First Principles Investigation for H\textsubscript{2} Dissociative Adsorption on Ni and Cr-Decorated Ni Surfaces – An Application to Alkaline Polymer Electrolyte Fuel Cell

Allan Abraham B. Padama, Mary Clare S. Escaño, and Hideaki Kasai*

Department of Precision Science & Technology and Applied Physics, Graduate School of Engineering, Osaka University, Suita, Osaka 565-0871, Japan

Melanie Y. David
Physics Department, College of Science, De La Salle University, Taft Avenue, Manila 1004, Philippines

Hiroyuki Kawai
Toyota Motor Corporation, Susono, Shizuoka 410-1193, Japan

(Received 1 June 2010; Accepted 24 June 2010; Published 10 July 2010)

In this research, density functional theory (DFT) calculations for H\textsubscript{2} dissociative adsorption on Ni(111) and Cr-decorated Ni surfaces are performed to understand the adsorption mechanism on both surfaces as an application to alkaline polymer electrolyte fuel cell (APEFC). The Cr-decorated Ni (Cr\textsubscript{ML}/Ni(111)) surface is constructed by placing a monolayer of Cr atoms on the topmost layer of a Ni (111) surface. The potential energy scans for H\textsubscript{2} dissociative adsorption on both surfaces reveal that the activation barrier of Cr-decorated Ni surface is lower than that of the pristine Ni surface. For both surfaces, the H atoms are dissociated with a distance of 1.8 Å, but H\textsubscript{2} on Cr-decorated Ni surface has greater adsorption energy than for H\textsubscript{2} on Ni(111) surface. The density of states (DOS) shows that the presence of Cr increased the unoccupied states in the region around the Fermi level as compared to clean Ni surface. The increase in unoccupied states is supported by the computed total charges of the atoms before and after the Cr monolayer is added on the Ni surface which also implies a strong metal-to-metal interaction between Ni and Cr atoms. The difference in the charges of the H atoms and the surface atoms before and after the adsorption shows an easier transfer of charges between H atoms and surface atoms of Cr-decorated Ni surface than the surface atoms of Ni(111) surface. [DOI: 10.1380/ejssnt.2010.325]

Keywords: Density Functional Theory; Alkaline Polymer Electrolyte Fuel Cell; Dissociative Adsorption; Ni(111); Cr-decorated Ni(111)

I. INTRODUCTION

Alkaline fuel cells (AFC) are one of the oldest fuel cell technologies developed in the attempt of using hydrogen as an alternative energy source. Evidently, it is used by NASA in their space exploration programs in the 1960’s [1, 2]. The conventional AFC uses liquid electrolyte and non-noble catalysts such as Ni and Ag for the anode and cathode electrodes, respectively. This gives advantage over other types of fuel cells due to the cheaper costs of the materials. Despite the good internal thermal management provided by the circulating electrolyte, problems on leakage and precipitation had always been an issue. Exposure of the KOH electrolyte on air causes it to react with CO\textsubscript{2} and leads to carbonate precipitation which affects the performance of the fuel cell [3]. Moreover, electrolyte leakage on the electrodes that leads to degradation has been observed and usually marks the lifetime of an AFC.

Due to these encountered problems, AFC lost its popularity and proton exchange membrane fuel cell (PEMFC) had become the interest of scientists and engineers. The use of Nafion membrane became very convenient and had solved the problem of leakage. However, this requires precious metals as catalyst due to the membrane’s high acidity that causes corrosion [4]. The Nafion itself is an expensive material and thus, the aim of having cheap source of energy still requires intensive research and investigation. Based on these circumstances, improvements on AFC have been studied for these past years. The degradation of the electrodes is investigated thoroughly and the performance of AFC has been reported [1, 5–9].

