Water Adsorption and Dissociation on Ni$_3$ and Ni$_5$ Decorated Y- and Sc-stabilized Zirconia: Insights from Density Functional Theory Investigation

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Received: 29 March, 2019; Accepted: 21 August, 2019; Published: 31 August, 2019

In this work, water adsorption and dissociation on Ni$_3$- and Ni$_5$-decorated Y- and Sc-stabilized zirconia (YZO and ScZO respectively), were probed using planewave, pseudopotential-based density functional theory calculations, to assess water splitting and subsequent hydrogen evolution potential of these metal-on-zirconia structures. It is found that the strength of Ni cluster binding on zirconia depends on the size of the cluster, at least for Ni$_3$ and Ni$_5$, and on the nature of the stabilizing atom. The Ni$_3$ and Ni$_5$ clusters tend to bind more favorably on the Sc site of ScZO compared to that of the Y site of YZO. Water is found to adsorb strongly on Ni$_3$-YZO, Ni$_3$-ScZO, and Ni$_5$-ScZO. Water dissociation barrier for both the first and second hydrogen atoms tends to decrease for larger Ni cluster, with the Ni$_5$-YZO system giving the lowest energy barriers. With relatively fine dissociation barriers, such systems could potentially be tapped for electrocatalytic water dissociation reactions leading to hydrogen evolution. These results are of importance and could contribute significantly in the further search and design of electrocatalytic materials for water dissociation and eventual hydrogen evolution for sustainable hydrogen production.

Keywords: Density functional theory; Solid oxide electrolysis cell; Energy conversion; Water adsorption and dissociation; First-principles calculations

I. INTRODUCTION

Hydrogen is considered to be a clean alternative energy carrier that is important in fuel cells, in particular, solid oxide fuel cells (SOFC) as fuel in electricity generation [1–6]. One of sustainable methods of producing hydrogen is through photocatalytic water-splitting, usually via a photocatalyst/co-catalyst combination [6, 7]. In addition, typical water electrolysis is also done utilizing energy derived from renewable sources such as solar and wind. In recent years, solid oxide electrolysis cells (SOEC) attracted attention as an efficient water electrolysis media, especially at high temperature applications [2, 6, 8–10]. SOECs are basically SOFCs working in reverse, thereby generating hydrogen and oxygen via electrolysis instead of combining them to produce water [8, 11]. In this respect, water electrolysis on SOEC electrodes provide the needed starting ingredients for SOFCs. Thus, a SOFC that works as SOEC in the reverse operation mode can be considered as a closed, economical process of energy generation.

As such, it is of interest to deal with common SOFC electrodes as water electrolysis materials in SOEC. Accordingly, water dissociation process proceeds at the cathode via the half-cell water splitting, as shown in Eq. (1) [12]:

$$\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{O}^{2-}_{\text{electrolyte}} + \text{H}_2(\text{g}).$$  (1)
In Eq. (1), a water molecule (usually in the form of steam) acquires 2 electrons from the SOEC cathode in order to form oxygen anions (to be deposited in the electrolyte) and hydrogen gas. In an SOEC system, consideration of the operating temperature is important, as most SOECs are Ni-based that oxidize rapidly (and degrading its stability) with increasing temperature and steam pressure. Thus, it is of significance to have a low-temperature SOEC operation.

In a typical electrode material for SOEC, a metal-ceramic composite which provides good electronic, catalytic activity, and oxide-ion conductivity is required. The electronic and catalytic activity is provided by the metal component while the ionic conductivity is provided by the ceramic oxide. Nickel is one of the typically used metal component due mainly to its advantageous properties such as high electronic conductivity and very good compatibility with other electrode components [13] while yttrium-scandium co-doped zirconia is one of the promising oxide-ion conductor due to its higher conductivity at intermediate temperatures than pure yttrium-stabilized zirconia (YSZ) and good structural stability than pure scandium-stabilized zirconia (ScSZ) [13–17].

Ni-based SOECs are the most commonly utilized electrodes for water electrolysis due mainly to its advantageous properties such as high conductivity and very good compatibility with other electrode components [4, 5, 9–12, 18–24]. Thus, it is imperative to do further studies on the catalytic properties of Ni especially in water electrolysis. In general, the sought after characteristics of SOEC electrode materials revolve around high catalytic activity and low resistance at intermediate temperatures, that is around 500–800°C [25–27]. Several techniques have been investigated in order to improve such properties of Ni-based SOECs, for instance alloying with certain transition metals [28] and utilization of low-dimensional materials such as nanotubes and nanowires to where Ni is embedded [21].

