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Computational design of Ni-Zn based catalyst for direct hydrazine fuel cell catalyst using density functional theory

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Abstract

Direct Hydrazine Fuel Cell (DHFC) is a promising alternative for the hydrogen fuel cell because hydrazine (N_2H_4) is much easier to produce and store than hydrogen. Research into DHFC catalyst has shown that use of Ni-Zn compound as catalyst produces higher power density than using pure Ni as catalyst. This paper presents some findings of our investigation on Ni-Zn based catalyst for DHFC applications by using density functional theory (DFT). Multiple configurations of Ni-Zn DHFC catalysts were modeled using DFT. Hydrazine adsorption onto (111) catalyst surface was studied with adsorption energy and density of states (DOS) collected as data and used in analysis. The supercells consist of 4 layers of 4x4 atoms forming the (111) surface, with structure variation for the top 2 layers and the other 2 bottom layers comprised of Ni atoms to simulate the bulk of the electrodes. The adsorption sites used were the top sites, either Zn or Ni atoms. For every structure variation, adsorption on Ni atoms results in lower adsorption energies than on Zn atoms. Increasing concentration of Zn atoms on catalyst surface raises the adsorption energy of hydrazine on Zn atoms. Adsorption energies of hydrazine were higher on every configurations than on pure Ni (111) surface except for one catalyst surface in which Zn concentration was 25% and hydrazine was adsorbed atop a Ni atom. There was also rotation of hydrazine molecule from its usual *anti* adsorption conformation for that particular configuration.

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1. Introduction

Fuel cell is probably the most viable alternative to the internal combustion engine for automotive applications. Moreover, since it essentially converts chemical fuel into electricity (without the carbon emission by-product of conventional engines), its application is not limited to the automotive field. The development of hydrogen fuel cell, long considered to be the simplest and best type of fuel cell, has been focused for a long time on the problem of production and safe storage of hydrogen[1,2]. Efficient hydrogen production still requires fossil fuels, while safely storing it without the risk of explosion or leakage is an exceedingly difficult proposition.

Hydrazine fuel cell is a lesser-known alternative to the hydrogen fuel cell. Hydrazine (N_2H_4) is a by-product of ammonium production, a well-established method in the industrial world. The compound is liquid in room temperature and pressure, making it easier to store and transport than hydrogen[3]. These qualities make hydrazine fuel cell a promising alternative to hydrogen fuel cell.

To facilitate the reactions in a fuel cell and produce more electric power from a single cell, a catalyst is necessary. Heterogeneous catalysis (solid catalyst) is often used and platinum (Pt) is now considered vital in catalysts of various fuel cells[4]. It is virtually irreplaceable for proton exchange membrane (PEM) fuel cells because the catalyst must have stability in the acidic work environment in addition to delivering good performance. However, Pt is relatively expensive due to its scarcity, which in turn raises the production cost of fuel cells and negatively affecting market demand for them.

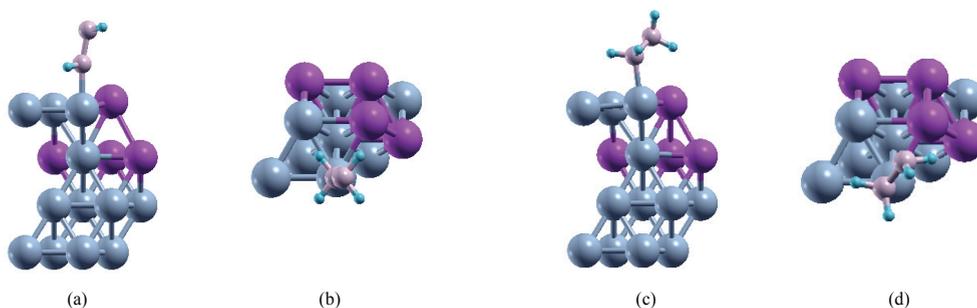


Fig. 1. Visualization of hydrazine adsorption on Ni₂₅ surface, with gray spheres representing Ni, purple representing Zn, pink representing N, and cyan representing H atoms, initial condition (a) side and (b) top views, as well as optimized coordinates (c) side and (d) top views