As a result, alkaline polymer electrolyte fuel cell (APEFC) technology is developed which uses alkaline polymer electrolytes instead of the traditional liquid electrolyte. Recently, the group of Pan synthesized quaternary polysulfone electrolyte (QAPS) with microstructure characteristic comparable to Nafion, and can be dissolved and be processed into thin films [10]. They tested the performance of QAPS using Pt electrodes and have proven the strong alkaline nature of QAPS-OH by the clear electrochemical behavior of the Pt/QAPS interface. This evaluation has promoted the feasibility of QAPS for fuel cell applications. Earlier, the group of Lu had tested the performance of QAPS using Ni surface alloyed with Cr-decorated Ni surface for anode and Ag surface for cathode [11]. Although it is a prototype, their work represents an important advancement in the science and technology of fuel cells. They have proven the feasibility of polymer electrolyte fuel cells independent of precious metal catalysts. Lastly, they have predicted that Ni-based electrocatalysts might come back to center stage for research. Indeed, APEFC technology offers a great future as an alternative source of energy despite the needed improvements and intensive study on its performance, especially on the electrodes.

On the other hand, multilayer and heterogeneous catalysts have attracted interests in electronic structure engineering due to considerable number of applications and enhanced properties of the resulting material as compared to the parent metals. As a matter of fact, several stud-
ies have proven that formation of bimetallic surfaces produces large perturbations and changes in the electronic, chemical and catalytic properties of the entire system as compared to the characteristics and properties of the parent metals [12–14].

Thus, this present study is developed to investigate and compare the dissociative adsorption mechanism of H₂ molecule on Ni and Cr-decorated Ni surfaces using density functional theory. Basically, Ni(111) and a monolayer of Cr atoms on Ni(111)–CrML/Ni(111)–surfaces are used for this purpose. Alloying and multilayer formation of Ni to other metals are some of the possible solutions to improve its reactivity while solving the problem on degradation [15, 16]. Cr electrodeposits have been proven and are used extensively to protect the base metal from corrosion [17]. The incorporation of Cr to Ni also enhances the electrical and magnetic properties as compared to pristine Ni, thus giving the desired characteristic of an anode for fuel cells [18–20]. Consequently, theoretical description and comparison on the reactivity of H₂ on Ni and Cr-decorated Ni surfaces are necessary and will be a substantial contribution for the realization of fuel cell technology that is free from noble metal catalysts.

In this study, potential energy scans (PES) are used to describe the mechanism of H₂ dissociative adsorption on the surfaces. The density of states of the surfaces are analyzed to predict the changes in the properties of the Ni(111) surface after placing the monolayer of Cr atoms on the topmost layer of Ni. Moreover, the total charges of the Ni atoms before and after placing the Cr atoms are compared to verify the results obtained from the density of states. The charges of the Cr atoms before and after placing them on the Ni surface are also analyzed. Finally, the difference on the charges of the H and the surface atoms before and after the adsorption process are determined to confirm the results of the potential energy curves. These factors and properties completely explain the details of H₂ dissociative adsorption on Ni and Cr-decorated Ni surfaces.

II. COMPUTATIONAL DETAILS

Density functional theory is employed in this study using Vienna ab initio simulation package (VASP) [21–24]. The exchange-correlation energy is treated using generalized gradient approximation (GGA) within the Perdew-Burke-Ernzerhof (PBE) functional [25, 26]. Ionic cores are described by projector augmented wave (PAW) potentials [27] and the Kohn-Sham one-electron valence states are expanded in a basis of plane waves with energy cutoff of 270 eV. Convergence tests are performed for the equilibrium lattice constant of the bulk Ni, the number of layers to be used and for the allowed number of k-points. The equilibrium lattice constant of Ni obtained is 3.52 Å which is in agreement with experimental results [28]. In all the calculations performed, Brillouin-zone integrations are used on a grid of 8×8×1 Monkhorst-Pack k points. Five layers of Ni in (111) facet is used with four atoms in each layer. A monolayer of Cr is placed on the top-most layer of the Ni(111) surface to define the Cr-decorated Ni surface. The Cr atoms are initially placed on top of the Ni atoms in the topmost layer of Ni(111) surface. In the optimization process, all the atoms of the three bottom layers are kept fixed to maintain the bulk parameter of the Ni while allowing full relaxation for the remaining atoms. The optimized structures of both surfaces are shown in Fig. 1.
For the dissociative adsorption configuration, the hollow-bridge-hollow conformation is adopted from the works of Nobuhara et al. [29] where the center-of-mass of H$_2$ is kept fixed on the bridge site while the hydrogen atoms are dissociated towards the hollow sites as shown in Fig. 2. In this mechanism, H$_2$ is allowed to approach the surface, decreasing the height $Z$, while performing dissociation, that is, increasing the bond length $r$. In each conformation, a static calculation of the total energy of the system is performed. The calculated potential energies are used to construct the potential energy surface (PES) for H$_2$ dissociative adsorption on the surfaces. Details of the analysis using density of states (DOS) and charge distribution are used to support the result of the calculation. In this regard, a 6-layer Cr(001) surface is also constructed in which the equilibrium lattice constant obtained for the bulk Cr is 2.84 Å. This is in good agreement with experimental result, 2.88 Å [30]. The dissociative adsorption mechanism for both surfaces are presented and explained in the next section.