In this work, we looked into the water dissociation potential of small Ni clusters (Ni3 and Ni5) on Sc- and Y-stabilized zirconia, ScZO, and YZO, respectively, via density functional theory calculations with spin polarization as implemented in Quantum Espresso package suite [33]. Ultra-soft pseudopotentials (via the Andrea Dal Corso code rijk3), scalar-relativistic calculation following the Troullier-Martins pseudization method [34] within the Perdew-Burke-Ernzerhof (PBE) parametrization of the generalized gradient approximation (GGA) were used. Throughout the calculations, a cut-off energy of 60 Ry was used, and configurations were relaxed until the atomic forces were below 0.001 a.u. Electronic convergence is set to 0.00001 a.u. All structural images were rendered using xcrysden software [35].

For our structural slab, we considered a 2 × 2 supercell of the (111) surface of a four-layer cubic zirconia (ZrO2) with one surface atom replaced by Y (for YZO stabilization) and Sc (for ScZO stabilization). The (111) surface was considered as it is known that for ZrO2, this surface is stable and catalytically more active compared to others [36, 37]. In our model, atom replacement was only done on the surface, with an effective Y (or Sc) concentration of 4.17%. A k-point mesh of 7 × 7 × 1 following the Monkhorst-Pack scheme was utilized. A vacuum space of more than 18 Å was used to avoid inter-slab interactions. The lowest energy Ni3 and Ni5 cluster configurations were searched using ab initio random structure searching. Here, Ni atoms were randomly placed in an effectively huge cubic supercell to create 30 different initial structures (both for Ni3 and Ni5 small clusters). These structures were then relaxed, and the one with the lowest energy was chosen as the most stable local minimum for each cluster. In our model, the Ni clusters sat on top of the Y (Sc) site of the stabilized YZO (ScZO). This was done to analyze the effect of Y and Sc stabilization on the binding of Ni clusters on the (111) surface. We then probed water adsorption on four different (111) surface models (Ni3-YZO, Ni5-ScZO, Ni3-YZO, and Ni5-ScZO). Finally, we calculated water dissociation for the first and second hydrogen atoms utilizing these structural models via nudged elastic band method with linearly-interpolated seven images.

III. RESULTS AND DISCUSSION

A. Structure and binding properties of Ni3 and Ni5 clusters

We first discuss the structure of Ni3 and Ni5 clusters. As per random structure searching, we obtained an isoceles triangular configuration for Ni3 and a square pyramid

Figure 1: Optimized structures of (a) Ni3 and (b) Ni5 atomic clusters searched using ab initio random structure searching.
(slightly trigonal bipyramid) structure for \( \text{Ni}_5 \) (shown in Figure 1), both of which are consistent with previous theoretical and experimental results [38−40]. In terms of their magnetic properties, \( \text{Ni}_3 \) cluster has a total magnetization of 2.94 Bohr magneton per cell, while \( \text{Ni}_5 \) has a total magnetization of 4.85 Bohr magneton per cell. We then looked into the charge redistribution effects of Y and Sc on \( \text{ZrO}_2(111) \) surface by analyzing their charge difference isosurfaces defined by \( \Delta \rho = \rho_{\text{Sc(Y)ZO}} - \rho_{\text{ZO}} - \rho_{\text{Sc}} \) (Figure 2). Here, \( \rho_{\text{Sc(Y)ZO}}, \rho_{\text{ZO}}, \) and \( \rho_{\text{Sc}} \) are charge densities of the Sc(Y)ZO system, ZO, and Sc (Y) atom, respectively. In this respect, it is found that the charge distributions within the vicinity of Sc and Y do not differ appreciably, implying that the two atoms almost have the same stabilization effect on \( \text{ZrO}_2(111) \).

We now proceed to Ni cluster adsorption on Y and Sc sites (Table 1). The binding energy per Ni atom is calculated using

\[
E_{\text{Ni per atom}} = \frac{(E_{\text{YZO/ScZO+Ni}} - E_{\text{YZO/ScZO}} - E_{\text{Ni}})}{n}. \tag{2}
\]