Direct hydrazine fuel cell (DHFC) is a form of hydrazine fuel cell classified as an alkaline anion-exchange membrane fuel cell (AAEMFC). It uses hydrazine (N₂H₄) as its fuel and produces nitrogen and water as waste. The full reaction taking place inside of DHFCs[5]:



can be expanded in terms of the reactions taking place in the anode:



and cathode:



The hydrazine oxidation reaction (Reaction II) occurs in the anode and is assisted by heterogeneous catalysis, which serves to lower the activation energy of said reaction. Hydrazine adsorption onto catalyst surface precedes the reaction. This raises the importance of adsorption energy as one of the physical quantities affecting the reaction; if adsorption is more energetically favorable, it will further lower the activation energy and increase the reaction rate in the anode in accordance with Arrhenius equation. An improved reaction rate naturally leads to improvement of fuel cell power density.

The alkaline working environment of DHFC means that other transition metals are possible alternatives for the more expensive noble metal Pt[6]. These include iron (Fe), nickel (Ni), cobalt (Co), zinc (Zn), palladium (Pd), and more. So far none have been able to deliver performance on par with Pt, although Ni, Co, and Zn have experimentally been proven to generate greater power density than Pt when used as DHFC catalyst[7].

Computational modelling of materials has an advantage over experimental pursuits in that more investigations can be carried out with less cost. This includes binary and ternary compounds with varying compositions. The binary compound of Ni-Zn was chosen in the hope that its surface can produce better performance than pure Ni. This paper presents some findings of our investigation into Ni-Zn based catalyst for DHFC applications by using density functional theory (DFT).

2. Model

Spin polarized plane-wave DFT [8,9] calculations were done as implemented in the Quantum ESPRESSO code[10] using PBE-GGA exchange correlation functionals[11,12]. Core electrons were treated with Projector Augmented Wave (PAW) method[13,14]. Cutoff energy of 30 Ry (408.17 eV) was used for all calculations. Hydrazine adsorption onto DHFC anode surface was simulated by structure relaxation of Ni-Zn (111) surface and hydrazine molecule (N₂H₄) initially located 2 Å on top of the active site. Marzari-Vanderbilt smearing was used to treat the metallic Fermi surface[15]. Calculations involving catalyst surface used 7x7x1 mesh of k-points in the Brillouin Zone per the Monkhorst-Pack sampling method[16]. Surfaces were visualized using the XCrySDen code[17].

Catalyst surface was modeled using the slab model. The supercell used was comprised of 4 layers of 4x4 atoms (corresponding to 0.25 ML coverage) and a gap of 12 Å between the surface and the top of the supercell so that interactions

between slabs are negligible. Zn atoms are only located near the surface of the catalyst; 2 top layers of atoms are composed of 8 Ni and 8 Zn atoms, while the 2 bottom layers are fully composed of Ni atoms to duplicate the effect of the catalyst bulk. Structure variation was made with the parameter of Zn concentration on the topmost layer of the catalyst (111) surface. The active sites chosen for hydrazine adsorption were top sites (either of Zn or Ni atom) according to a previous study by Aji, Purwoko, et al[18].

3. Methods

3.1. Catalyst surface

(111) surface was chosen because it is the most stable among (111), (110), and (100) surfaces and thus would be energetically favorable in formation of the catalyst surface. Atomic positions of pure Ni (111) surface were used as initial positions. 8 Ni atoms from the top 2 layers were then substituted by 8 Zn atoms according to the structure variations considered. The catalyst surface then underwent structural optimization, changing its atomic positions slightly (surface reconstruction) due to the different atomic radii between the substituted Ni and Zn atoms.

Structure variations were based on Zn atom concentration on the topmost layer of the catalyst surface, giving 5 variations: 0%, 25%, 50%, 75%, and 100%. 2 possible active sites (Zn and Ni top sites) are available for 25%, 50%, and 75% structures and only 1 possible active site (Zn or Ni top site) for both 0% and 100% structures. As a result, there were a total of 8 adsorption possibilities considered. Listed according to the active site and top layer Zn concentration, in that order, they are Ni0, Ni25, Zn25, Ni50, Zn50, Ni75, Zn75, and Zn100.