### III. RESULTS AND DISCUSSIONS

The parameters of the optimized structures of the surfaces are shown in Fig. 1. Cr is bcc in nature. However, the optimized structure shows that the atoms take the fcc structure of the Ni(111) surface. This is in good agreement with experiments where electron diffraction pattern results reveal the fcc structure of such system [18, 31]. It is also observed in an experiment that diffusion of the Cr and Ni elements across the interfaces between the layers does not occur, which further supports the result of the optimized structure [20]. It can be noticed that the distance between layers 1 and 2 of the Ni surface has increased with the presence of the Cr atoms while the distance between layers 2 and 3 decreased. From this, one can say that there is a strong metallic interaction between the monolayer of Cr and layer 1 of the Ni. The result of this interaction will be discussed later in this section.

The PES for the dissociative adsorption of H$_2$ on Ni(111) surface is shown in Fig. 3(a). Far from the surface, at $Z = 3.0$ Å, the H$_2$ molecule bond length is 0.75 Å, which is the equilibrium bond length. H$_2$ is gradually stretched wherein, at $Z = 1.6$ Å, the distance between the H atoms is increased to 1.0 Å. At this value of $Z$, the molecule overcomes an activation barrier of $\sim 0.25$ eV to continue the adsorption process. The calculated activation barrier is in good agreement with existing results [29, 32, 33]. H$_2$ is totally dissociated when $Z = 1.4$ Å where the distance between the H atoms is 1.8 Å. The dissociative adsorption ends at $Z = 1.0$ Å, where the two H atoms are adsorbed and became stable on the Ni(111) surface.

On the other hand, the potential energy curve for the dissociative adsorption of H$_2$ on Cr$_{ML}$/Ni(111) surface is shown in Fig. 3(b). The initial conditions of the system are the same with that of the H$_2$–Ni(111) system. H$_2$ is gradually elongated to 1.0 Å when it is 1.8 Å above the surface while overcoming a $\sim 0.18$ eV activation barrier. It will totally dissociate when $Z = 1.7$ Å where the distance between the H atoms is 1.8 Å. The most stable configuration is when the two H atoms are adsorbed with $Z = 1.2$ Å above the surface. For both systems, the H$_2$ molecule is totally dissociated with a distance of 1.8 Å between the H atoms. This distance is more than twice of the equilibrium bond length, 0.75 Å which implies that there is already no interaction between the H atoms in such case.

The insets in each figure describe the reaction path of H$_2$ on the surfaces. These also show the difference on
The activation and adsorption energies on each surface. The presence of Cr atoms reduced the activation barrier for the dissociative adsorption of H$_2$, from $\sim$0.25 eV for Ni(111) to $\sim$0.18 eV for Cr$_{ML}$/Ni(111). This result is remarkably good for the objective of this present work and is quite comparable to the activation barrier obtained for H$_2$ adsorption on Pt surface [34, 35]. The distance of the most stable position of the H atoms from the surface is increased, from 1.0 Å for Ni(111) to 1.2 Å for Cr$_{ML}$/Ni(111). Furthermore, the adsorption energies of H$_2$ are $\sim$0.75 eV and $\sim$1.32 eV for Ni(111) and Cr$_{ML}$/Ni(111) surfaces, respectively.