In the above, \( E_{\text{YZO/ScZO+Ni}} \) is the energy of YZO/ScZO with \( \text{Ni}_n \) cluster system, \( E_{\text{YZO/ScZO}} \) is the energy of the YZO/ScZO substrate, and \( E_{\text{Ni}} \) is the energy of the \( \text{Ni}_n \) cluster. In this definition, the more negative the value of \( E_{\text{Ni per atom}} \) is, the more stable is the binding. It is found that the binding energy of Ni clusters depend on the cluster size, and the stabilizing atom. \( \text{Ni}_3 \) binds more than twice as strong as \( \text{Ni}_5 \) on ScZO. On the other hand, \( \text{Ni}_3 \) binding energy on YZO is comparable to that on ScZO, although \( \text{Ni}_3 \) appears to have a very minimal interaction with YZO (binding energy of 0.09 eV atom\(^{-1}\)). As such it can be inferred that Ni clusters bind more favorably on ScZO, on Sc site, compared to YZO’s Y site. This could be attributed to the slightly higher electronegativity of Sc (1.36, Pauling scale) compared to Y (1.22, Pauling scale), causing a more defined overlap between Ni and Sc bonding states that resulted to a more stable binding. Furthermore, we calculated the charge difference isosurfaces between the Ni clusters and the stabilizing atoms (Sc and Y), defined by \( \Delta \rho = \rho_{\text{NiX-Sc(Y)ZO}} - \rho_{\text{Sc(Y)ZO}} - \rho_{\text{NiX}} \), where \( \rho_{\text{NiX-Sc(Y)ZO}}, \rho_{\text{Sc(Y)ZO}}, \) and \( \rho_{\text{NiX}} \) are the charge densities of the NiX/Sc(Y)ZO system, the Sc(Y)ZO substrate, and the NiX/NiX cluster (shown in Figure 3). It can be observed that in the case of \( \text{Ni}_3 \) on ScZO and YZO (Figure 3(a, c)), an electron-rich region (denoted by yellow isosurface) exist between the Ni clusters and the stabilizing atoms. This interacts with a modest electron-deficient region on top of the stabilizing atoms, giving an effective electrostatic interaction that binds the two together. As for \( \text{Ni}_5 \) on ScZO and YZO (Figure 3(b, d)), it is noticeable

| Substrate | \( \text{Ni}_3 \) binding energy per atom (eV/Ni) | \( \text{Ni}_5 \) binding energy per atom (eV/Ni) |
|-----------|---------------------------------|---------------------------------|
| YZO(111)  | −0.42                           | 0.09                            |
| ScZO(111) | −0.55                           | −0.17                           |

Figure 2: Charge difference isosurface for (a) YZO and (b) ScZO. Green and red denote electron-rich and deficient regions, respectively. An isosurface level is set to 0.06 e per Bohr\(^3\).

Figure 3: Charge difference isosurface for (a) \( \text{Ni}_3 \)-ScZO, (b) \( \text{Ni}_5 \)-ScZO, (c) \( \text{Ni}_3 \)-YZO, and (d) \( \text{Ni}_5 \)-YZO. Yellow and blue-green denote electron-rich and deficient regions, respectively. An isosurface level is set to 0.05 e per Bohr\(^3\).
that there is a significant reduction of the electron-rich region beneath the Ni$_5$ cluster, although such reduction is much more pronounced in the case of Ni$_3$ on YZO. This explains the reduced adsorption energy of Ni$_3$ on ScZO, and its positive adsorption energy on YZO. Furthermore, using NEB calculations, an effective activation barrier (0.15 eV) in adsorbing Ni$_3$ on YZO is found. This implies that energy is needed to bring Ni$_3$ closer to YZO, and this further verifies that Ni$_3$ does not adsorb spontaneously on YZO as demonstrated by the positive adsorption energy. The observed trend in adsorption energy strength is consistent with that of Ni$_3$ and Ni$_5$ cluster adsorption on pristine oxygen-terminated ZrO$_2$(111) [41]. Although the adsorption energy values for these two systems cannot be directly compared due to differences in the calculation parameters and surface feature, it can be noted that the calculated adsorption energies of Ni$_3$ and Ni$_5$ clusters on Sc- and Y-stabilized zirconia are smaller in magnitude, and it is suggested that the stabilizing effect of Sc and Y could have reduced the strength of binding between the Ni clusters and the Sc and Y sites on the surface. Looking into the magnetic properties of the system, the following magnetizations were obtained upon adsorption of Ni clusters (in Bohr magneton per cell): Ni$_3$-ScZO, 6.76; Ni$_5$-ScZO, 8.01; Ni$_3$-YZO, 6.79; and Ni$_5$-YZO, 8.74.

