AB – INITIO DEVELOPMENT OF Ca-Ni BASED ALLOYS FOR METAL HYDRIDE BATTERIES

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submitted by **ORKUN MUĞAN** in partial fulfillment of the requirements for the degree of **Master of Science in Metallurgical and Materials Engineering Department, Middle East Technical University** by,

Prof. Dr. Canan Özgen ______________
Dean, Graduate School of **Natural and Applied Sciences**

Prof. Dr. Hakan Gür ______________
Head of Department, **Metallurgical and Materials Engineering**

Prof. Dr. M. Kadri Aydınol ______________
Supervisor, **Metallurgical and Materials Eng. Dept., METU**

Examining Committee Members:

Prof. Dr. Tayfur Öztürk ______________
Department of Metallurgical and Materials Engineering, METU

Prof. Dr. M. Kadri Aydınol ______________
Department of Metallurgical and Materials Engineering, METU

Assoc. Prof. Dr. Zafer Evis ______________
Department of Engineering Sciences, METU

Assist. Prof. Dr. Y. Eren Kalay ______________
Department of Metallurgical and Materials Engineering, METU

Assoc Prof. Dr. Yener Kuru ______________
Department of Materials Science and Engineering, Akdeniz University

Date: 11.09.2012

I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

Name, Last name : Orkun MUĞAN

Signature :

ABSTRACT

AB – INITIO DEVELOPMENT OF Ca-Ni BASED ALLOYS FOR METAL HYDRIDE BATTERIES

MUĞAN, Orkun

Master of Science, Department of Metallurgical and Materials Engineering

Supervisor: Prof. Dr. M. Kadri AYDINOL

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Ni-MH battery today is one of the most widely used secondary battery type because of its properties like secure use at high voltages, excellent thermal properties and consisting of environmentally acceptable materials. $LaNi_5$, as an anode material, is the dominant commercial active material for the Ni-MH battery industry. $CaNi_5$, belonging to same crystal structure, is an alternative for $LaNi_5$, due to higher hydrogen storage capacity, higher theoretical discharge capacity, light weight and low cost. However, low cycle life is the main restriction for the use of $CaNi_5$. In this study, effects of alloying was studied using an ab initio pseudo potential method. In this regard, formation energies of the $CaNi_5$ compounds having different alloying elements were calculated for the understanding of the effect of the alloying element on the stability of the compound. It was found that, all lanthanides and actinides and early transition metals (Sc, Y, Zr, Hf) replacing Ca and early transition metals (Sc, Ti, Zr, Hf) plus elements like Al, Si, P, Ge, Zn, Sn and Sb replacing Ni, decrease the formation energy of $CaNi_5$. Lower formation energy, compared to the pure compound, increases the stability which could improve the cyclic durability of $CaNi_5$ to be used as an anode in Ni-MH batteries. In addition, in order to investigate effects of alloying on Ca diffusion in $CaNi_5$, activation energies of Ca diffusion for different alloys were calculated by Nudged Elastic Band method (NEB) method.

Keywords: *Ni-MH battery, ab-initio development,* $CaNi_5$*,*

ÖZ

METAL HİDRİD BATARYALAR İÇİN Ca-Ni ALAŞIMLARININ AB INITIO İLE GELİŞTİRİLMESİ

MUĞAN, Orkun

Yüksek Lisans, Metalurji ve Malzeme Mühendisliği Bölümü

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Günümüzde, kullanım alanlarının geniş olması yüksek voltajlarda bile güvenli oluşları ve çevre dostu olmaları nedeniyle, Nikel – Metal Hidrid bataryaları en yaygın olarak kullanılan ikincil bataryalardan biridir. $LaNi_5$, Nikel – Metal Hidrid batarya endüstrisinde anot malzemesi olarak en fazla kullanılan aktif malzemedir. $LaNi_5$ ile aynı kristal yapıda olan $CaNi_5$ ise daha fazla hidrojen depolama kapasitesi, daha fazla deşarj kapasitesi, daha hafif ve ucuz oluşundan dolayı $LaNi_5$'in en büyük alternatifi konumundadır. Ancak çeviri ömrünün çok kısa olmasından dolayı bataryalarda aktif anot malzemesi olarak kullanılamamaktadır. Bu bağlamda, yapılan teorik çalışmada alaşımlı bileşiklerin ve hidrürlerinin formasyon enerjileri temel prensipler yöntemiyle hesap edilmiştir. Buna ek olarak NEB (nugged elastic band) yöntemiyle Ca atomunun yapı içindeki yayınım aktivasyon enerjileri hesap edilmiştir. Elde edilen sonuçlara göre, nadir toprak elementlerinin Ca yerine kullanılarak alaşımlandırılma yapıldığında sistemin kararlılığını arttırdığını görmekteyiz. Ayrıca bazı geçiş elementlerinin de (Hf, Sc, Y, Zr) Ca yerine kullanıldığında sistemin enerjisini düşürdüğü görülmüştür. Ni yerine yapılan alaşımlandırmalarda ise özellikle Al, Si, Ge ve P' nin çok etkili olduğu Sb, Sn, Sc, Zn, Zr, Hf ve Ti gibi elementlerin ise kısmen yararlı etki yaratacağı tespit edilmiştir.

Anahtar Kelimeler: *Ni-MH bataryalar, ab initio çalışmaları,* $CaNi_5$, $LaNi_5$

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INTRODUCTION

New technological developments on electronic devices increase the importance of the energy storage. Smaller and more efficient electrical and electronic systems make the batteries key product for portable applications for example cell phones, cameras, vehicles, etc. Energy can be stored by many ways but secondary batteries are more economical because of their rechargeable characteristic and they have been used since middle of 1800. First battery type was lead batteries developed by Gaston Planté in 1859. About in 1950s , first alkaline electrolyte using Ni-Cd batteries were produced [1]. These technological developments were followed by development of different battery types. Today, there are many secondary battery types such as lead - acid batteries, nickel - cadmium batteries (Ni-Cd batteries), nickel - metal hydride batteries (Ni-MH batteries) and lithium-ion batteries (Li-ion batteries). However, Ni – MH batteries have some advantages over other secondary battery types such as excellent thermal properties, secure use at high voltages, consisting environmentally acceptable and recyclable materials and safety in charge, discharge characteristics [2]. In this manner, since the developments in the late 1980s, popularity of Ni-MH battery have increased and used in many portable electrical devices such as laptop computers, cell phones, cassette players, toys etc [3]. Properties of a Ni – MH battery are given on following table.

Table 1. Common properties of a Ni – MH battery [2].

	Ni – MH battery
Nominal Voltage	1.2 V
Specific Energy	75 Wh/kg
Energy Density	240 Wh/L
Operating Temperature	-20 to 50 ^{0}C
Cycle Life	300-600
Discharge Profile	Flat

Chemistry of a Ni – MH battery have some similarities with the Ni - Cd battery. As in Ni – Cd battery, positive electrode is nickel oxyhydroxide (NiOOH) in charged state. On the other hand, differently from Ni – Cd battery, hydrogen is stored in negative electrode as a metal hydride at charged state. Charge and discharge reactions of Ni – MH battery can be seen on following formulas [2].

Positive electrode:

$$NiOOH + H_2O + e^- \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftarrows}} Ni(OH)_2 + (OH)^- \tag{1}$$

Negative electrode:

$$MH_x + OH^- \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftarrows}} MH_{x-1} + H_2O + e^- \tag{2}$$

As can be seen, in negative electrode, hydrogen is absorbed and desorbed during charging and discharging. Therefore, hydrogen storage should be reversible. In this context, intermetalics are used as negative electrode materials in Ni – MH battery. The most important intermetallic groups are tabulated on Table 2. These intermetallic groups mostly determine capacity, cycle life and electrochemical characteristic of Ni – MH battery. AB_5 is the most widely used intermetallic group in Ni – MH batteries because it has some advantages over other intermetallic groups such as better cycling properties, better long term cycling stability and higher volumetric storage density [4]. On the other hand, intermetallics on this group can lose their reversible hydrogen storage capacity.

Table 2. The most important hydride-forming intermetallic groups, prototypes and their hydrides.

Intermetallic Compound	Prototype	Hydrides
AB_5	$LaNi_5$	$LaNi_5H_6$
AB_2	ZrV_2	$ZrV_2H_{5.5}$
AB_3	$CeNi_3$	$CeNi_3H_4$
A_2B_7	Th_2Fe_7	$Th_2Fe_7H_3$
AB	FeTi	$FeTiH_2$
A_2B	$NiMg_2$	Mg_2NiH_4

$LaNi_5$, belonging to $CaCu_5$ crystal structure, is the most widely used commercial active materials of this group. However, in order to increase cycle life and reduce the cost, $LaNi_5$ is used as an alloy with $MmNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75}$ composition where Mm represents a mixture of rare earth elements [5]. Unfortunately, since La is a relatively expensive rare earth element, other alternatives for $LaNi_5$ are searched because according the researches, 45 % of the total cost of a Ni – MH battery belongs to negative electrode of the battery [6]. In this manner, $CaNi_5$ turns out to be an important alternative. $CaNi_5$ has higher specific hydrogen storage capacity than $LaNi_5$. Also, theoretical capacity of $CaNi_5$ is 482 $mAhg^{-1}$, while it is 372 $mAhg^{-1}$ for $LaNi_5$ [7] Therefore, $CaNi_5$ has a very important potential to be an alternative for $LaNi_5$. However, very low cycle life of $CaNi_5$ limits its use in commercial applications. Low cycle life is used to be the problem of $LaNi_5$ too, but with proper alloying additions it was solved to a certain extent. Same approach can also be used to solve the cycle life problem of $CaNi_5$. Therefore, in this study, the effects of different alloying elements on the stability of the $CaNi_5$ compound were investigated because thermodynamic stability may be one of the reasons of low cycle life. In this manner, 48 different alloying elements were selected from the periodic table and the formation energy of the Ca-Ni based alloys were calculated using first principle theories. In addition, in literature it is seen that corrosion is a very important factor for low cycle life. Therefore, the effect of alloying on a probable corrosion mechanism, which is the disintegration of $CaNi_5$ due to Ca hydroxide formation via Ca diffusion, is also investigated by first principle methods.

In literature there are limited studies for $CaNi_5$. Therefore, it is difficult to discuss and comment on results of proper alloying of $CaNi_5$. In this manner, same study has been carried on for $LaNi_5$ because low cycle life problem of $LaNi_5$ were solved by proper alloying and today $LaNi_5$ is the commercial active material for Ni-MH batteries. Therefore, as done for $CaNi_5$ effects of alloying was studied using an ab initio pseudo potential method. Formation energies of the $LaNi_5$ compounds having different alloying elements were calculated for the understanding of the effect of the alloying element on the stability of the compound. Also, NEB study was also carried on for $LaNi_5$.

As known, properties of materials are strongly related with the interactions of electrons and nuclei. Therefore, Schrodinger Equation (S. E.) has opened a new gateway for materials science. However, analytical and numerical solutions of S. E. were invaluable for chemistry and materials science until 1964 [8]. In the mid-1960s two fundamental mathematical theorems proved by Kohn and Hohenberg and the derivation of a set of equation by Kohn and Sham have formed the basis of Density Functional Theory (DFT) [9]. DFT is mainly based on the cast of the intractable complexity of the electron-electron interactions in many electron systems into an effective one-electron potential, which is a functional of the electron density only[10].

There are a number of methods for computer simulation techniques for materials science and chemistry. DFT has some advantages over other techniques such as less demanding computational effort, less computer time and better agreement with the experimental studies[11].

Today, DFT calculations have become a main stay of materials science and play an important role in many material research efforts. There are some reasons for this success. First of all, DFT can convert the many-body electronic problem to a self-consistent-field single particle calculations. In addition, despite the severe approximations such as exchange and correlation energy functional, DFT calculations have sufficient accuracy. Combination of high accuracy of

DFT calculations with the currently available computational power and modern numerical algorithms makes DFT calculations feasible for realistic models of systems[12].

LITERATURE REVIEW

First principle studies are playing a very important role in many field of material science because they guide experimental works and save time. First principle studies are used to understand and optimize electrode materials in the battery industry since many of the relevant properties of battery such as voltage, capacity, structural stability, etc. are directly related with the electrode material [13].

In this manner, there are a number of studies for electrode materials of Li – ion batteries, Ni – MH batteries. Especially, studies for Li – ion batteries are very common. For example, Reed and Van Der Ven have investigated activation barriers of two stages of the transformation from layered Li_xMnO_2 to defective spinel-like form upon cycling by first principle studies [14]. In a different study, Aydinol et al. have used first principle's method to predict the intercalation voltage for lithium in metal oxides. In this study, average intercalation voltage of $LiMO_2$ cathodes was computed for different elements such as M = Ti, V, Co, Ni and Cu using pseudopotential technique[15]. In addition, Ouyang et al. have investigated the energy barriers for possible spatial hopping pathways for diffusion of Li ions in the olivine $LiFePO_4$ by adiabatic trajectory method which is based on density functional based total energy calculations [16]. It is possible to increase different examples of first principle studies for Li – ion batteries.

First principle methods are used not only for prediction of properties of Li – ion battery electrodes, but also they are used for optimize properties of intermetallics which are used as hydrogen storage materials and electrode materials of Ni – MH batteries. For example, Kecik and Aydinol has investigated the adsorption characteristic of hydrogen on magnesium surface. In this manner, Mg surface was alloyed with selected elements in order to calculate substitutional and on-surface adsorption energies. In addition, charge density differences of substitutionally doped surface configurations were investigated [17]. In their study, Pauw et al. tried to find solutions for high stability of MgH_2 and extremely slow desorption rate of MgH_2 by density functional theory. For this purpose, stability of two different crystallographic modifications of Mg-transition metal (Sc, Ti, Zr, Hf) dihydrides was investigated [18]. In an another study, dissociative adsorption of H_2 on FeTi surface was investigated via ab initio pseudopotential-plane wave method by Izanlou and Aydinol. For this purpose, adsorption energies of H atom and H_2 molecule on Fe and Ti terminated surfaces were calculated. Also, activation energies for possible dissociation paths of H_2 molecule were investigated by climbing image nudged elastic band method [19]. NEB studies are also very common in literature. For example, Tezuka et al.

have investigated hydrogen hopping paths in $LaNi_5H$ solid solution by first principle calculations. In this study, activation energy for diffusion of hydrogen atoms in the structure were calculated by NEB method [20].