3.2. Hydrazine molecule

The 3 conformations of hydrazine molecule (*gauche*, *anti*, and *cis*) were considered. An isolated hydrazine molecule is most stable under the *gauche* conformation, while its adsorption on pure Ni (111) surface is most stable under *anti* conformation[19]. As such, in this study, *anti* conformation was used as initial position (pre-relaxation) for all surfaces, with a 2 Å initial distance from a N atom and the active site and an arbitrary 80° angle between the N-N bond and the xy plane as shown in Figure 1a and 1b. To calculate the adsorption energy, the total energy of a single isolated hydrazine molecule, in *gauche* conformation, is also computed using a 20 Å x 20 Å x 20 Å cell with a uniform 5x5x5 mesh of k-points in the Brillouin Zone.

3.3. Adsorption energy

Adsorption energy or E_{ads} is obtained for every catalyst surface using Equation (1):

$$E_{ads} = E_{tot} - E_{surf} - E_{isol} \quad (1)$$

Where E_{tot} is the total energy of catalyst surface and adsorbed hydrazine molecule, E_{surf} is the total energy of the catalyst surface, and E_{isol} is the total energy of an isolated hydrazine molecule in *gauche* conformation. Total energy was obtained by means of a self-consistent field (scf) calculation done after structure optimization.

4. Results and Discussion

4.1. Hydrazine adsorption on catalyst surfaces

Table 1. Adsorption energy of hydrazine on catalyst surfaces

| Zn concentration on top layer (%) | Adsorption energy on Ni (eV) | Adsorption energy on Zn (eV) |
|-----------------------------------|------------------------------|------------------------------|
| 0 | -0.522 | |
| 25 | -0.634 | -0.514 |
| 50 | -0.299 | -0.181 |
| 75 | -0.486 | -0.151 |
| 100 | | -0.071 |

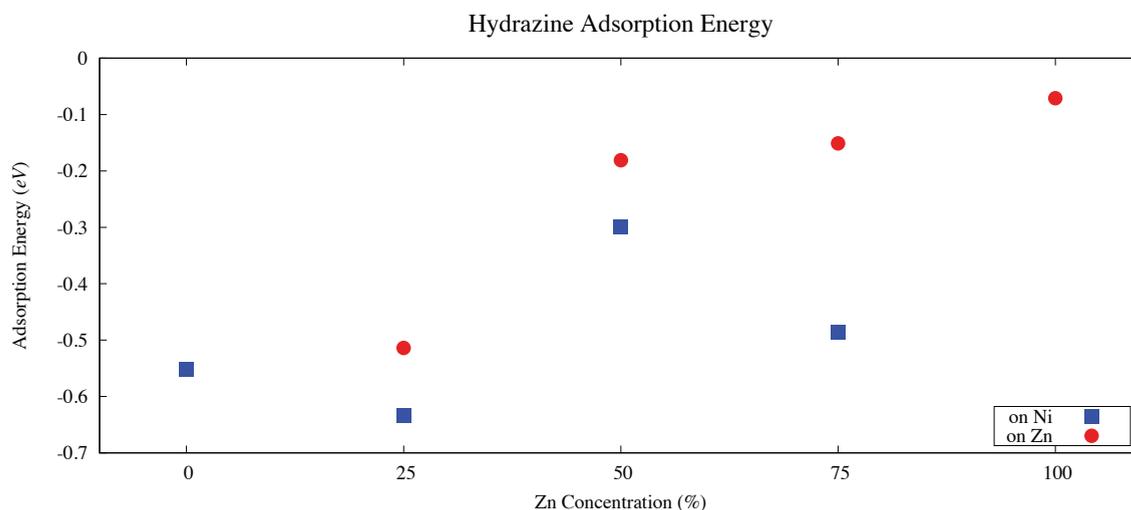


Fig. 2. Adsorption energy of hydrazine molecule with 0.25 ML coverage on various Ni-Zn (111) surfaces with Ni and Zn active sites

In general, adsorption of hydrazine molecule on top of Ni atom is energetically favorable; adsorption on Ni atoms result in lower adsorption energies than on Zn atoms. The concentration of Zn atoms on the top layer of catalyst surface also increases repulsion between hydrazine molecule and catalyst surface. As seen in Table 1 and Figure 2, increasing the concentration of Zn atoms on the catalyst surface generally increases the adsorption energy to the point where hydrazine adsorption on Zn100 surface can no longer be classified as chemisorption. One surface, Ni25, is promising in terms of adsorption energy; hydrazine adsorption on this surface resulted in an adsorption energy of -0.634 eV, slightly more stable compared with that of on pure Ni (111) surface of -0.6 eV.

