-OH	−100.25	NiO-OH	−114.914
Adsorption energy	**−3.1122**	Adsorption energy	**−4.666**

In the equation above, negative value of ΔG indicates more preferred (stronger) binding. When both surfaces are compared, the binding of OH turned out to be stronger with the (111) surface than with the (100) surface. This observation can be predicted from the number of binding points of OH as captured in the figure above: 1 vs. 3 for (100) and (111) surfaces, respectively.

Aside from Gibbs free energy, the Ni−O bond length can be retrieved from DFT calculations. The Ni−O bond length was 1.807 Å and 1.988 Å for (100) and (111) surfaces, respectively. Combining all of this information, I reached the conclusion that although the Ni−O bond length of the (111) surface is shorter, its triple-coordination bonds are the main origin of the stronger bond with OH.

From catalytic activity viewpoint, it was known that moderate binding with reactants with active sites on the catalyst is more suitable for activating the reaction because too strong binding hinders proceeding the series of elementary reactions. In this sense, I speculated that the (100) surface might play a more crucial role in the OER experiment I performed previously. I plan to perform a more in-depth investigation to elucidate this discussion as a future study.

3. CONCLUSION

The OER imposes energetically a high barrier and is thus the main hurdle to overcome in water splitting. NiO and $Ni(OH)_2$ are well-known nickel-based catalysts for OER. My simulations indicated the dependence of the surface orientation of a NiO catalyst as the surface orientation determines the binding strength of OH reactant with the catalyst. The simulations portray detailed atomic structures with respect to coordination number of the reactant and its bond length to the active site. This computational study helps understanding my previous experiment using the Ni-based catalyst at the atomic level and therefore implies the usefulness in designing catalyst materials.

4. REFERENCES

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