As mentioned below, today, $LaNi_5$ is used as anode material in Ni – MH battery. Therefore, first principle studies about $LaNi_5$ were investigated. In one of the first first principles study about $LaNi_5$, Malik et al. have calculated the spin-polarized energy bands, the density of states, and the magnetic moments using the self-consistent augmented-plane-wave method [21]. Later, In 1998, Nakamura et al. have investigated the electronic structure and energetics of $LaNi_5$, its hydrogen solution ($La_2Ni_{10}H$) and its hydride ($LaNi_5H_7$) by the tight-binding linear muffin-tin orbital method [22]. In a different study, first principles electronic structure calculations have been used to investigate vacancy formation in $LaNi_5$. It was found on this study that, Ni vacancies are mainly formed at the 2c sites in the hydrogen absorption–desorption cycle in $LaNi_5$ [23]. In their study, Yu et al. have calculated phonon dispersion curves and the phonon density of states in order to investigate thermodynamic and dynamical properties of $LaNi_5$. In this study, it was found that, lattice parameters didn't differ more than 0.6 % from experimental data. Also, using the calculated phonon density of states, thermodynamic functions of $LaNi_5$ were determined with the harmonic approximation [24]. In an another study, Zhang et al. have investigated the structure and elasticity of $LaNi_5$ and $LaNi_{4.25}Al_{0.75}$. They have indicated that, Al atoms prefer to substitute Ni atoms in the 3g site [25]. Moreover, Herbst and Hector have discussed the systematic theoretical results for $La(TM)_5H_n$ materials (TM = Fe, Co and Ni) where enthalpies of formation and saturation hydrogen contents derived from density functional theory and Miedema's model were compared [26]. As can be seen, there are many different first principles studies about $LaNi_5$. These studies generally give background information for experimental studies.

As mentioned above, $LaNi_5$ the most widely used commercial active materials for Ni – MH battery. However, there were some problems with the $LaNi_5$ such as low cycle life and relatively high cost of $LaNi_5$. Low cycle life is strongly related with the instability and corrosion sensitivity of $LaNi_5$ [27]. Therefore, storage capacity of $LaNi_5$ decreases during charging and discharging cycles dramatically because $LaNi_5$ decomposes to $La(OH)_3$, $Ni(OH)_2$ and Ni as can be seen on following reaction.

$$LaNi_5 + 13\ OH^- \longleftrightarrow La(OH)_3 + 5\ Ni(OH)_2 + 13\ e^- \qquad (3)$$

Decomposition to $La(OH)_3$ and Ni was proved in many studies. For example, Boonstra et al. have found that, capacity decay of $LaNi_5$ electrode is related with the degradation process of $LaNi_5$ with the formation of $La(OH)_3$ and $Ni(OH)_2$ by x-ray diffraction measurements. Also it was stated that, equation 3 is the dominant degradation mechanism of $LaNi_5$ during charge discharge cycle [28]. In addition, Han and Lee have investigated the hydrogen absorption and desorption behavior of $LaNi_5$. In their study, Ni clusters were found on the surface of alloys by magnetization measurements [29]. Moreover, formation of $La(OH)_3$ needles on surface of $LaNi_5$ after about 12 electrochemical cycles was determined by TEM [30].

Investigation of corrosion mechanism of $LaNi_5$ is very important in order to understand capacity decay and low cycle life. For this purpose, Willems and Buschow have investigated the degradation mechanism in their study. According to their study, corrosion reaction entails the diffusion of La from bulk to surface. Normally, La in the crystal structure of $LaNi_5$ is immobile at room temperature. However, as can be seen in equation (2), there is a hydrogen storage while charging and because of this hydrogen storage, hydrogen-rich and hydrogen-poor regions occurs in the structure. Difference in volume between these regions severely distort lattice which distortion enhances mobility of La atom in the structure. Therefore, near the surface, a zone with a lower La concentration than the average concentration occurs. Lattice defects introduced during charging creates short-circuit diffusion paths for La atoms. Therefore La atoms move gradually and step by step into La depleted zone. From the La depleted zone, La atoms continue to diffuse to surface in order to form $La(OH)_3$ by reacting with the alkaline solution. Formation of thick $La(OH)_3$ layer on surface and decrease in La content in the structure inhibit hydrogen absorption [30]. Pulverization of $LaNi_5$ is an another problem for capacity decay because oxidized surface area increases. Probable reason of pulverization is the internal stresses due to the volume expansion during hydrogen absorption since volume expansion of $LaNi_5$ on hydriding is about 24 % [30]. In this manner, Sakai et al. have examined the mechanical properties of alloys. It was determined that the lower the Vickers hardness leads to the slower the pulverizing rate which increase cycle life of alloys [31, 32].

In this regard, scientist tried to solve capacity decay problem of $LaNi_5$ by proper alloying. Generally, studies focused to Ni site substitution. For example, Willems and Buschow have investigated charge and discharge behaviors of $LaNi_{5-x}Co_x$, $LaNi_4Cu$ and $LaNi_{5-x}Co_xAl_{0.1}$. According to results of this study, Cu substitution has no considerable effect on cycle life of $LaNi_5$. On the other hand, it was observed that, Co substitution improves cycle life of $LaNi_5$. In fact, increase in x values up to 3.3 in $LaNi_{5-x}Co_x$ gives better results. Also, Al addition to Co substitution gives very good results. Therefore, $LaNi_{1.9}Co_3Al_{0.1}$ gives the best overall performance [30]. These positive results of Co substitution can be explained by the study of Van Mal. According to Van Mal et al., partial substitution of Co for Ni in $LaNi_5$ results in a considerable reduction of the volume expansion on hydrogen absorption [33]. Finally, Willems and Buschow have studied the behavior of compounds in which La was partially substituted such as $La_{0.8}Nd_{0.2}Ni_{2.5}Co_{2.4}S_{0.1}$. With this compound, excellent stability obtained and after one thousand cycles capacity have decreased only 30% [30]. In an another study, Sakai et al. have investigated the properties of $LaNi_{5-x}M_x$(M=Ni, Mn, Cu, Cr, Al and Co). In their study, capacity decay ratios after 150 cycles at a cut-off voltage of –0.5 V were calculated for alloys $LaNi_{4.5}M_{0.5}$, $LaNi_4M$ (M=Mn, Cu, Cr, Al) and $LaNi_{2.5}Co_{2.5}$. It was found that, increase in M content decreases capacity but increases cycle life. In addition, Al and Co are very effective in order to increase cycle life of $LaNi_5$. On the other hand, Mn adversely affect cycle life of $LaNi_5$ [31]. Similarly, Chartouni et al. have investigated mechanical and electrochemical properties of $LaNi_5$, $LaNi_4Co$, $LaNi_{4.5}Al_{0.5}$, $Zr_{0.2}La_{0.8}Ni_{4.5}Al_{0.5}$, $Er_{0.2}La_{0.8}Ni_{4.5}Al_{0.5}$ and $LaNi_{3.5}CoAl_{0.5}$ alloys. According to their results, after 150 cycles, $LaNi_{3.5}CoAl_{0.5}$ has lost its capacity only 90 %. Also partial substitution of La with Er and Zr gave very good cycle life in this study. In addition, direct relationship between hardness of the alloy and cycle life has been shown. It was found that, decrease in Vickers hardness leads to increase in cycle stability. For example, $LaNi_5$ with the lowest cycle stability has 809 $kg.mm^{-2}$ Vickers hardness, on the other hand, $LaNi_{3.5}CoAl_{0.5}$ with the best cycle stability has 762 $kg.mm^{-2}$ Vickers hardness. Moreover, it was determined that, $LaNi_{3.5}CoAl_{0.5}$ shows the slowest decrease in surface La content which is the reason for highest cyclic stability [32]. In an another study, Sakai et al. have partially substituted La with Ce, Nd and Zr, Ni with Co and Al. It was observed that, these elements are effective in order to improve cycle life of $LaNi_5$. In this study, alloy of $La_{0.8}Nd_{0.15}Zr_{0.05}Ni_{3.8}Co_{0.7}Al_{0.5}$ has best overall performance [34]. Also, Mg was substituted with La atom by Cuscueta et al. and positive effect of Mg substitution on cycle life was determined. it was found that $La_{0,85}Mg_{0,15}Ni_{3,8}Co_{0,3}Mn_{0,3}Al_{0,4}$ alloy has performed the best results on cyclic stability, with a capacity reduction of 4.4% at cycle 50 and a reduction rate of 0.117mAh/g per cycle [35]. As can be seen similar elements were studied by different scientists. In a comparative study, $LaNi_{4.7}M_{0.3}$ (M = Ni, Co, Mn and Al) alloys were investigated by Liu et al. As found on previous studies, Mn decreases cycle life of $LaNi_5$, on the other hand, Co and Al increases cycle life of $LaNi_5$ and it was stated that Co is more effective that the Al in order to improve cycle life of $LaNi_5$ [36]. Positive effects of Co and Al were discussed by Reilly et al. Formation of stable Co and Al oxide layer on the surface of alloys restrict further corrosion of alloy. Since Co oxide layer is conductive and more stable than the Al oxide layer, Co is more effective in order to improve cycle life of $LaNi_5$ [27]. For Ni site substitution different elements were tried also. For example, Meli et al. have studied iron-containing $LaNi_5$ alloys. It was found on this study that partial substitution of Ni with Fe has no effect on cyclic durability of $LaNi_5$. According to capacity measurements, after 200 cycle, capacity of $LaNi_{4.5}Fe_{0.5}$ decreases about 60 %. On the other hand, it was observed that, combined substitution of Fe and Al increases cyclic durability of $LaNi_5$. After electrochemical cycling, on the surface of alloys, no Fe enrichment was observed but a small amount Al enrichment observed by XPS [37]. In addition, Züttel et al. have observed that, partial replacement of La with Al, Mn, Co and Fe gives better cyclic durability than the non-iron containing alloys because of the smaller volume expansion [38]. Deng et al. have studied the electrochemical performance of $LaNi_5Sn_x$ alloys. It was stated on this study that Sn improves cycle life of $LaNi_5$, but there is no a linear relationship between amount of Sn and electrochemical performance. It was found that $LaNi_{4.58}Sn_{0.42}$ gives the best overall performance [39]. Witham et al. have compared $LaNi_{5-x}Si_x$ and $LaNi_{5-x}Ge_x$ alloys in their studies. They have found that, Ge is more effective than the Si in order to improve cycle life of $LaNi_5$ and the optimum Ge content for $LaNi_{5-x}Ge_x$ alloys is in the range $0.4 < x < 0.5$ [40]. Effect of Ti and Zr additions were also investigated by Seo et al. and it was stated that only small amount Ti and Zr addition are effective in order to improve cycle life of the alloy $(LMNi_{3.6}Al_{0.4}Co_{0.7}Mn_{0.3})M_y$ (LM = La – rich mischmetal, M = Ti and Zr). It was found that, addition of Ti with $y = 0.05$ and Zr with $y = 0.02$ improve cycle life of the alloy. On the other hand, addition of higher amounts Ti and Zr adversely affect cycle life of the alloy [41]. There are also studies for La site substitution. For example, effect of partial substitution of La with Ce, Pr and Nd were investigated by Chen [42]. It was observed that, $La_{0.7}Ce_{0.3}B_5$ ($B = Ni_{3.55}Co_{0.75}Mn_{0.4}Al_{0.3}$) gives the best cycle life. Effect of Ce on cycle life of alloys was explained by formation of protective CeO_2 oxide layer [42]. In addition, Moussa et al. have compared the electrochemical properties of $MmNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75}$ and $LaNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75}$ alloys and it was found that, capacity decay in Mm containing alloy is slower than the $LaNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75}$. Also Mm containing alloy has better electrochemical properties [43].

As can be seen on studies, low cycle life due to the rapid capacity decay problem of $LaNi_5$ was solved by proper alloying. Today, different $LaNi_5$ alloys are used in Ni – MH batteries. For example, Moussa et al. have showed that, compared to the $LaNi_5$ compound, $MmNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.6}Fe_{0.15}$ has a better stability in the alkaline solution, a good reversibility and a good kinetic of the electrochemical reaction [44]. However as mentioned above, La is a relatively expensive rare earth element. Therefore, other alternatives for $LaNi_5$ are searched. $CaNi_5$, belonging to same crystal structure with $LaNi_5$, turns out to be an important alternative. $CaNi_5$ has higher specific hydrogen storage capacity than $LaNi_5$. Also, theoretical capacity of $CaNi_5$ is $482 mAhg^{-1}$, while it is $372\ mAhg^{-1}$ for $LaNi_5$ [7]. In this regard, $CaNi_5$ has a very important potential to be an alternative for $LaNi_5$. However, very low cycle life of $CaNi_5$ limits its use in commercial applications. Like $LaNi_5$, during charge and discharge cycle, capacity decays because of the electrochemical corrosion of Ca as can be seen in equation (4) [45]. Calcium segregation from bulk to surface was also detected in studies [46, 47]. Therefore, scientists tried to improve cycle life of $CaNi_5$ by proper alloying as in $LaNi_5$.

$$CaNi_5 + 2\ H_20 \longleftrightarrow Ca(OH)_2 + 2\ H^+ + 5\ Ni + 2\ e^- \qquad (4)$$

In literature, the number of studies related to the effect of alloying on the cycle life of $CaNi_5$ is quite low. Li and Suda have studied Ca and Ni site substitutions. Generally, they have stated that, instead of Ni site substitution, Ca site substitution would be more effective in order to increase cycle life of $CaNi_5$ [45]. According to their results, Al substitution with Ni cannot improve cycle life of alloy. On the other hand, combined substitution of Ca with La and Ni with Al have improved cycle life of $CaNi_5$, where substitution also restricts the formation of Ca_2Ni_7 and Ni-rich phases. In fact, increase in amount of La content gives better results until the x = 0.7 in the alloy of $Ca_{1-x}La_xNi_{4.7}Al_{0.3}$. This positive effect of La substitution might be caused by the increase of the pulverization easiness of the alloy. Co substitution with Ni site was combined with La substitution and it was found that there is no any effect of Co substitution on cycle durability of $Ca_{0.5}La_{0.5}Ni_{5-x}Co_x$ alloy. In addition, it was found in this study that, instead of La substitution with Ca, Ce substitution gives better results in the same alloy for x = 0.2 amount since it can not only decrease pulverization easiness of the alloy but also improve the lattice stability. Moreover, it was stated that, Mg substitution have also positive effect on cycle durability of $CaNi_5$ with the formation of more stable protective surface layer of $Mg(OH)_2$ [7]. In an another study of Li and Suda, effects of Ti and Zr additions on cycle durability of $Ca_{0.4}La_{0.6}Ni_{4.7}Al_{0.3}$ alloy were investigated. It was found that, Ti and Zr improves cycle durability of alloy with the formation of protective oxide layer on the surface of alloy [48] and $Ca_{0.4}La_{0.6}Zr_{0.15}Ni_{4.7}Al_{0.3}$ alloy gives the best overall cyclic durability performance [45]. On the other hand, Jensen and Bjerrum, alloyed $CaNi_5$ by adding 10 at. % Al, Cr, Mn, Fe, Co, Cu, Zn, Sn and Mg. They found that, there was no improvement in the cycle life. It was also stated that, crystal structure of $CaNi_5$ cannot be preserved [49]. Moreover for hydrogen storage, Liang et al. (2001) found that, Sn substitution for Ni by mechanical alloying resulted in new phase formation after heat treatment and this new phase cannot absorb hydrogen [50].