B. Water adsorption and dissociation on Ni$_3$-YZO, Ni$_5$-ScZO, and Ni$_5$-ScZO

Water adsorption energy is obtained via

$$E_{\text{H}_2\text{O}}\text{ adsorption} = E_{\text{YZO}/\text{ScZO}+\text{Ni}_n+\text{H}_2\text{O}} - E_{\text{YZO}/\text{ScZO}+\text{Ni}_n} - E_{\text{H}_2\text{O}},$$

(3)

where $E_{\text{YZO}/\text{ScZO}+\text{Ni}_n+\text{H}_2\text{O}}$ is the energy of the YZO/ScZO + Ni$_n$ with adsorbed water, $E_{\text{YZO}/\text{ScZO}+\text{Ni}_n}$ is the energy of the YZO/ScZO-Ni$_n$ substrate, and $E_{\text{H}_2\text{O}}$ is the energy of a single water molecule. Water binds strongly on Ni$_3$ on both ScZO and YZO, at around $-0.6$ eV (see Figure 4). The same order of magnitude of adsorption energy is found for Ni$_5$ on ScZO (water adsorption on Ni$_5$-YZO was not considered since Ni$_5$ did not bind on YZO Y site). In comparison to bulk Ni(100) and Ni(111) surfaces (with water adsorption energies of $-0.26$ eV and $-0.17$ eV, respectively [42]), water adsorption on these nickel clusters are more stable. Furthermore, the obtained water adsorption energies are much higher that those on Ni$_x$/Cu(111) ($x = 1, 2, 3, 4$) surface alloys [43]. As such, Ni$_3$ and Ni$_5$ clusters on Y/Sc-stabilized ZrO$_2$(111) are much better systems for water adsorption than bulk nickel surface and alloys. With these observations, it can be noted that water adsorption does not depend on Ni cluster size, at least in the case of Ni$_3$ and Ni$_5$ clusters on ScZO and YZO. As hydrogen evolution starts with the presence of hydrogen atoms on the electrode material, dissociation activation barriers were calculated to gauge the feasibility of these structures for such process. To note, the calculated water adsorption energies on Ni$_3$-ScZO and Ni$_5$-YZO are comparable to those on YZO and ZrO$_2$ [7, 44]. In particular, using combined TPD, XPS, and STM approach, it was reported that the average water adsorption energy on ZrO$_2$ is around 0.57 eV that agrees well with DFT calculations [44]. This indicates that such adsorption energy range is good enough for typical SOEC operations. To further analyze the adsorption mechanism, we analyze the projected density of states (PDOS) between the oxygen 2p states of water (as the stable water adsorption orientation is that of oxygen interacting with nickel) and that of nickel 3d states. These are shown in Figure 5. As such processes occur near the Fermi level, we looked into the states hybridization and changes in the vicinity of this region. In the case of

Figure 4: Optimized water adsorption configurations on (a) ScZO-Ni$_3$, (b) YZO-Ni$_3$, and (c) ScZO-Ni$_5$.

Figure 5: Projected density of states for (a) Ni$_3$-ScZO, (b) Ni$_3$-YZO, and (c) Ni$_5$-ScZO systems.
Ni$_3$-ScZO and Ni$_3$-YZO, the hybridization of the O 2p and Ni 3d states near the Fermi level is effectively the same, resulting to the same water adsorption energy. As for the Ni$_5$-ScZO case, it can be observed that supposedly, since there are more available O 2p and Ni 3d states near the Fermi level, the resulting water adsorption energy should be higher compared to Ni$_3$-ScZO and Ni$_3$-YZO. However, it is also noticeable that the hybridization between these states is in a way not as good as that of the Ni$_3$ cases. As such, even though there are more available states near the Fermi level, the relatively poor hybridization between the O 2p and Ni 3d states could have reduced water adsorption energy. This might explain the resulting very close water adsorption energy values among the Ni$_3$-ScZO, Ni$_3$-YZO, and Ni$_5$-ScZO systems.

In terms of water dissociation (first hydrogen), activation energy barriers of 2.77 eV and 2.74 eV were obtained for Ni$_3$-ScZO and Ni$_3$-YZO, respectively, indicating that there is a very small dissociation energy barrier difference between the two (see Figure 6). Interestingly, the activation energy for the dissociation of the first hydrogen atom from water on Ni$_5$-ScZO is 1.70 eV, quite a significant reduction from the Ni$_3$ case. This could imply that the larger the Ni cluster is, the lower is the dissociation energy barrier. The only caveat of large Ni cluster is the smaller binding energy on either ScZO or YZO (as Ni$_5$ does not bind to YZO, water dissociation energy barriers on it were not calculated). Analyzing the transition state structures, it is noted that in the case of Ni$_5$-ScZO and Ni$_3$-YZO, the transition state is that configuration where one hydrogen atom detaches from water, forming an OH group and a free hydrogen atom. On the other hand, the transition state structure for Ni$_3$-ScZO is the stretching of one H bond before being detached and adsorbed on one of the nickel atoms. Such mechanisms explain why a relatively smaller activation barrier was obtained for Ni$_5$-ScZO system. The calculated water dissociation barriers are quite higher compared to those on Ni(100) and Ni(111) surfaces [42], but the dissociation barrier on Ni$_5$-ScZO is comparable to those on Ni cluster/Cu(111) alloy [43].