To further understand the decrease in the activation barrier in the presence of Cr on Ni surface, the density of states (DOS) of both surfaces is analyzed. The total DOS of both surfaces (Figs. 4(a) and 4(b)) are almost the same. However, a closer look on the region near the Fermi level defines the difference (Fig. 4(c)). This is consistent with experiment where results of electron energy loss spectroscopy (EELS) exhibit similar intensity variations but a shift of the maximum density of states near the Fermi level is observed upon alloying of Cr in Ni [36]. The density of states of a 6-layer Cr(001) slab was also presented in Fig. 4(c) to give a more clear interpretation for the DOS obtained with Cr$_{ML}$/Ni(111).

It is evident that there is a greater number of unoccupied states in the Cr$_{ML}$/Ni(111) surface as compared with the Ni(111) surface in the region near the Fermi level. Looking at the figure, one can say that donation of states happened when the monolayer of Cr is placed on top of the Ni surface. Thus, it can be assumed that the electrons of Cr atoms have occupied the available states of the Ni atoms below them. This results to the strong interaction between the Ni and Cr atoms as mentioned in the first part of this section. The transfer of electrons increased the unoccupied states of Cr$_{ML}$/Ni(111) surface as observed in the DOS (Fig. 4(c)). This is further supported from the figure which shows that pure Cr has greater unoccupied states as compared to Cr$_{ML}$/Ni(111) surface—corresponding to the charge transfer from Cr to Ni atoms.

To prove this, the total charges of the atoms are calculated with the aid of Bader charge analysis [37–39]. Fig-
TABLE I: The charge difference of the H and the surface atoms of (a) Ni(111) and (b) Cr\textsubscript{ML}/Ni(111) surfaces before and after the adsorption of H\textsubscript{2}. The positive (+) and negative (−) values represent gain and lose of charge, respectively. The numbers indicated for each atom correspond to their positions as illustrated in Fig. 2.

(a) Atoms Charge Difference (e)  
Ni (1) −0.0986  
Ni (2) −0.1094  
Ni (3) −0.1261  
Ni (4) −0.1313  
H (5) +0.2971  
H (6) +0.1544  

(b) Atoms Charge Difference (e)  
Cr (1) −0.2301  
Cr (2) −0.2458  
Cr (3) −0.2270  
Cr (4) −0.2319  
H (5) +0.5978  
H (6) +0.3966  

Figure 5(a) shows the charges of the Ni atoms before and after the Cr layer has been added on the topmost layer of the Ni surface. Atoms of layers 1 and 2 of the Ni(111) have a redistribution of charges and gained considerable amount of charges when the Cr atoms are placed above them. These charges definitely came from the Cr atoms because the total charge of the Ni atoms below layer 2 did not change. This phenomenon (metal to metal interaction) is also observed experimentally for the case of Pt-Ru bimetallic cluster complexes wherein the reactivity is enhanced due to donation of states and transfer of charges between the Pt and Ru atoms [40]. Moreover, the Cr atoms have decreased in charges when placed on top of the Ni surface as shown in Fig. 5(b). These support the result obtained for the DOS of Cr\textsubscript{ML}/Ni(111) surface where the unoccupied states near the Fermi level have increased. Furthermore, the results obtained completely elaborate and verify the donation of states and the transfer of charges from Cr to Ni that is explained above using the density of states.