As listed above, there are many studies in order to improve cycle life and decrease cost of $LaNi_5$ and $CaNi_5$. Generally, cycle life was improved by several mechanism such as formation of protective surface layer on surface of alloy, reduction of volume expansion on hydrogen absorption and decrease pulverization rate of alloy. However, according to Willems and Buschow, oxide layer on the surface inhibits hydrogen absorption and desorption. In addition, protective effect of surface layer can only be present when volume expansion is not too much. Therefore, protective effect of surface layer decreases; because, $LaNi_5$ expands about 24 % while hydrogen storage [30].

In this manner, in this study, in order to investigate the stability of different La-Ni and Ca-Ni based alloys, 48 different alloying elements were selected from the periodic table and the formation energy of the La-Ni and Ca-Ni based alloys were calculated using ab initio pseudo potential method because phase stability would be one of the important factors on cycle life like formation of stable oxide layer on surface of alloy. In addition, as mentioned above, La atoms diffuse from bulk to surface due to several distortions in the crystal structure of the $LaNi_5$ in order to form $La(OH)_3$ by reacting with the alkaline solution [30]. Same corrosion mechanism can be possible in $CaNi_5$ because of the same crystal structure, same hydrogen absorption desorption mechanism and charge discharge mechanism. Therefore, in order to understand effects of alloying on diffusion barriers, diffusion of La atom in the crystal structure of $LaNi_5$ and Ca atom in the crystal structure of $CaNi_5$ was investigated by NEB method. Moreover, in order to understand the hydride stability in alloyed $CaNi_5$, formation energies of $Ca_7Ni_{40}MH_{48}$ and $Ca_8Ni_{39}MH_{48}$ were calculated.

CHAPTER 2

COMPUTATIONAL METHODOLOGY

In this study, formation energies of La-Ni and Ca-Ni based alloys were calculated. In addition, in order to understand effects of alloying on diffusion barriers, diffusion of La atom in the crystal structure of $LaNi_5$ and Ca atom in the crystal structure of $CaNi_5$ was calculated by NEB method. All calculations were performed in a plane wave basis set using the projector augmented wave (PAW) method [51] within the formalism of density functional theory as implemented in the VASP program [52-54]. In the calculations, PAW potentials [55] were used, where exchange-correlation functional with the generalized gradient approximation (GGA) is in Perdew-Burke-Ernzerhow functional (PBE) form [56].

3.1 Bulk Calculations for $CaNi_5$ and $LaNi_5$

Bulk calculations in $CaNi_5$ structure were performed for several test purposes. $CaNi_5$ adopt the hexagonal $CaCu_5$ crystal structure, Fig. 1, in which there are five nickel atoms (2c and 3g Wyckoff positions) and one calcium atom (1a Wyckoff position) within the unit cell having the symmetry of the P6/mmm space group. After setting up the simulation cells in the bulk sense with periodic boundary conditions, the cell volume and the atomic positions are allowed to relax to find the minimum energy configuration. During these calculations, sampling in the reciprocal space (*k*-point grid size) and spin polarization effect were considered to attain a few meV convergence. It was found that, 16×16×16 gamma centered grid of *k*-point sampling is adequate for $CaNi_5$. Expectedly, since Ni is a magnetic element, electronic structure and the density of states (DOS) of the compound changes with respect to spin polarization Fig 2. Therefore, spin polarization has been taken into account in all calculations hereafter. The calculated lattice parameters of the compound were found to be in agreement with the experimental values with less than 0.5% error.

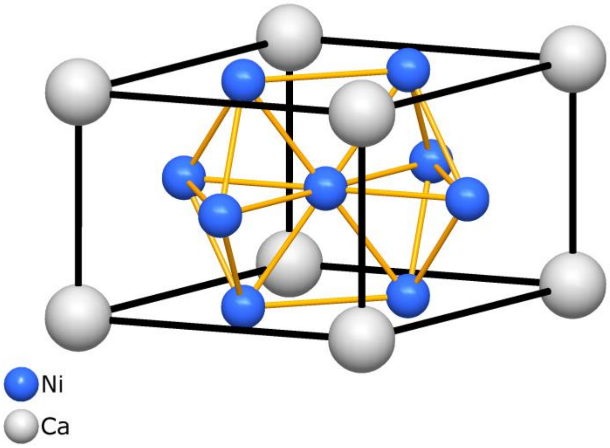

Figure 1. Crystal structure of $CaNi_5$ and $LaNi_5$.

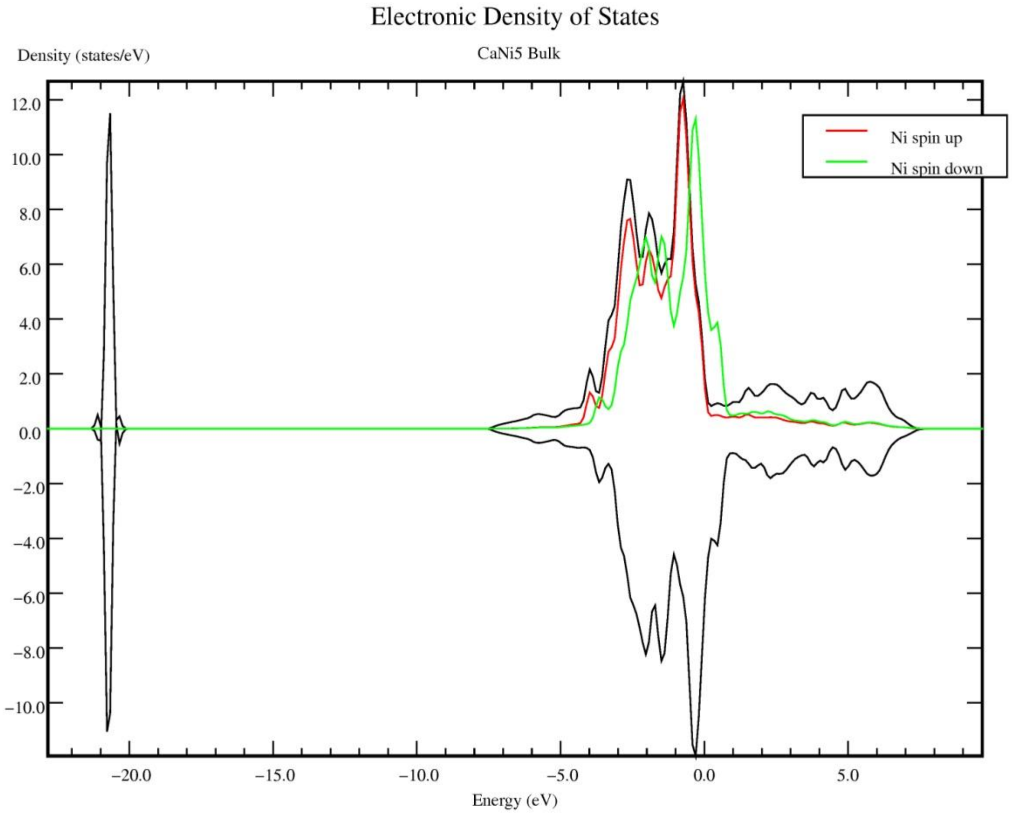

Figure 2. Electronic density of states of $CaNi_5$, showing spin up and spin down states.

For the alloying calculations a super-cell, composed of 2×2×2 unit cells was constructed, Fig. 3. for $CaNi_5$. Therefore there are a total of 8 calcium and 40 nickel atoms in this cell, in which either one calcium or one nickel atom will then be substituted by the alloying element later in the calculations. There are, however, two non-equivalent Ni sites in the structure. One is at the same crystal plane as that of Ca (called as Ni-1 site) and the other one lies above this plane (called Ni-2 site). In order to understand which Ni site is preferred by the alloying element, we therefore considered both. Once the alloyed super cell is formed, cell volume and atomic positions are all allowed to relax again to find the minimum energy configuration. In all alloying calculations, spin polarization was taken into account and a gamma centered grid of 3×3×4 *k*-point set was used corresponding to 9 *k*-points in the irreducible Brillouin zone. In the expansion of the plane-wave basis set, a kinetic energy cut off of 400 eV was used. The overall convergence in the total energy is less than about 10 meV per unit cell.

Since $LaNi_5$ has the same $CaCu_5$ crystal structure, a similar 2x2x2 unit cell constructed for $LaNi_5$ calculations. In addition, same *k*-point sampling and kinetic energy cutoff values were used.

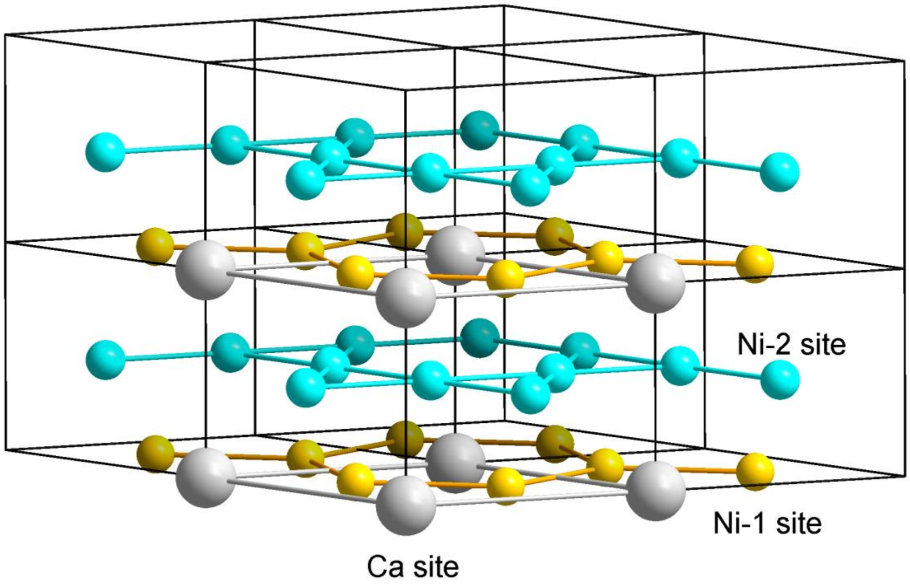

Figure 3. The super-cell used in alloying calculations. Ca, Ni-1 and Ni-2 sites are shown.

In case of La-site substitution, the structure has a unit formula of $La_7Ni_{40}M$, M being one of the 48 alloying elements. For Ni-site substitution we have $La_8Ni_{39}M$. The composition of the alloy in terms of the alloying element is, therefore 2.08 at.%. The corresponding alloying reactions are,

(5)

(6)

for La and Ni-site substitution respectively. Formation energy of the alloy then can be calculated by taking the difference of the calculated total energies of the product and the reactants of the above alloying reactions. More specifically, for La and Ni-site substitution they are given as below.

(7)

(8)

Similarly, for Ca-site substitution, the structure has a unit formula of $Ca_7Ni_{40}M$, M being one of the 48 alloying elements. For Ni-site substitution we have $Ca_8Ni_{39}M$. The composition of the alloy in terms of the alloying element is, therefore 2.08 at.%. The corresponding alloying reactions are,

(9)

(10)

for Ca and Ni-site substitution respectively. Formation energy of the alloy then can be calculated by taking the difference of the calculated total energies of the product and the reactants of the above alloying reactions. More specifically, for Ca and Ni-site substitution they are given as below.

(11)

(12)

As known from electrochemical reactions of a Ni – MH battery, hydrogen atoms are stored on anode materials. Current density, capacity and other properties of battery is directly related with the release of these hydrogen atoms from anode. In this manner, effect of alloying on formation energy of hydride compounds of $CaNi_5$ were calculated and compared with the pure hydride compound.

Unfortunately, there are very limited study about hydride compounds of $CaNi_5$. Therefore, literature of $LaNi_5$ was surveyed and it was found that $LaNi_5$ can store six hydrogen atoms per formula. When crystal structure of these hydride compounds were investigated, it was understood that hydrogen atoms does not fill Wyckoff positions exactly [57]. Therefore, there are different crystal structures which have different space groups because of the different positions of hydrogen atoms. However, when hydrogen atoms are deleted, crystal structure is $CaCu_5$ crystal structure. Therefore, one of the crystal structure of hydride compounds of $LaNi_5$ was selected for $CaNi_5$ calculations because $CaNi_5$ also belongs to $CaCu_5$ crystal structure. Selected crystal structure for calculation of formation energy of hydride compounds of $CaNi_5$ belongs to space group of 157, Ca atom are positioned at 1a, Ni atoms are positioned at 2b and 3c and H atoms are positioned at 3c and 6d Wyckoff positions. However, only half of the 6d Wyckoff position is filled by hydrogen atoms Fig. 4. Therefore, in order to calculate formation energies of hydride compounds of $CaNi_5$, exact position of hydrogen atoms should be determined. In this manner, for six position, total energies of ten possible combination structures were calculated and positions were named by their position number Fig. 4. Total energies of ten possible combination is given on following table.