Ni25 also produced an interesting effect on hydrazine adsorption conformation. As stated earlier, for all surfaces an *anti* conformation was used for the hydrazine molecule's initial positions. This *anti* conformation was broken for Ni25, Zn25, and Ni75; structural optimization caused the hydrazine molecule to be rotated on its N-N bond, resulting in a configuration not unlike the *gauche* conformation (see Figure 1c and 1d). This phenomenon might be correlated with the effect of Zn atoms on the catalyst surface and also with the increase in stability relative to other surfaces.

4.2. Density of states (DOS)

Density of states (DOS) and projected density of states (PDOS) were obtained and observed for all surfaces, particularly the PDOS from the adsorbed hydrazine N atom p states and from the active site (either Zn or Ni) metallic atom d states. The result mostly agrees with a previous investigation into hydrazine adsorption on Ni (111) surfaces by Agusta and Kasai[19]. Adsorbate-substrate interactions give rise to three states marked in Figure 3: antibonding (AB) states were found just below the Fermi energy, while bonding (B) and dative (D) states were found further below.

The substitution of Ni atoms with Zn atoms severely reduces the magnetic property of the catalyst surface. This is seen in the PDOS profile of all catalyst surfaces. Peaks for the majority spin occur in the same energy levels as for the minority spin. For pure Ni (111) surface, part of the AB state (contribution from minority spin) lies above the Fermi energy. This lessens the repulsion between catalyst surface and the hydrazine molecule, thus increasing stability compared with Ni-Zn (111) surfaces.

For hydrazine adsorption on metallic surfaces, the highest occupied molecular orbital (HOMO) would be an antibonding (AB) orbital, while the bonding (B) orbital is lower in energy. For a free hydrazine molecule, the *gauche* conformation creates degeneracy between this AB orbital (HOMO) and the lower energy bonding (B) orbital (HOMO-1), resulting in more stability as a consequence of Walsh's rule. This degeneracy is broken in adsorption onto pure Ni (111) surface, resulting in the *anti* configuration being more favorable than *gauche*[19]. This is exactly what happened for most of the Ni-Zn surfaces in this work.

Different results were obtained for 3 particular surfaces, however. The hydrazine molecule rotation on surfaces Ni25, Zn25, and Ni75 naturally produced different PDOS profiles than the other surfaces, seen in Figure 4; the D peaks in between -6 and -8 eV disappeared, the B peaks were shifted further below the Fermi energy, and the AB peaks were severely delocalized. The delocalization of AB peaks were also accompanied by weaker hybridization between N atoms' p_z orbitals and metallic atoms' d_z^2 orbitals for the AB orbital. This weakens the repulsion between catalyst surface and hydrazine molecule, thus producing relatively stronger adsorption than on other surfaces.