To determine the transfer of charges before and after the adsorption of H\textsubscript{2}, the charge difference of the H atoms and surface atoms for both surface are also calculated. Tables I(a) and I(b) shows the charge difference for H\textsubscript{2} and the surface atoms of Ni(111) and Cr\textsubscript{ML}/Ni(111). The positive (+) and negative (−) values represent gain and lose of charge, respectively. The greater values for Table I(b) as compared to Table I(a) indicate a better interaction between the H atoms and the surface atoms of Cr\textsubscript{ML}/Ni(111) than that of the surface atoms of Ni(111). This means an easier adsorption which results to lower activation energy. This further implies stronger binding energy for H\textsubscript{2} on Cr\textsubscript{ML}/Ni(111) surface which is supported by the results of the calculations. More importantly, this proves and elaborates the enhanced catalytic activity of the Ni surface in the presence of the monolayer of Cr towards H\textsubscript{2}.

IV. CONCLUSIONS

H\textsubscript{2} dissociative adsorption on Ni and Cr-decorated Ni surfaces are investigated using density functional theory. Specifically, Ni(111) and monolayer of Cr on Ni (Cr\textsubscript{ML}/Ni(111)) surfaces are used. The results show that the catalytic activity of Ni is enhanced by the presence of monolayer of Cr on the surface. Lower activation barrier is calculated for H\textsubscript{2} dissociative adsorption on Cr\textsubscript{ML}/Ni(111) than on clean Ni(111) as shown using the potential energy curves. For both surfaces, the H atoms are dissociated with a distance of 1.8 Å between them; but the H\textsubscript{2} on Cr\textsubscript{ML}/Ni(111) has greater adsorption energy than for H\textsubscript{2} on Ni(111) surface. This has originated from the increased number of unoccupied states in the region around the Fermi level of Cr\textsubscript{ML}/Ni(111) surface. Charges from the Cr atoms transferred to the Ni atoms, leaving the Cr atoms with unoccupied states. The total charge of the atoms has indeed verified this phenomenon and further implied the strong metal-to-metal interaction between Cr and Ni atoms. The charge difference of the surface atoms and the H atoms before and after the adsorption process indicates an easier but stronger interaction between the H atoms and the Cr\textsubscript{ML}/Ni(111) surface. This causes the decrease in the activation barrier as shown in the potential energy curves. Therefore, Cr\textsubscript{ML}/Ni(111) surface will be an efficient H\textsubscript{2} catalyst for the realization of precious-metal free APEFC.

Acknowledgments

We acknowledge Prof. Hiroshi Nakanishi for helpful discussion and contribution for the success of this research. This work is supported and in collaboration with Toyota Motor Corporation. This is also supported by the Ministry of Education, Culture, Sports, Science and Technology of Japan (MEXT) through Special Coordination Funds for the Global Center of Excellence (GCOE) program (H08) “Center of Excellence for Atomically Controlled Fabrication Technology”. AABP would like to personally thanks and acknowledge MEXT for the scholarship grant; the Physics Department, De La Salle University–Manila, Philippines and the Department of Science and Technology-Science Education Institute (DOST-SEI) of the Philippine Government for giving him the opportunity to pursue his studies in Osaka University. Some of the calculations were done using computer facilities of the ISSP Super Computer Center (University of Tokyo), the Yukawa Institute (Kyoto University) and the Japan Atomic Energy Research Institute (ITBL, JAERI).

[1] B. Y. S. Lin, D. W. Kirk, and S. J. Thorpe, J. Power Sources 161, 474 (2006).  
[2] F. Bidault, D. J. L. Brett, P. H. Middleton, and N. P.
Brandon, J. Power Sources **187**, 39 (2009).

[3] M. A. Al-Saleh, S. Gültekin, A. S. Al-Zakri, and H. Celiker, J. Appl. Electrochem. **24**, 575 (1994).

[4] S. Xue and G. Yin, Polymer **47**, 5044 (2006).

[5] E. Gülzow, M. Schulze, and G. Steinhalber, J. Power Sources **106**, 126 (2002).

[6] M. Schulze and E. Gülzow, J. Power Sources **127**, 252 (2004).

[7] M. Schulze, E. Gülzow, and G. Steinhalber, Appl. Surf. Sci. **179**, 251 (2001).

[8] J. Shim and H. Lee, Mater. Chem. Phys. **69**, 72 (2001).