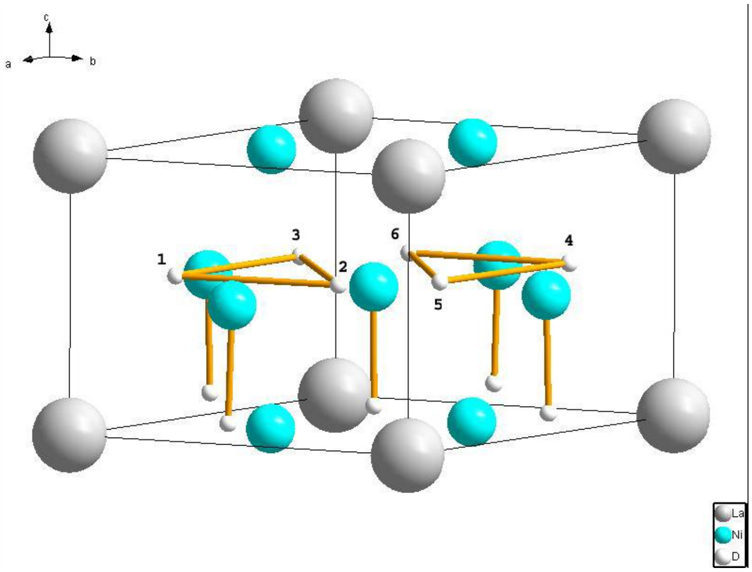

Figure 4. Six possible position for three hydrogen atoms named by numbers.

Table 3. Total energies of ten possible combination

Combination of Positions	**Total Energy (eV)**
(123)	-51.988
(134)	-51.925
(136)	-51.924
(126)	-51.928
(156)	-51.919
(253)	-51.930
(256)	-51.930
(362)	-51.972
(356)	-51.973
(456)	-51.993

As can be seen on Table 3. the most stable combinations are (123) (and its crystallographic equivalent (456)) and (356) (and its crystallographic equivalent (362)) because of the lower energy state. In this manner, by using these hydrogen atom positions, total energies and formation energies of $Ca_7Ni_{40}MH_{48}$ and $Ca_8Ni_{39}MH_{48}$ compounds were calculated according to corresponding reactions for Ca and Ni-site substitution respectively,

(13)

(14)

Formation energy of the hydrides then can be calculated by taking the difference of the calculated total energies of the product and the reactants of the above hydriding reactions. More specifically, for Ca and Ni-site substitution they are given as below.

(15)

(16)

3.2 NEB calculations for $CaNi_5$ and $LaNi_5$

The NEB method is used to find the minimum energy path (MEP) between a given initial and final state of reaction [58, 59] and the MEP can be used to estimate the activation energy barrier for transition between the initial and final states. Any maximum along the MEP is a saddle point on the potential surface and energy of the highest saddle point gives the activation energy of the reaction [59].In this study, the climbing image NEB (CI-NEB) method which is a modified version of NEB is used [58]. By this method, with a rigorous convergence to a saddle point, exact position of saddle point can be obtained.

For CI-NEB calculations, diffusion path of Ca atom determined and as can be seen on Fig. 5 Ca atoms diffuse through Ni tubes. For initial state Fig. 6, one Ca atom was taken out from 2x2x2 super cell and system was relaxed without cell shape relaxation. Similarly for final state, next Ca atom on Ni tube was taken out and system was relaxed without cell shape relaxation Fig. 7. For calculations as a kinetic energy cutoff of 400 eV and gamma centered grid of 2×2×3 *k*-point set were used.

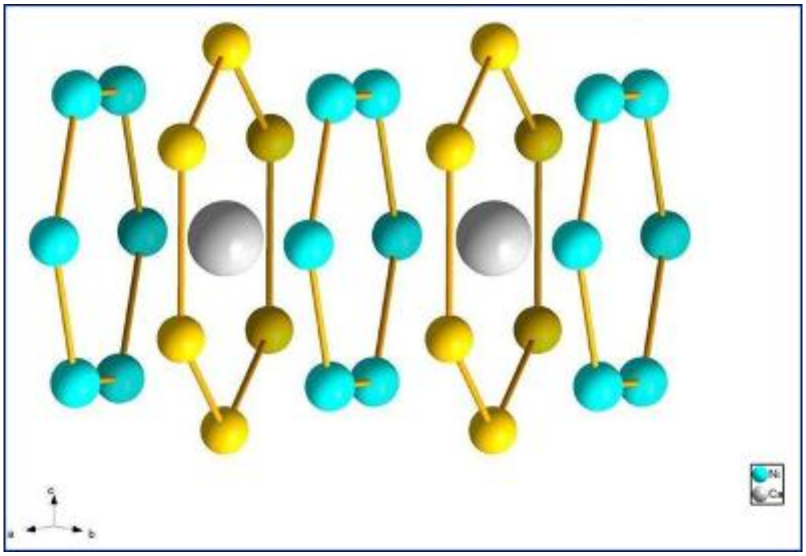

Figure 5. Ca atoms diffuse through these Ni tubes.

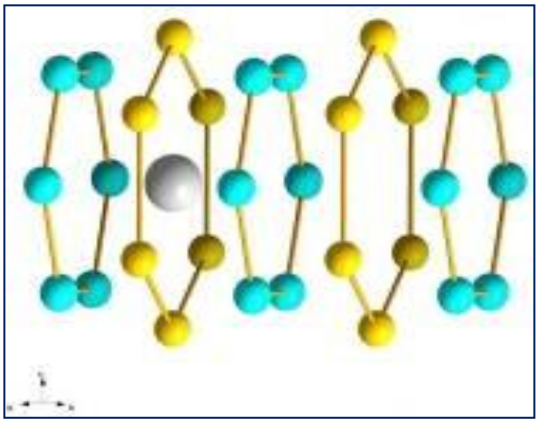

Figure 6. Initial state for NEB calculations.

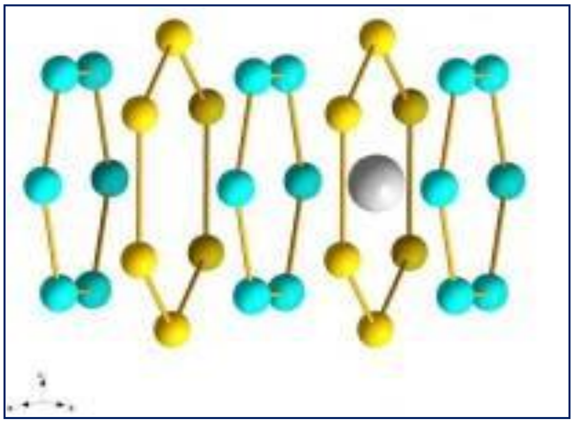

Figure 7. Final state for NEB calculations.

Due to the same crystal structure, same procedure was used for CI-NEB calculations of $LaNi_5$. Also same *k*-point sampling and kinetic energy cutoff values were used for CI-NEB calculations of $LaNi_5$.

CHAPTER 3

RESULTS AND DISCUSSION

4.1 Calculations for CaNi5

4.1.1 Calculation of Formation Energy

As mentioned above, firstly bulk calculations were performed. As can be seen on equation 7, 8 10 and 11 for calculation of formation energies, total energies of pure structures are needed. Therefore, pure $LaNi_5$, $CaNi_5$ and alloying elements were relaxed and total energies were calculated Table 4.

From Table 4, it can be concluded that, the difference between calculated lattice parameters and experimental results does not change more than % 3 except for a few elements. Also, for $CaNi_5$ and $LaNi_5$, difference is lower than %0.5. These differences between calculated and experimental lattice parameters are very successful for a first principle study. In addition, as can be seen on Table 4. $LaNi_5$ is more stable than $CaNi_5$ because of the lower energy state. Therefore, it would be more difficult to make $CaNi_5$ more stable than $LaNi_5$.

Then, as mentioned above, different alloying elements were replaced with one calcium atom, with one nickel atom in plane with calcium atom (Ni – 1 site) and with one nickel atom out of plane with calcium atom (Ni – 2 site). Therefore, $Ca_7Ni_{40}M$ and $Ca_8Ni_{39}M$ alloys were obtained and relaxed. Formation energies of $Ca_7Ni_{40}M$ and $Ca_8Ni_{39}M$ alloys were calculated by equations 11 and 12. Lattice parameters, total energies and formation energies of $Ca_7Ni_{40}M$ and $Ca_8Ni_{39}M$ alloys were tabulated on Tables 5, 6, and 7.

Table 4. Experimental and calculated lattice parameters CaNi$_5$, LaNi$_5$ and alloying elements.

Element	**Experimental Results**		**Calculated Results**			
	Lattice Parameters (Å)		**Lattice Parameters (Å)**		**% Difference**	
	a	**c**	**a**	**c**	**a**	**c**
CaNi$_5$	4.960	3.948	4.940	3.935	-0.404	-0.325
LaNi$_5$	5.017	3.986	5.002	3.980	-0.298	-0.155
Ag	4.086		4.156		1.712	
Al	4.010		4.040		0.737	
B	10.170	8.82	10.101	65.367	-0.675	0.256
Ba	5.128		5.016		-2.177	
Bi	4.545	11.859	4.594	11.990	1.082	1.108
Ca	5.585		5.500		-1.521	
Cd	2.979	5.617	3.028	5.679	1.632	1.107
Ce	3.680	11.833	3.788	12.179	2.928	2.928
Co	2.507	4.070	2.492	4.036	-0.606	-0.823
Cr	2.888		2.838		-1.742	
Cu	3.620		3.630		0.283	
Dy	3.588	5.646	3.615	5.662	0.744	0.290
Er	3.550	5.600	3.590	5.564	1.139	-0.648
Fe	2.870		2.830		-1.403	
Gd	3.678	5.860	3.634	5.750	-1.183	-1.869
Hf	3.198	5.053	3.193	5.043	-0.144	-0.203
K	5.328		5.302		-0.487	
La	3.765	12.150	3.764	12.094	-0.032	-0.464
Li	3.513		3.440		-2.079	
Mg	3.223	5.219	3.192	5.177	-0.957	-0.811
Mn	8.538		8.539		0.015	
Mo	3.147		3.150		0.096	
Nb	3.294		3.323		0.888	
Nd	3.660	11.801	3.704	11.935	1.191	1.139
Ni	3.524		3.520		-0.111	
Pb	4.950		5.028		1.584	
Pd	3.890		3.952		1.588	
Sb	4.306	11.250	4.383	11.488	1.799	2.118
Sc	3.304	5.225	3.318	5.172	0.448	-1.004
Si	5.431		5.468		0.686	
Sm	3.611	26.220	3.661	26.356	1.395	0.519
Sn	5.833	3.182	5.929	3.225	1.643	1.369
Ta	3.305		3.308		0.104	
Th	5.087		5.044		-0.839	
Ti	2.943	4.698	2.918	4.644	-0.865	-1.152
V	3.030		2.980		-1.665	
W	3.191		3.172		-0.590	
Y	3.649	5.744	3.649	5.695	-0.009	-0.855
Yb	5.480		5.427		-0.962	
Zn	2.666	4.947	2.654	4.963	-0.446	0.319
Zr	3.232	5.147	3.238	5.163	0.172	0.309
Na	4.221		4.191		-0.730	
Ac	5.311		5.669		6.743	
Au	4.079		4.174		2.327	
Hg	3.458	6.684	3.716	6.860	7.465	2.638
In	3.253	4.946	3.306	5.033	1.642	1.759
Ge	5.658		5.782		2.204	
P	3.313	10.473	3.302	11.070	-0.344	5.703
	b= 4.374		b=4.534		3.649	

Table 5. Lattice parameters, total energies and formation energies of Ca-site substitution alloys.