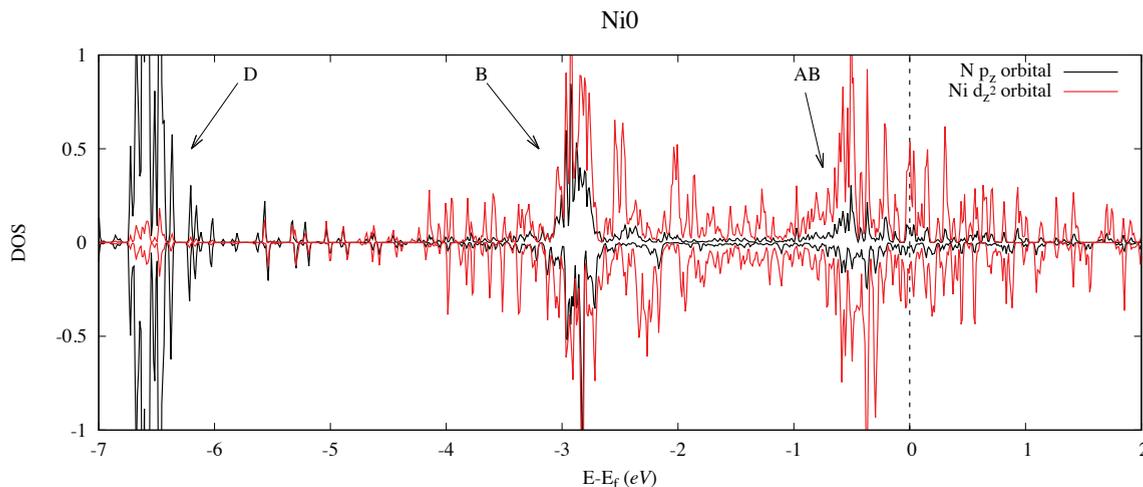


Fig. 3. PDOS of a bonded N atom p_z orbital (black) and the active site Ni atom d_z^2 orbital (red) of the Ni0 catalyst surface

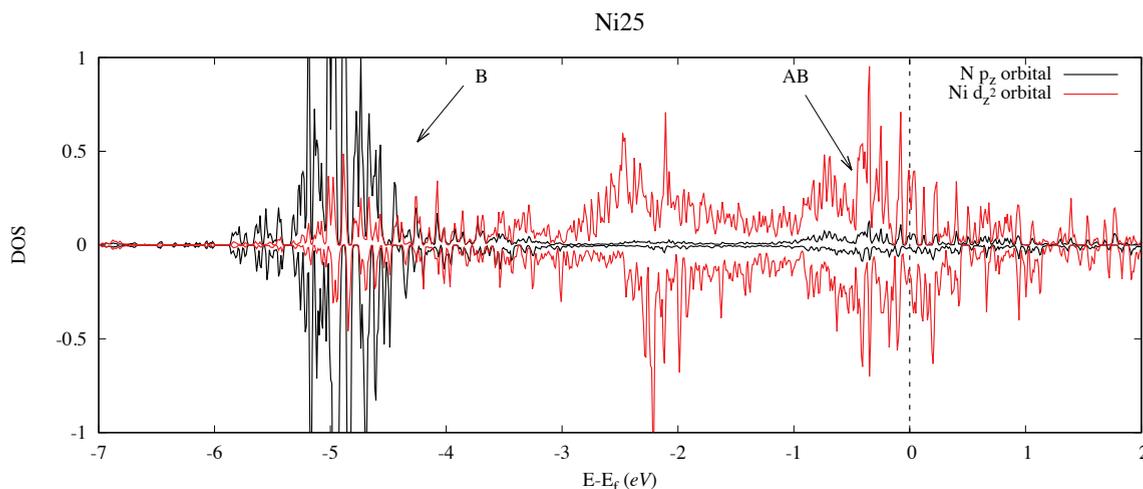


Fig. 4. PDOS of a bonded N atom p_z orbital (black) and the active site Ni atom d_z^2 orbital (red) of the Ni25 catalyst surface

The rotation of hydrazine molecule can be seen as a tendency to revert to *gauche* conformation to gain stability in the same way that a free hydrazine molecule gains stability with the *gauche* conformation. The full occupation of the AB and B states introduces lone-pair repulsion and prevents charge transfer between adsorbate and surface. Adsorption in *gauche* conformation then provides a stabler configuration than in *anti* (where stability is derived from charge transfer between hydrazine and catalyst surface).

Why these three particular surfaces induced a conformation shift in the hydrazine molecule is not known. Since one surface (Ni25) produced a higher adsorption energy than pure Ni (111) surface, we believe that further investigation is necessary.

5. Conclusion

Hydrazine adsorption on Ni-Zn based catalyst for DHFC application was studied. The Zn atom was found unsuitable as an active site for hydrazine adsorption, with a highest adsorption energy value of -0.071 eV for a catalyst surface completely covered in Zn. The stablest adsorption achieved, with energy of -0.634 eV, was hydrazine adsorption onto Ni atom on catalyst surface with 25% concentration of Zn atoms on the topmost layer. On this surface and 2 others (Zn₂₅, Ni₇₅) hydrazine was adsorbed with the *gauche* conformation as opposed with the usually more stable *anti*. Why these 3 surfaces in particular induced hydrazine conformation change is unknown.

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