[9] E. Agel, J. Bouet, and J. F. Fauvarque, J. Power Sources **101**, 267 (2001).

[10] J. Pan, S. Lu, Y. Li, A. Huang, L. Zhuang, and J. Lu, Adv. Funct. Mater. **20**, 312 (2010).

[11] S. Lu, J. Pan, A. Huang, L. Zhuang, and J. Lu, Proc. Natl. Acad. Sci. USA **105**, 20611 (2008).

[12] J. Rodriguez and D. Goodman, Science **257**, 897 (1992).

[13] M. Escaño, T. Kishi, S. Kunikata, H. Nakanishi, and H. Kasai, e-J. Surf. Sci. Nanotech. **5**, 117 (2007).

[14] M. C. Escaño, T. Q. Nguyen, H. Nakanishi, and H. Kasai, J. Phys.: Condens. Matter **21**, 492201 (2009).

[15] A. Kellou, N. Fenineche, A. Tadjer, and H. Aourag, Mater. Chem. Phys. **80**, 215 (2003).

[16] M. Singh, V. Kulshershtha, A. Kumar, N. K. Acharaya, and Y. K. Vijay, Pramana – J. Phys. **68**, 75 (2007).

[17] C. Huang, C. Chen, C. Hsu, and C. Lin, Scripta Mater. **57**, 61 (2007).

[18] S. Petrović, N. Bundaleski, M. Radović, Z. Ristić, G. Gligorijević, D. Perusko, M. Mitrić, B. Pravec, A. Zalar, and Z. Rakovečević, Nucl. Instrum. Methods Phys. Res. B **256**, 368 (2007).

[19] S. Brossard, P. Munroe, A. Tran, and M. Hyland, Surf. Coat. Technol. **204**, 1599 (2010).

[20] C. Huang and C. Chen, Surf. Coat. Technol. **203**, 3320 (2009).

[21] G. Kresse and J. Furthmuller, Comput. Mater. Sci. **6**, 15 (1996).

[22] G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11169 (1996).

[23] G. Kresse and J. Hafner, Phys. Rev. B **47**, 558 (1993).

[24] G. Kresse and J. Hafner, Phys. Rev. B **49**, 14251 (1994).

[25] J. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

[26] J. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **78**, 1396 (1997).

[27] P. E. Blöchl, Phys. Rev. B **50**, 17953 (1994).

[28] H. Robota, W. Vielhaber, M. Lin, J. Segner, and G. Ertl, Surf. Sci. **155**, 101 (1985).

[29] K. Nobuhara, H. Kasai, W. A. Diño, and H. Nakanishi, Surf. Sci. **566-568**, 703 (2004).

[30] J. Schäfer, E. Rotenberg, S. D. Kevan, and P. Blaha, Surf. Sci. **454-456**, 885 (2000).

[31] S. Brossard, P. Munroe, A. Tran, and M. Hyland, Surf. Coat. Technol. **204**, 1608 (2010).

[32] G. Kresse, Phys. Rev. B **62**, 8295 (2000).

[33] R. Baer, Phys. Rev. B **55**, 10952 (1997).

[34] N. Arboleda, H. Kasai, W. A. Diño, and H. Nakanishi, Jpn. J. Appl. Phys. **46**, 4233 (2007).

[35] N. Arboleda, H. Kasai, W. A. Diño, and H. Nakanishi, Thin Solid Films **509**, 227 (2006).

[36] H. A. E. Hagelin-Weaver, J. F. Weaver, G. Hoffund, and G. Salaita, J. Alloy. Compounds **389**, 34 (2005).

[37] G. Henkelman, A. Arnaldsson, and H. Jónsson, Comput. Mater. Sci. **36**, 354 (2006).

[38] E. Sanville, S. D. Kenny, R. Smith, and G. Henkelman, J. Comp. Chem. **28**, 899 (2007).

[39] W. Tang, E. Sanville, and G. Henkelman, J. Phys.: Condens. Matter **21**, 084204 (2009).

[40] R. Adams and T. Barnard, Organometallics **17**, 2885 (1998).