Alloy	**Lattice Parameters (Å)**		**$\Delta E(Ca_7N_{40}M)$ (eV/cell)**
	a	**c**	
$CaNi_5$ (8)	4.925	3.950	-0.715
Ca-Ag	4.907	3.952	-0.450
Ca-Al	4.885	3.964	-0.640
Ca-B	4.874	3.965	-0.159
Ca-Ba	4.952	3.953	-0.531
Ca-Bi	4.915	3.968	-0.522
Ca-Cd	4.903	3.962	-0.538
Ca-Ce	4.930	3.948	-0.807
Ca-Co	4.881	3.959	-0.376
Ca-Cr	4.883	3.962	-0.318
Ca-Cu	4.892	3.959	-0.413
Ca-Dy	4.918	3.947	-0.878
Ca-Er	4.918	3.949	-0.883
Ca-Fe	4.890	3.966	-0.440
Ca-Gd	4.924	3.950	-0.872
Ca-Hf	4.890	3.973	-0.841
Ca-K	4.944	3.935	-0.305
Ca-La	4.925	3.955	-0.842
Ca-Li	4.901	3.949	-0.539
Ca-Mg	4.904	3.956	-0.641
Ca-Mn	4.909	3.947	-0.516
Ca-Mo	4.877	3.962	-0.434
Ca-Nb	4.880	3.956	-0.653
Ca-Nd	4.933	3.957	-0.836
Ca-Pb	4.918	3.966	-0.518
Ca-Pd	4.904	3.957	-0.462
Ca-Sb	4.888	3.971	-0.560
Ca-Sc	4.904	3.952	-0.839
Ca-Si	4.881	3.973	-0.525
Ca-Sm	4.925	3.948	-0.854
Ca-Sn	4.892	3.985	-0.608
Ca-Ta	4.872	3.957	-0.659
Ca-Th	4.927	3.964	-0.950
Ca-Ti	4.881	3.963	-0.708
Ca-V	4.885	3.958	-0.519
Ca-W	4.875	3.962	-0.424
Ca-Y	4.916	3.950	-0.871
Ca-Yb	4.918	3.942	-0.789
Ca-Zn	4.896	3.961	-0.529
Ca-Zr	4.893	3.957	-0.841
Ca-Ca	4.925	3.950	-0.715
Ca-Ni	4.886	3.959	-0.374
Ca-Na	4.928	3.942	-0.465
Ca-Ac	4.942	3.945	-0.783
Ca-Au	4.906	3.958	-0.471
Ca-Hg	4.905	3.961	-0.480
Ca-In	4.907	3.965	-0.595
Ca-Ge	4.894	3.969	-0.531
Ca-P	4.879	3.977	-0.429

Table 6. Lattice parameters, total energies and formation energies of Ni-1 site substitution alloys

Alloy	**Lattice Parameters (Å)**		**ΔECa$_8$N$_{39}$M) (eV/cell**
	a	**c**	
CaNi$_5$ (8)	4.925	3.950	-0.715
Ni-Ag	4.943	3.975	-0.649
Ni-Al	4.938	3.942	-0.869
Ni-B	4.944	3.886	-0.701
Ni-Ba	4.993	3.986	-0.314
Ni-Bi	4.980	3.975	-0.625
Ni-Cd	4.948	3.974	-0.669
Ni-Ce	4.985	3.978	-0.548
Ni-Co	4.930	3.941	-0.666
Ni-Cr	4.934	3.932	-0.616
Ni-Cu	4.922	3.950	-0.725
Ni-Dy	4.971	3.978	-0.673
Ni-Er	4.966	3.971	-0.693
Ni-Fe	4.930	3.941	-0.690
Ni-Gd	4.980	3.979	-0.653
Ni-Hf	4.959	3.962	-0.773
Ni-K	4.971	3.996	-0.205
Ni-La	4.981	3.969	-0.621
Ni-Li	4.922	3.937	-0.716
Ni-Mg	4.951	3.971	-0.720
Ni-Mn	4.942	3.955	-0.705
Ni-Mo	4.951	3.961	-0.595
Ni-Nb	4.954	3.959	-0.683
Ni-Nd	4.973	3.975	-0.589
Ni-Pb	4.963	3.969	-0.630
Ni-Pd	4.939	3.978	-0.737
Ni-Sb	4.957	3.965	-0.776
Ni-Sc	4.951	3.960	-0.777
Ni-Si	4.952	3.932	-0.902
Ni-Sm	4.952	3.932	-0.621
Ni-Sn	4.952	3.960	-0.770
Ni-Ta	4.956	3.957	-0.708
Ni-Th	4.986	3.967	-0.696
Ni-Ti	4.936	3.944	-0.788
Ni-V	4.938	3.938	-0.683
Ni-W	4.948	3.961	-0.584
Ni-Y	4.972	3.977	-0.654
Ni-Yb	4.963	3.973	-0.664
Ni-Zn	4.936	3.947	-0.789
Ni-Zr	4.966	3.963	-0.744
Ni-Ca	4.965	3.979	-0.558
Ni-Ni	4.925	3.950	-0.715
Ni-Na	4.948	3.982	-0.498
Ni-Ac	4.996	3.982	-0.509
Ni-Au	4.942	3.974	-0.735
Ni-Hg	4.951	3.978	-0.661
Ni-In	4.948	3.964	-0.718
Ni-Ge	4.946	3.935	-0.855
Ni-P	4.945	3.911	-0.923

Table 7. Lattice parameters, total energies and formation energies of Ni-2 site substitution alloys.

Alloy	Lattice Parameters (Å)		ΔE($Ca_8N_{39}M$) (eV/cell)
	a	c	
$CaNi_5$ (8)	4.925	3.950	-0.715
Ni-Ag	4.972	3.963	-0.645
Ni-Al	4.935	3.960	-0.875
Ni-B	4.882	3.921	-0.693
Ni-Ba	5.032	3.996	-0.346
Ni-Bi	4.974	3.968	-0.663
Ni-Cd	4.958	3.960	-0.656
Ni-Ce	5.014	3.994	-0.546
Ni-Co	4.928	3.949	-0.674
Ni-Cr	4.931	3.955	-0.628
Ni-Cu	4.941	3.960	-0.709
Ni-Dy	4.988	3.980	-0.670
Ni-Er	4.986	3.979	-0.690
Ni-Fe	4.932	3.951	-0.692
Ni-Gd	4.982	3.976	-0.649
Ni-Hf	4.965	3.979	-0.765
Ni-K	5.029	3.981	-0.234
Ni-La	4.996	3.995	-0.627
Ni-Li	4.939	3.947	-0.674
Ni-Mg	4.972	3.971	-0.707
Ni-Mn	4.939	3.957	-0.694
Ni-Mo	4.928	3.954	-0.615
Ni-Nb	4.939	3.962	-0.684
Ni-Nd	5.005	3.987	-0.590
Ni-Pb	4.989	3.979	-0.647
Ni-Pd	4.963	3.956	-0.743
Ni-Sb	4.969	3.973	-0.818
Ni-Sc	4.957	3.963	-0.765
Ni-Si	4.910	3.940	-0.932
Ni-Sm	5.001	3.986	-0.624
Ni-Sn	4.965	3.969	-0.792
Ni-Ta	4.943	3.967	-0.719
Ni-Th	4.976	3.986	-0.715
Ni-Ti	4.931	3.953	-0.791
Ni-V	4.919	3.951	-0.710
Ni-W	4.927	3.956	-0.624
Ni-Y	4.988	3.978	-0.649
Ni-Yb	4.990	3.976	-0.655
Ni-Zn	4.936	3.954	-0.778
Ni-Zr	4.972	3.976	-0.731
Ni-Ca	5.009	3.986	-0.562
Ni-Ni	4.925	3.950	-0.715
Ni-Na	4.999	3.975	-0.489
Ni-Ac	5.017	3.998	-0.536
Ni-Au	4.967	3.962	-0.747
Ni-Hg	4.984	3.970	-0.673
Ni-In	4.969	3.963	-0.731
Ni-Ge	4.939	3.953	-0.872
Ni-P	4.898	3.934	-0.952

In order to see effect of alloying on stability of $CaNi_5$, formation energies of alloys were compared with the formation energy of the pure $CaNi_5$, Table 8 and Fig 8. As can be seen from Table 8, early transition metals of group 3 and 4, lanthanides and actinides are all effective in lowering the formation energy of $CaNi_5$ and they preferentially replace the calcium atom in the structure. Sc, Ti, Zr and Hf can also substitute Ni in both Ni-1 and Ni-2 sites. In addition, Al, Si, Ge and P were found to be very effective and they can replace Ni in both Ni sites. Less effective than these, Ni can also be substituted by Zn, Sn and Sb. All of the above elements lower the formation energy of $CaNi_5$, therefore a more stable alloy is formed which may increase the cyclic durability.

Table 8. Percent change in the formation energy of $CaNi_5$ due to alloying at Ca, Ni-1 and Ni-2 sites.

Alloying Element	Ca Site	Ni-1 Site	Ni-2 Site	Alloying Element	Ca Site	Ni-1 Site	Ni-2 Site
Ac	-9.53	28.82	25.00	**Mg**	10.44	-0.68	1.18
Ag	37.11	9.31	9.84	**Mn**	27.82	1.42	3.03
Al	10.54	-21.49	-22.35	**Mo**	39.31	16.81	14.01
Au	34.18	-2.75	-4.39	**Na**	34.94	30.33	31.71
B	77.77	1.97	3.10	**Nb**	8.74	4.52	4.37
Ba	25.74	56.14	51.65	**Nd**	-16.89	17.69	17.52
Bi	27.02	12.56	7.29	**Ni**	47.77	0.00	0.00
Ca	0.00	22.05	21.42	**P**	40.03	-29.03	-33.08
Cd	24.75	6.54	8.24	**Pb**	27.62	11.92	9.49
Ce	-12.81	23.36	23.70	**Pd**	35.35	-3.08	-3.84
Co	47.46	6.85	5.74	**Sb**	21.77	-8.47	-14.33
Cr	55.50	13.85	12.21	**Sc**	-17.32	-8.67	-6.90
Cu	42.33	-1.42	0.87	**Si**	26.60	-26.16	-30.24
Dy	-22.80	5.85	6.32	**Sm**	-19.42	13.18	12.76
Er	-23.38	3.07	3.54	**Sn**	15.04	-7.66	-10.76
Fe	38.44	3.60	3.25	**Ta**	7.89	1.04	-0.54
Gd	-21.92	8.68	9.32	**Th**	-32.81	2.74	0.07
Ge	25.82	-19.48	-21.92	**Ti**	1.09	-10.18	-10.51
Hf	-17.54	-8.11	-6.97	**V**	27.41	4.55	0.73
Hg	32.85	7.57	5.89	**W**	40.72	18.38	12.77
In	16.78	-0.33	-2.15	**Y**	-21.71	8.56	9.22
K	57.33	71.34	67.22	**Yb**	-10.32	7.11	8.41
La	-17.76	13.12	12.34	**Zn**	26.09	-10.24	-8.76
Li	24.60	-0.07	5.74	**Zr**	-17.55	-4.02	-2.19

% Change in the Formation Energy of CaNi$_5$ with Alloying

M	Alloying element
Ca	replaces Ca
Ni in	replaces in plane Ni
Ni out	replaces out of plane Ni

H																	**He**
Li	**Be**											**B**	**C**	**N**	**O**	**F**	**Ne**
24,60												77,77					
-0,07												1,97					
5,74												3,10					
Na	**Mg**											**Al**	**Si**	**P**	**S**	**Cl**	**Ar**
34,94	10,44											10,54	26,60	40,03			
30,33	-0,68											-21,49	-26,16	-29,03			
31,71	1,18											-22,35	-30,24	-33,08			
K	**Ca**	**Sc**	**Ti**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**	**Ga**	**Ge**	**As**	**Se**	**Br**	**Kr**
57,33	0,00	-17,32	1,09	27,41	55,50	27,82	38,44	47,46	47,77	42,33	26,09		25,82				
71,34	22,05	-8,67	-10,18	4,55	13,85	1,42	3,60	6,85	0,00	-1,42	-10,24		-19,48				
67,22	21,42	-6,90	-10,51	0,73	12,21	3,03	3,25	5,74	0,00	0,87	-8,76		-21,92				
Rb	**Sr**	**Y**	**Zr**	**Nb**	**Mo**	**Tc**	**Ru**	**Rh**	**Pd**	**Ag**	**Cd**	**In**	**Sn**	**Sb**	**Te**	**I**	**Xe**
		-21,71	-17,55	8,74	39,31				35,35	37,11	24,75	16,78	15,04	21,77			
		8,56	-4,02	4,52	16,81				-3,08	9,31	6,54	-0,33	-7,66	-8,47			
		9,22	-2,19	4,37	14,01				-3,84	9,84	8,24	-2,15	-10,76	-14,33			
Cs	**Ba**	**Lan***	**Hf**	**Ta**	**W**	**Re**	**Os**	**Ir**	**Pt**	**Au**	**Hg**	**Tl**	**Pb**	**Bi**	**Po**	**At**	**Rd**
	25,74		-17,54	7,89	40,72					34,18	32,85		27,62	27,02			
	56,14		-8,11	1,04	18,38					-2,75	7,57		11,92	12,56			
	51,65		-6,97	-0,54	12,77					-4,39	5,89		9,49	7,29			
Fr	**Ra**	**Act***															
		La	**Ce**	**Pr**	**Nd**	**Pm**	**Sm**	**Eu**	**Gd**	**Tb**	**Dy**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**	
		-17,76	-12,81		-16,89		-19,42		-21,92		-22,80		-23,38		-10,32		
		13,12	23,36		17,69		13,18		8,68		5,85		3,07		7,11		
		12,34	23,70		17,52		12,76		9,32		6,32		3,54		8,41		
		Ac	**Th**	**Pa**	**U**												
		-9,53	-32,81														
		28,82	2,74														
		25,00	0,07														

Figure 8. On the periodic table % change in the formation energy of CaNi$_5$ with alloying.

If these results are compared with the results found in literature, some agreement can be seen. For example, according to Li and Suda [7], La and Ce addition improves cycle life, while they are also found to lower the formation energy. A similar agreement can also be seen in Al, Zr and Ti added alloys. However, in literature it was stated that, Ce, Zr and Ti improves cycle life with increasing lattice stability or formation of stable oxide layer on surface [7, 45, 48]. This means that, there would be different mechanisms to improve cycle life of $CaNi_5$ and it is hard to discuss which one more effective. On the other hand, according to Willems and Bushow's study [30], protective effect of the surface layer will be present only when the volume expansion while hydrogen absorbing is not too much. Therefore, increasing thermodynamical stability of the alloy would be also effective and important to increase cycle stability of $CaNi_5$. In addition, it was reported in literature that, Fe and Co elements do not have any effect on the cycle life of $CaNi_5$ [7, 49]. As can be seen in Table 8, these elements cause an increase in the formation energy of the system, which means that the compound becomes less stable.

In addition, it is known from literature that [30], lattice distortions enhance mobility of Ca atom and which leads to corrosion of $CaNi_5$. Therefore, effect of alloying on lattice parameters were investigated. According to Table 5, 6 and 7, it is seen that, for Ca site substitution, especially rare earth elements has little effect on lattice parameters. Ac has maximum effect relative to other rare earth elements on lattice parameters with 0.34 % increase in a and 0.14 % decrease in c. On the other hand, early transition metals such as Hf, Zr, Sc and Y distort lattice about between 0.17 % and 0.7 %. For Ni site substitution, except Al, Cu, Ti and Zn, all elements which decrease formation energy of alloy distort lattice much more relative to Ca site substitution. For example rare earth elements distort lattice parameters more than 1 % and also some transition metals effect about 0.8 %.