To further assess the water electrolysis potential of these systems, dissociation barriers of the second hydrogen atom from OH were also calculated (Figure 7). Looking at the calculated minimum energy pathways (MEP), it can be ob-

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**Figure 6**: Minimum energy pathway (MEP) of first hydrogen dissociation from water molecule adsorbed on (a) Ni$_3$-ScZO, (b) Ni$_3$-YZO, and (c) Ni$_5$-ScZO.

**Figure 7**: Minimum energy pathway (MEP) of hydrogen dissociation from OH (second hydrogen dissociation from water molecule) adsorbed on (a) Ni$_3$-ScZO, (b) Ni$_3$-YZO, and (c) Ni$_5$-ScZO.
served that there are two transition states from which an effective energy barrier can be extracted. This feature of the MEP suggests that the processes involve in dissociating the second hydrogen atom are more sophisticated compared to the first one. Regardless, we are only after the effective energy barrier, and as such, we consider the transition state with the highest relative energy with reference to the initial state as the effective dissociation barrier. In light of the obtained complex MEPs, for all cases, the first transition state structure points to the onset of stretching of the second hydrogen bond, while a second local minima appeared wherein the structure is that of a stretched second hydrogen bond. Such structures imply that in the case of second hydrogen dissociation, a stretched hydrogen bond is a local minimum (although higher in energy compared to the fixed points local minima). On the other hand, the second transition state structure is a configuration in which the second dissociated hydrogen atom adsorbs on a nickel atom. This denote that adsorbing another hydrogen atom on nickel clusters requires additional energy. This might be due to an already adsorbed hydrogen atom, which give a repulsive interaction to the other. Going back to the effective activation barriers, in the case of Ni$_3$-ScZO, taking the second hydrogen atom from OH requires an effective energy of around 2.90 eV. This is a jump of just 0.13 eV from the dissociation barrier of the first hydrogen atom, indicating that dissociating the second hydrogen atom from OH on Ni$_3$-ScZO is almost as feasible as that of the first. For Ni$_3$-YZO, the dissociation barrier for taking out the second hydrogen atom from OH is found to be 3.43 eV. This value is significantly higher than the first hydrogen dissociation barrier of 2.74 eV, implying that on Ni$_3$-YZO taking out the second hydrogen atom requires an essentially higher energy. Finally, the second hydrogen dissociation energy barrier for water on Ni$_3$-ScZO is found to be 2.16 eV, significantly lower than the calculated values for Ni$_3$-ScZO and Ni$_3$-YZO. This implies that water dissociation via removal of its first and second hydrogen atoms is most feasible on Ni$_3$-ScZO, albeit still relatively a little high. However, this high activation energy barriers could be lowered via external energy source (e.g., applied electrode potential, relatively higher operating temperature, etc), which is typical in most SOEC operations. And this 2.16 eV is not that much, the operating temperature of such SOEC material would be much lower than 800°C. As an overall outlook, this work demonstrates that the size of small Ni clusters affects water dissociation activation barriers, while the stabilization agent (Sc or Y) influence the binding stability of small Ni clusters on zirconia.

**IV. CONCLUSIONS**

To conclude, this work investigated the binding of small Ni clusters Ni$_3$ and Ni$_5$ on Y- and Sc-stabilized zirconia, and subsequently, water adsorption and dissociation on these systems. Our calculations revealed that the binding of Ni clusters depend on the cluster size and the stabilizing atom in zirconia. In this case, Ni$_3$ and Ni$_5$ tend to adsorb better on ScZO compared to that on YZO. This could be attributed to the higher electronegativity of Sc compared to Y. On the other hand, water adsorption is found to be strong on both ScZO and YZO, regardless of the size of the Ni cluster. As hydrogen evolution depends on the availability of hydrogen atoms on the surface, dissociation activation energy for the first hydrogen atom is calculated and is found to be the lowest for Ni$_3$-ScZO. The same is true for the second hydrogen atom. As such, the dissociation barriers tend to be reduced for larger Ni clusters. These insights are of importance in the design of electrocatalytic systems, especially SOECs, for eventual hydrogen evolution and production.

**Acknowledgments**

We would like to acknowledge the Commission on Higher Education-Philippine California Advanced Research Institute (CHED-PCARI) for grant support under Project 1 of the GREEN POWER program: Hydrogen Generation Using Solid Oxide Electrolysis Cells (SOEC) (IID 2015-009).

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DOI: 10.1380/ejssnt.2019.117
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