As mentioned above, activation energies of diffusion of Ca atom in crystal structure were calculated for different alloying elements and different substitution sites by NEB method. To select alloying elements for NEB calculations, firstly effects of alloying elements of formation energy (Table 8) were investigated and alloying elements which decrease formation energy of $CaNi_5$ were selected. Secondly, as mentioned before, there are nickel tubes in $CaCu_5$ structure and alloying elements which makes nickel tubes narrow were selected. For this purpose, distance between two opposite nickel atom on nickel tube was found and compared with the pure $CaNi_{5,}$ Table 8. In all substitutions, three distances were identified for six nickel atoms and it was found that two distances are same with each other and only one is different. Therefore, there are same distances and different distance titles on Table 9. In this manner, alloying elements for NEB calculations were selected according to Table 8 and 9 and tabulated on Table 10, Table 11 and Table 12. For Ca site substitution, Dy, Er, Gd, Hf, La, Sm, Ti, Y and Zr, elements were selected and for Ni site substitution, Al, Fe, P, Si, Sn, V and Zn were selected for

NEB calculations. Activation energies can be seen on graphs of diffusion of Ca atom in Figure 9, 10 and 11. It was found that, activation energy of Ca atom on pure $CaNi_5$ structure is 0,89191 eV.

Table 9. % Change in distance between opposite nickel atoms according to pure $CaNi_5$

	Ca-Site Substitution		**Ni1-Site Substitution**		**Ni2-Site Substitution**	
Alloying Elements	**Same Distances**	**Different Distance**	**Same Distances**	**Different Distance**	**Same Distances**	**Different Distance**
Ac	0.341	-0.613	1.500	1.790	4.573	0.372
Ag	-0.369	0.439	0.375	0.552	2.942	-0.251
Al	-0.808	0.433	0.270	0.329	0.353	0.292
Au	-0.383	0.374	0.369	0.626	2.727	-0.352
B	-1.042	-1.500	0.452	0.060	-2.937	0.617
Ba	0.556	-1.386	1.462	1.777	6.132	-0.200
Bi	-0.195	-0.301	1.135	1.520	2.611	0.115
Ca	-	-	0.850	0.949	4.792	-0.113
Cd	-0.446	0.097	0.483	0.681	2.143	-0.358
Ce	0.108	-0.229	1.277	1.556	4.578	0.157
Co	-0.886	0.373	0.110	0.116	-0.258	0.255
Cr	-0.852	0.696	0.185	0.206	-0.276	0.481
Cu	-0.677	0.168	-0.051	-0.034	0.909	0.105
Dy	-0.144	0.170	0.958	1.146	3.387	0.075
Er	-0.137	0.639	0.859	1.024	3.218	0.103
Fe	-0.703	1.237	0.092	0.120	-0.513	0.447
Gd	-0.019	0.276	1.163	1.387	3.345	-0.096
Ge	-0.633	-0.272	0.418	0.526	0.025	0.553
Hf	-0.721	1.027	0.707	0.886	1.135	0.869
Hg	-0.416	-0.023	0.552	0.825	3.627	-0.204
In	-0.376	0.253	0.475	0.581	2.666	-0.056
K	0.386	0.047	0.999	1.117	6.514	-0.793
La	-0.011	-0.542	1.174	1.438	3.508	0.327
Li	-0.481	0.039	-0.051	-0.102	1.578	-0.215
Mg	-0.418	0.412	0.530	0.565	2.429	0.266
Mn	-0.332	1.017	0.350	0.471	0.281	0.340
Mo	-0.971	1.412	0.537	0.679	-1.317	0.806
Na	0.058	0.082	0.477	0.474	4.123	-0.318
Nb	-0.917	1.062	0.594	0.740	-0.477	0.793
Nd	0.172	0.140	1.019	1.217	4.098	0.235
Ni	-0.782	0.328	-	-	-	-
P	-0.926	-0.914	0.423	0.411	-2.442	0.625
Pb	-0.146	-0.277	0.794	1.249	3.167	0.309
Pd	-0.422	0.782	0.304	0.339	2.298	-0.106
Sb	-0.742	-0.330	0.651	1.054	1.642	0.713
Sc	-0.421	0.736	0.539	0.625	1.737	0.072
Si	-0.896	-0.425	0.545	0.598	-1.481	0.513
Sm	-0.003	0.130	0.660	0.791	3.850	0.120
Sn	-0.665	-0.061	0.555	0.867	2.017	0.213
Ta	-1.067	0.987	0.630	0.828	-0.512	0.964
Th	0.033	0.170	1.257	1.537	1.981	0.786
Ti	-0.896	0.610	0.226	0.211	-0.570	0.469
V	-0.817	1.359	0.266	0.241	-1.727	0.756
W	-1.022	1.326	0.460	0.656	-1.370	0.890
Y	-0.175	0.256	1.004	1.201	3.593	-0.063
Yb	-0.138	0.004	0.801	0.866	3.911	0.045
Zn	-0.595	0.188	0.219	0.266	1.177	-0.068
Zr	-0.658	0.881	0.846	0.984	1.393	0.720

Table 10. Activation energies and change in the activation energy for Ca site substitution

Element	Activation Energy (eV)	% Change in Activation Energy	% Change in Formation Energy	Activation Energy of Pure $CaNi_5$ (eV)
Dy	0.925	3.777	-22,80	0.8919
Er	0.932	4.516	-23,38	0.8919
Gd	0.910	2.132	-21,92	0.8919
Hf	1.032	15.711	-17,54	0.8919
La	0.897	0.597	-17,76	0.8919
Sm	0.899	0.799	-19,42	0.8919
Ti	1.091	22.412	1,09	0.8919
Y	0.915	2.654	-21,71	0.8919
Zr	1.027	15.176	-17,55	0.8919

It can be concluded from Table 10 that, Ti has little effect on formation energy of $CaNi_5$, but it increases activation energy for diffusion of Ca atom about %22. Therefore, for Ca site substitution, addition to formation of sable oxide layer on surface, Ti can improve cycle life by increasing activation energy for diffusion of Ca atom in the structure. Interestingly, Hf and Zr not only decrease formation energy of system but they also increase activation energy for diffusion of Ca atom considerably which makes diffusion of Ca atom in the structure more difficult. Therefore, it can be concluded that, these elements would be effective to improve cycle life of $CaNi_5$. Also rare earths which decrease formation energy of system has little effect on activation energy for diffusion of Ca atom.

Table 11. Activation energies and change in the activation energy for Ni-1 site substitution

Element	Activation Energy (eV)	% Change in Activation Energy	% Change in Formation Energy	Activation Energy of Pure $CaNi_5$ (eV)
Al	1.057	18.524	-21.49	0.8919
Fe	0.949	6.413	3.60	0.8919
P	0.853	-4.254	-29.03	0.8919
Si	0.982	10.105	-26.16	0.8919
Sn	1.251	40.367	-7.66	0.8919
V	1.212	35.982	4.55	0.8919
Zn	0.950	6.536	-10.24	0.8919

Table 12 Activation energies and change in the activation energy for Ni-2 site substitution.

Element	Activation Energy (eV)	% Change in Activation Energy	% Change in Formation Energy	Activation Energy of Pure $CaNi_5$ (eV)
Al	0.753	-15.513	-22.35	0.8919
Fe	0.814	-8.699	3.25	0.8919
P	0.770	-13.559	-33.08	0.8919
Si	0.813	-8.752	-30.24	0.8919
Sn	0.748	-16.103	-10.76	0.8919
V	0.709	-20.424	0.73	0.8919
Zn	0.797	-10.566	-8.76	0.8919

As can be seen in Table 11 and Table 12, for Ni-1 site substitution, except P, all elements which decrease formation energy of system also increase the activation energy of diffusion of Ca atom. However, if we look for change in energy on formation energy of system, all these elements, except Zn, prefer Ni-2 site substitution because of lower energy state. As can be seen on Table 12, if these elements substitute with Ni-2 site all elements decrease activation energy of diffusion of Ca atom, which makes diffusion of Ca atom easier.

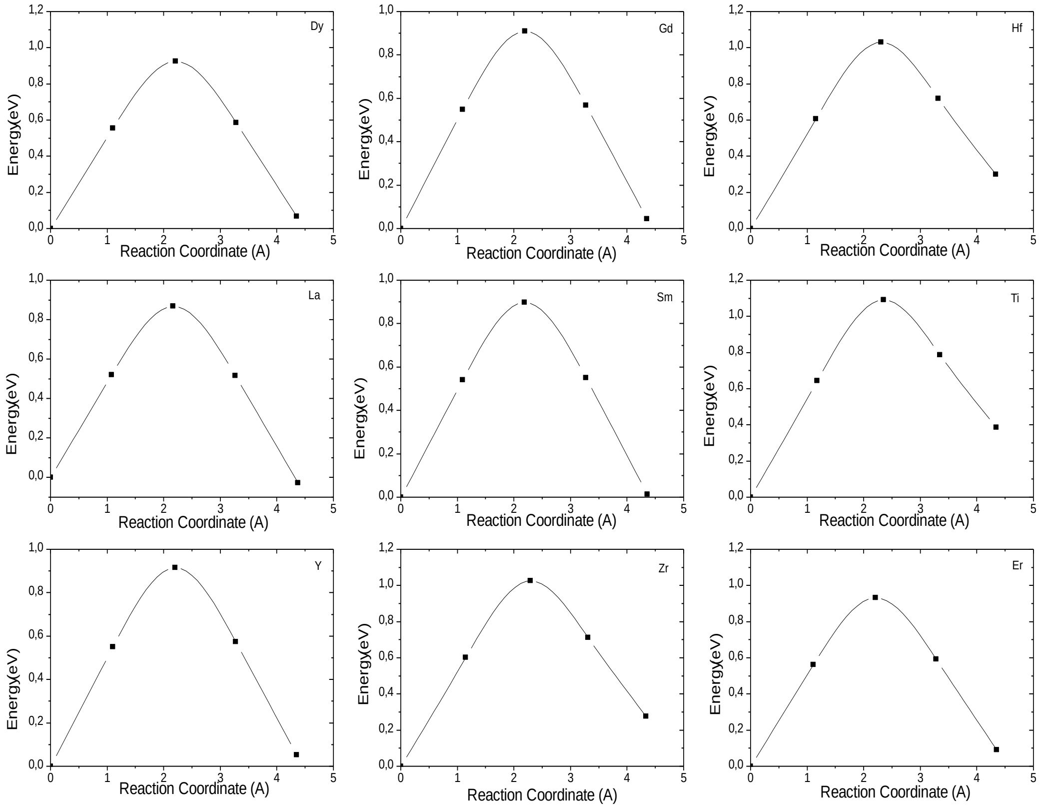

Figure 9. Activation energies of diffusion of Ca atom in the structure for Ca site substitution

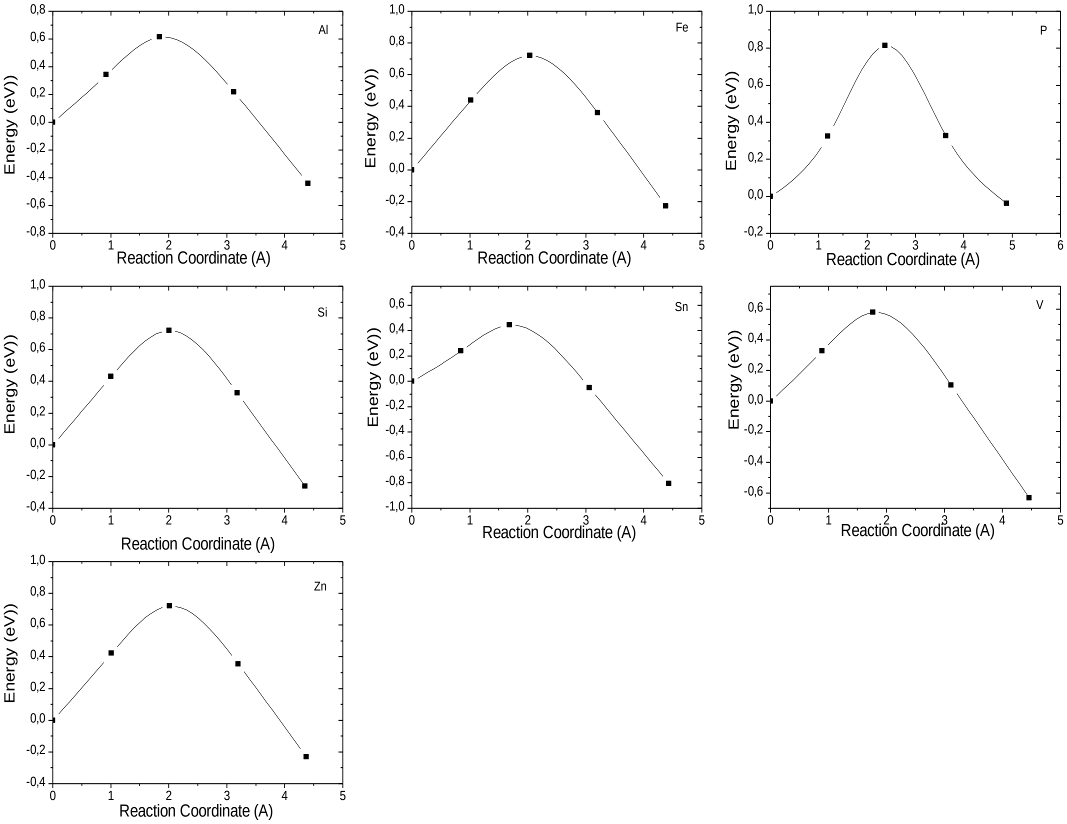

Figure 10. Activation energies of diffusion of Ca atom in the structure for Ni–1 site substitution

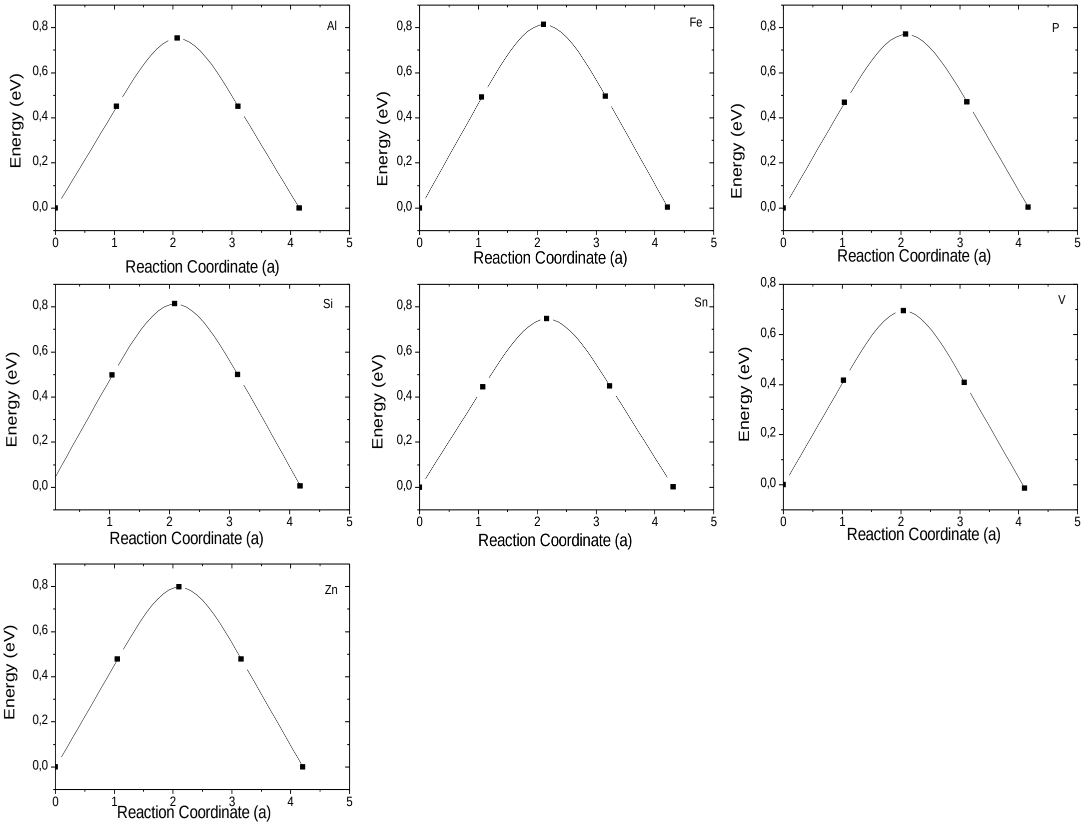

Figure 11. Activation energies of diffusion of Ca atom in the structure for Ni–2 site substitution

4.1.2 Formation Energy Calculations for Hydride Compounds of $CaNi_5$

As known from electrochemical reactions of a Ni – MH battery, hydrogen atoms are stored on anode materials. Current density, capacity and other properties of battery is directly related with the release of these hydrogen atoms from anode. In this manner, effect of alloying on formation energy of hydride compounds of $CaNi_5$ were calculated and compared with the pure hydride compound. When hydrogen atoms were positioned at (123) Fig. 3, formation energy of pure $CaNi_5H_6$ was calculated as -1.233 eV and when hydrogen atoms were positioned at (356) Fig. 3, formation energy of pure $Ca_8Ni_{40}H_{48}$ was calculated as -1.27 eV. In addition, calculations were done for $Ca_7Ni_{40}MH_{48}$ and $Ca_8Ni_{39}MH_{48}$ compounds and effect of alloying on formation energy of these alloys were investigated and compared with the pure $Ca_8Ni_{40}H_{48}$, Table 13.

Table 13. % Change in the formation energy of hydride compounds of $CaNi_5$ for alloying elements.

Element	Ca		Ni – 1		Ni - 2	
	(123)	(356)	(123)	(356)	(123)	(356)
Ag	-4.204	-3.121	-3.746	-1.917	0.317	-4.037
Al	-11.436	-10.846	-8.125	-4.465	-4.670	-5.325
B	5.312	7.553	-8.703	-7.635	-3.936	-12.157
Ba	10.117	8.385	20.177	16.170	20,708	12.332
Bi	-7.280	-7.558	3.743	-0.266	9.426	1.428
Cd	-5.619	-6.186	4.132	-1.636	5.011	3.266
Ce	0.073	-2.629	16.757	13.090	13.907	14.108
Co	-3.625	-6.261	4.654	-0.113	1.677	0.591
Cr	2.090	-22.428	4.503	1.068	3.037	3.027
Cu	-5.439	-5.108	-3.321	-4.971	0.201	-4.505
Dy	-5.400	-7.425	14.693	11.819	11.647	12.045
Er	-6.642	-8.399	14.205	11.284	9.467	10.785
Fe	-14.428	-23.101	-1.332	-6.644	-4.900	-4.489
Gd	-4.300	-6.388	14.972	12.248	11.951	11.690
Hf	-17.425	-18.956	8.139	3.567	3.309	6.589
K	12.828	10.400	20.092	19.380	16.830	15.932
La	0.553	-2.520	13.905	10.549	9.835	8.238
Li	1.974	-0.757	7.441	3.362	8.231	5.406
Mg	-5.548	-5.636	4.819	1.743	5.714	3.372
Mn	-10.370	-28.476	-0.620	-2.561	1.268	0.047
Mo	-10.649	-15.226	4.378	-1.115	1.433	0.892
Nb	-18.925	-18.270	4.821	-0.903	4.356	2.968
Nd	-1.556	-4.119	16.690	12.929	12.483	11.268
Pb	-7.212	-7.287	3.200	-0.961	8.800	1.169
Pd	-7.999	-7.363	-2.477	-2.589	0.689	-3.188
Sb	-9.596	-8.544	-0.409	-4.532	7.084	-2.597
Sc	-9.852	-10.703	10.586	6.929	7.215	8.510
Si	-12.632	-8.807	-16.516	-8.796	-14.159	-8.659
Sm	-2.880	-5.382	16,299	12.605	12.802	11.878
Sn	-10.460	-8.906	1.159	-2.903	8.112	-0.245
Ta	-22.913	-23.889	3.141	-2.626	3.338	0.782
Th	-8.245	-10.309	11.205	6,522	4.688	4.401
Ti	-13.962	-15.135	5.200	0.607	1.544	3.062
V	-11.063	-16.003	4.493	-0.415	-1.490	0.368
W	-15.447	-19.296	1.794	-3.665	-0.511	-2.026
Y	-5.000	-7.074	16.455	13.859	12.879	12.489
Yb	1.202	-1.655	13.569	12.090	13.124	10.181
Zn	-7.151	-5.065	-7.203	-4.445	-3.574	-7.738
Zr	-14.808	-14.996	9.412	5.184	3.988	7.307
Ca			15.143	14.315	16.257	16.560
Ni	-1.73384	-2.296				
Na	5.329135	3.113	10.713	10.813	11.057	8.021
Ac	3.078796	-0.045	15.912	12.537	15.249	8.072
Au	-6.43054	-5.013	-10.277	-5.431	-3.576	-8.388
Hg	-5.45928	-4.378	1.532	-0.557	3.962	-0.295
In	-7.96274	-5.831	3.591	-2.846	5.943	1.401
Ge	-9.86163	-8.458	-5.830	-9.359	3.718	-5.820
P	-9.06185	-2.174	-20.621	-10.463	-13.979	-9.278

As mentioned above, capacity of battery is directly related with the release of the hydrogen stored. If hydride is too stable, capacity of active material may decrease because hydrogen cannot be released easily. Therefore, if proper alloying decrease formation energy of $Ca_{(1-x)}Ni_5M_x$

and $CaNi_{(5-x)}M_x$ compounds, cycle life would probably increase. However, if proper alloying decrease the formation energy of hydride compounds, reversible capacity of active material would probably decrease. In addition, contrary to decrease in formation energy of hydride compounds, if formation energy of hydride compounds increase, active material cannot be charged completely.

In this respect, when Table 8 and 13 investigated, it can be seen that, substitution of Ca with La, Ce and Yb do not change the formation energy of $CaNi_5H_6$ too much. Other rare earth elements and Y decrease formation energy of $CaNi_5H_6$ by 5 to 7 % when substituted with the Ca. Zr and Hf, however, decrease the formation energy of the hydride by more than 10% if replace with Ca atom. On the other hand, all early transition metals including Zr and Hf decrease the hydride stability if they substitute Ni sites. Other elements replacing Ni sites (Al, Si, Ge, P Sn and Zn) which decrease formation energy of $CaNi_5$, decrease the formation energy of the hydride too.

In addition, as mentioned above, lattice expansions because of the hydrogen absorption, enhance mobility of Ca atom [30]. According to lattice parameter calculations, volume of pure $CaNi_5$ increases about 22.53 % for (123) positions and 23.76 % for (356) positions while hydrogen absorbing. Therefore, in order to investigate effect of alloying on lattice parameters of $CaNi_5$ hydride compounds, lattice parameters of hydride compounds were calculated (Tables 14, 15 and 16). Also change in the volume while hydrogen absorbing were calculated and compared with that for pure $CaNi_5$ as seen in Table 17.

Table 14. Lattice parameters of Ca site substituted hydride alloys of $CaNi_5$.

Alloy	Calculated Lattice Parameters for (123)		Calculated Lattice Parameters for (356)	
	a	**c**	**a**	**c**
$CaNi_5H_6$	5.284	4.204	5.311	4.204
Ca-Ag	5.253	4.225	5.248	4.232
Ca-Al	5.224	4.247	5.224	4.254
Ca-B	5.229	4.210	5.242	4.216
Ca-Ba	5.312	4.207	5.339	4.222
Ca-Bi	5.266	4.228	5.287	4.249
Ca-Cd	5.249	4.229	5.274	4.251
Ca-Ce	5.281	4.217	5.315	4.223
Ca-Co	5.226	4.206	5.252	4.225
Ca-Cr	5.231	4.229	5.270	4.210
Ca-Cu	5.234	4.228	5.244	4.232
Ca-Dy	5.251	4.239	5.286	4.229
Ca-Er	5.259	4.241	5.289	4.233
Ca-Fe	5.226	4.206	5.264	4.219
Ca-Gd	5.271	4.230	5.293	4.230
Ca-Hf	5.224	4.253	5.264	4.240
Ca-K	5.302	4.214	5.315	4.217
Ca-La	5.278	4.221	5.312	4.229
Ca-Li	5.251	4.224	5.271	4.237
Ca-Mg	5.237	4.226	5.257	4.233
Ca-Mn	5.232	4.237	5.270	4.223
Ca-Mo	5.233	4.203	5.257	4.218
Ca-Nb	5.234	4.238	5.272	4.224
Ca-Nd	5.273	4.227	5.306	4.232
Ca-Pb	5.263	4.223	5.290	4.254
Ca-Pd	5.232	4.228	5.257	4.223
Ca-Sb	5.248	4.238	5.265	4.253
Ca-Sc	5.241	4.250	5.269	4.226
Ca-Si	5.216	4.262	5.217	4.237
Ca-Sm	5.275	4.227	5.305	4.233
Ca-Sn	5.238	4.231	5.260	4.258
Ca-Ta	5.214	4.255	5.252	4.241
Ca-Th	5.266	4.233	5.306	4.237
Ca-Ti	5.228	4.238	5.272	4.228
Ca-V	5.225	4.218	5.278	4.233
Ca-W	5.233	4.206	5.258	4.227
Ca-Y	5.259	4.238	5.298	4.235
Ca-Yb	5.257	4.229	5.300	4.229
Ca-Zn	5.230	4.235	5.240	4.249
Ca-Zr	5.238	4.250	5.275	4.229
Ca-Ni	5.220	4.221	5.247	4.232
Ca-Na	5.269	4.220	5.276	4.222
Ca-Ac	5.294	4.209	5.331	4.231
Ca-Au	5.245	4.227	5.270	4.247
Ca-Hg	5.249	4.227	5.270	4.248
Ca-In	5.240	4.229	5.255	4.253
Ca-Ge	5.230	4.249	5.226	4.238
Ca-P	5.216	4.255	5.234	4.232

Table 15. Lattice parameters of Ni - 1 site substituted hydride alloys of $CaNi_5$.

Alloy	Calculated Lattice Parameters for (123)		Calculated Lattice Parameters for (356)	
	a	c	a	c
$CaNi_5H_6$	5.284	4.204	5.311	4.204
Ni-Ag	5.280	4.244	5.308	4.242
Ni-Al	5.303	4.197	5.338	4.191
Ni-B	5.284	4.138	5.350	4.133
Ni-Ba	5.363	4.229	5.356	4.258
Ni-Bi	5.317	4.219	5.332	4.226
Ni-Cd	5.306	4.220	5.320	4.234
Ni-Ce	5.347	4.223	5.331	4.249
Ni-Co	5.273	4.233	5.293	4.224
Ni-Cr	5.277	4.240	5.302	4.232
Ni-Cu	5.277	4.219	5.308	4.226
Ni-Dy	5.318	4.224	5.332	4.248
Ni-Er	5.323	4.230	5.332	4.250
Ni-Fe	5.262	4.239	5.301	4.226
Ni-Gd	5.319	4.225	5.329	4.245
Ni-Hf	5.300	4.216	5.320	4.223
Ni-K	5.353	4.218	5.325	4.266
Ni-La	5.334	4.220	5.337	4.249
Ni-Li	5.270	4.222	5.286	4.239
Ni-Mg	5.287	4.220	5.308	4.233
Ni-Mn	5.282	4.244	5.305	4.223
Ni-Mo	5.274	4.231	5.305	4.222
Ni-Nb	5.281	4.230	5.318	4.223
Ni-Nd	5.339	4.223	5.332	4.251
Ni-Pb	5.319	4.216	5.330	4.223
Ni-Pd	5.275	4.239	5.294	4.247
Ni-Sb	5.309	4.207	5.335	4.202
Ni-Sc	5.302	4.234	5.308	4.236
Ni-Si	5.313	4.143	5.355	4.147
Ni-Sm	5.326	4.213	5.330	4.246
Ni-Sn	5.318	4.209	5.333	4.216
Ni-Ta	5.290	4.217	5.336	4.226
Ni-Th	5.325	4.217	5.350	4.241
Ni-Ti	5.280	4.223	5.308	4.216
Ni-V	5.278	4.226	5.313	4.209
Ni-W	5.266	4.235	5.331	4.224
Ni-Y	5.326	4.227	5.332	4.251
Ni-Yb	5.310	4.221	5.308	4.246
Ni-Zn	5.286	4.208	5.321	4.206
Ni-Zr	5.301	4.222	5.319	4.230
Ni-Ca	5.279	4.278	5.340	4.237
Ni-Na	5.312	4.232	5.308	4.258
Ni-Ac	5.335	4.232	5.338	4.249
Ni-Au	5.280	4.263	5.316	4.240
Ni-Hg	5.297	4.219	5.302	4.228
Ni-In	5.306	4.209	5.345	4.231
Ni-Ge	5.316	4.185	5.341	4.172
Ni-P	5.319	4.133	5.325	4.194

Table 16. Lattice parameters of Ni - 2 site substituted hydride alloys of $CaNi_5$.

Alloy	Calculated Lattice Parameters for (123)		Calculated Lattice Parameters for (356)	
	a	**c**	**a**	**c**
$CaNi_5H_6$	5.284	4.204	5.311	4.204
Ni-Ag	5.331	4.222	5.306	4.226
Ni-Al	5.275	4.232	5.281	4.236
Ni-B	5.261	4.207	5.314	4.197
Ni-Ba	5.382	4.265	5.360	4.290
Ni-Bi	5.299	4.259	5.322	4.263
Ni-Cd	5.331	4.246	5.320	4.240
Ni-Ce	5.367	4.261	5.332	4.279
Ni-Co	5.264	4.211	5.292	4.221
Ni-Cr	5.292	4.229	5.307	4.232
Ni-Cu	5.280	4.227	5.305	4.227
Ni-Dy	5.350	4.235	5.289	4.243
Ni-Er	5.349	4.244	5.295	4.239
Ni-Fe	5.274	4.215	5.308	4.230
Ni-Gd	5.351	4.239	5.302	4.258
Ni-Hf	5.316	4.230	5.290	4.228
Ni-K	5.375	4.250	5.387	4.270
Ni-La	5.355	4.262	5.298	4.269
Ni-Li	5.283	4.228	5.294	4.219
Ni-Mg	5.310	4.226	5.301	4.224
Ni-Mn	5.276	4.226	5.295	4.231
Ni-Mo	5.290	4.195	5.310	4.214
Ni-Nb	5.293	4.196	5.304	4.227
Ni-Nd	5.356	4.244	5.313	4.263
Ni-Pb	5.297	4.246	5.322	4.251
Ni-Pd	5.288	4.233	5.327	4.246
Ni-Sb	5.270	4.251	5.302	4.266
Ni-Sc	5.317	4.232	5.294	4.231
Ni-Si	5.286	4.220	5.253	4.240
Ni-Sm	5.361	4.250	5.307	4.258
Ni-Sn	5.292	4.246	5.303	4.245
Ni-Ta	5.287	4.196	5.307	4.231
Ni-Th	5.352	4.273	5.298	4.272
Ni-Ti	5.297	4.223	5.293	4.233
Ni-V	5.283	4.213	5.298	4.224
Ni-W	5.287	4.204	5.315	4.228
Ni-Y	5.360	4.233	5.294	4.248
Ni-Yb	5.341	4.231	5.301	4.239
Ni-Zn	5.291	4.240	5.307	4.232
Ni-Zr	5.323	4.240	5.308	4.241
Ni-Ca	5.326	4.225	5.321	4.261
Ni-Na	5.342	4.233	5.313	4.227
Ni-Ac	5.342	4.278	5.333	4.284
Ni-Au	5.317	4.233	5.300	4.248
Ni-Hg	5.320	4.252	5.319	4.245
Ni-In	5.306	4.239	5.313	4.243
Ni-Ge	5.260	4.235	5.270	4.245
Ni-P	5.337	4.205	5.250	4.248

Table 17. % change in volume expansion while hydrogen absorbing for different alloying elements compared to pure $CaNi_5$ and its hydride.

Element	Ca		Ni – 1		Ni - 2	
	(123)	(356)	(123)	(356)	(123)	(356)
Ag	-0.06	-5.30	-2.98	-2.89	-0.16	-9.54
Al	0.08	-4.34	1.21	2.01	-1.64	-5.17
B	-1.34	-3.07	-3.77	3.37	9.27	12.94
Ba	-0.29	1.73	-0.45	-3.40	-1.76	-8.16
Bi	-0.98	0.59	-6.66	-7.77	-3.16	-3.22
Cd	-0.91	1.58	-1.92	-2.48	6.50	-2.16
Ce	0.27	2.34	-1.64	-6.67	-1.20	-10.96
Co	-3.28	-0.93	1.56	-0.95	-3.80	-2.03
Cr	-0.15	0.13	3.54	2.12	2.71	0.89
Cu	-1.22	-3.81	0.98	2.76	-2.81	-2.97
Dy	-0.22	0.27	-4.26	-3.76	-0.48	-16.29
Er	1.12	1.01	-0.50	-1.40	0.91	-15.28
Fe	-6.26	-2.02	0.26	1.10	-2.49	1.00
Gd	0.79	-0.10	-6.09	-6.68	2.01	-10.40
Hf	-1.48	-0.25	-4.36	-4.60	-2.71	-13.07
K	2.99	0.51	-0.43	-5.21	-2.43	-2.80
La	0.49	2.75	-2.72	-3.60	0.14	-15.25
Li	1.22	1.41	1.73	1.85	0.17	-3.99
Mg	-3.04	-3.40	-5.76	-5.00	-5.06	-11.92
Mn	-2.48	-1.80	0.26	-3.04	-2.88	-3.65
Mo	-1.77	-0.23	-5.91	-5.82	-0.99	0.00
Nb	3.26	3.76	-4.76	-3.50	-4.03	-2.98
Nd	-2.12	-0.14	-0.16	-3.38	-2.80	-13.70
Pb	-2.63	1.38	-2.24	-4.31	-9.79	-9.09
Pd	-4.06	-4.71	-4.48	-4.76	-4.62	-0.45
Sb	2.11	2.04	-3.43	-4.01	-9.59	-6.26
Sc	1.38	-1.33	0.52	-3.28	1.54	-8.36
Si	-0.10	-7.98	-5.28	-1.66	7.26	-2.48
Sm	1.41	2.85	6.43	5.83	0.04	-14.47
Sn	-3.62	-1.04	0.26	-1.16	-4.39	-7.26
Ta	2.73	3.25	-4.79	0.24	-6.70	-3.25
Th	-2.23	1.08	-5.46	-2.76	6.70	-9.48
Ti	0.88	2.98	0.03	-0.47	3.55	-1.38
V	-2.54	4.85	0.30	-0.11	2.12	1.17
W	-0.79	1.58	-6.21	0.31	-0.55	2.59
Y	1.21	3.23	-2.56	-3.55	1.71	-14.58
Yb	0.38	3.69	-4.06	-6.41	-2.65	-14.38
Zn	-2.25	-3.69	-0.90	0.46	2.84	-0.22
Zr	2.64	2.11	-5.02	-5.36	-1.05	-9.13
Ca			-4.24	-2.11	-11.91	-13.14
Ni	-3.75	-2.11				
Na	-0.53	-4.17	0.14	-2.70	-4.18	-15.24
Ac	-0.21	4.58	-5.76	-8.08	-5.29	-11.17
Au	-2.02	0.21	-0.42	-1.19	-0.28	-6.98
Hg	-1.17	0.37	-5.00	-7.70	-2.18	-8.30
In	-3.77	-2.96	-1.72	3.37	-2.56	-5.76
Ge	-1.19	-8.30	1.55	-0.29	-4.24	-6.20
P	-0.94	-5.46	-1.10	2.53	19.54	1.40

According to Table 17, generally, change in the volume expansion for (356) position of hydrogen atoms is higher than that for (123) position of hydrogen atoms. For Ca site substitution, when hydrogen atoms are positioned at (356) position, there is a little increase in volume expansions for rare earths and some early transition metals which decrease formation energy of $CaNi_5$. On the other hand, when hydrogen atoms are positioned at (123) positions volume expansion decreases. However, according to Table 13. when Ca atom is replaced with these elements, hydrogen atoms prefer (356) positions because of the lower energy state. For Ni site substitution, generally, Ni-2 site substitutions lower volume expansion while hydrogen absorbing. Especially, Hf, Mg, Sb, Sc, Sn, Zr and Ge decrease volume expansion while hydrogen absorbing much more according to pure $CaNi_5$ and also these elements decrease formation energy of $CaNi_5$. Therefore, it can be concluded for these elements one can expect less protective oxide film degradation.

4.2 Calculations for $LaNi_5$

4.2.1 Formation Energy Calculations

In literature there are limited studies for $CaNi_5$. Therefore, it is hard to discuss and comment on results of proper alloying of $CaNi_5$. In this manner, same study have been carried on for $LaNi_5$ because low cycle life problem of $LaNi_5$ was solved by proper alloying and today $LaNi_5$ is commercially active material for Ni-MH batteries. Also, as mentioned above, there are many studies for alloying of $LaNi_5$.

Same elements used for alloying of $CaNi_5$ were used for also alloying of $LaNi_5$. Alloying elements were replaced with one lanthanum atom, with one nickel atom in plane with lanthanum atom (Ni – 1 site) and with one nickel atom out of plane with lanthanum atom (Ni – 2 site). Therefore, $La_7Ni_{40}M$ and $La_8Ni_{39}M$ alloys were obtained and relaxed. Formation energies of $La_7Ni_{40}M$ and $La_8Ni_{39}M$ alloys were calculated by equations 7 and 8. Lattice parameters, total energies and formation energies of $La_7Ni_{40}M$ and $La_8Ni_{39}M$ alloys were tabulated on Table 17, 18, and 19.

In order to see effect of alloying on stability of $LaNi_5$, formation energies of alloys were compared with the formation energy of the pure $LaNi_5$, Table 20. As can be seen from Table 20, for La site substitution, some of the lanthanides, actinides and early transition metals of group 3 are effective for decreasing formation energy of $LaNi_5$. On the other hand, for Ni sites substitution, Al, Ge, P, Se, Se, Si, Ti and Zn are very effective to decrease formation energy of the system. In addition, less effectively, Ni can also be substituted with Au, Hf, Sb, Sc, Sn in order to lower formation energy of $LaNi_5$. As can be seen, it was determined that, all above elements lower formation energy of $LaNi_5$, therefore a more stable alloy is formed which may increase the cyclic durability.

Table 18. Lattice parameters, total energies and formation energies of La-site substitution alloys.

Alloy	**Lattice Parameters (Å)**		**ΔE ($La_7N_{40}M$) (eV/cell)**
	a	**c**	
$LaNi_5$ (8*)*	5.000	3.998	-1.754
La-Ag	4.967	3.990	-1.372
La-Al	4.945	4.002	-1.543
La-B	4.933	4.012	-1.074
La-Ba	5.015	3.983	-1.459
La-Bi	4.973	3.997	-1.438
La-Cd	4.970	3.999	-1.457
La-Ce	5.010	3.988	-1.718
La-Co	4.947	3.993	-1.272
La-Cr	4.970	3.986	-1.348
La-Cu	4.960	3.999	-1.336
La-Dy	4.984	3.985	-1.783
La-Er	4.974	3.991	-1.784
La-Fe	4.945	4.001	-1.157
La-Gd	4.987	3.984	-1.777
La-Hf	4.970	3.997	-1.737
La-K	5.006	3.980	-1.240
La-Ca	4.989	3.989	-1.630
La-Li	4.967	3.980	-1.451
La-Mg	4.960	3.989	-1.550
La-Mn	4.954	3.993	-1.403
La-Mo	4.944	3.990	-1.327
La-Nb	4.954	3.991	-1.542
La-Nd	4.992	3.981	-1.744
La-Pb	4.979	3.972	-1.424
La-Pd	4.959	3.988	-1.394
La-Sb	4.976	3.992	-1.475
La-Sc	4.966	3.990	-1.739
La-Si	4.952	4.007	-1.436
La-Sm	4.992	3.989	-1.761
La-Sn	4.974	3.991	-1.519
La-Ta	4.945	3.989	-1.547
La-Th	4.995	3.984	-1.846
La-Ti	4.953	3.988	-1.595
La-V	4.950	4.000	-1.384
La-W	4.948	3.996	-1.315
La-Y	4.984	3.989	-1.776
La-Yb	4.991	3.974	-1.695
La-Zn	4.956	4.002	-1.441
La-Zr	4.959	3.991	-1.736
La-Se	4.979	3.994	-1.337
La-Ni	4.947	3.989	-1.288
La-Na	4.983	3.991	-1.386
La-Ac	5.016	3.999	-1.700
La-Au	4.959	3.995	-1.400
La-Hg	4.982	3.991	-1.402
La-In	4.966	3.991	-1.511
La-Ge	4.962	4.001	-1.445
La-P	4.949	3.999	-1.344

Table 19. Lattice parameters, total energies and formation energies of Ni-1 site substitution alloys.

Alloy	**Lattice Parameters (Å)**		**ΔE ($La_8N_{39}M$) (eV/cell)**
	a	**c**	
$LaNi_5$ (8)	5.000	3.998	-1,754
Ni-Ag	5.016	4.007	-1.659
Ni-Al	5.016	3.979	-1.866
Ni-B	5.017	3.931	-1.710
Ni-Ba	5.058	4.022	-1.325
Ni-Bi	5.047	3.992	-1.577
Ni-Cd	5.025	4.009	-1.668
Ni-Ce	5.055	4.014	-1.528
Ni-Co	5.003	3.993	-1.690
Ni-Cr	5.004	3.985	-1.633
Ni-Cu	5.004	3.991	-1.748
Ni-Dy	5.042	4.020	-1.683
Ni-Er	5.029	4.002	-1.701
Ni-Fe	5.008	3.990	-1.696
Ni-Gd	5.045	4.021	-1.662
Ni-Hf	5.030	3.996	-1.773
Ni-K	5.041	4.035	-1.218
Ni-La	5.041	4.007	-1.629
Ni-Li	4.998	3.997	-1.734
Ni-Mg	5.021	4.001	-1.727
Ni-Mn	5.006	3.994	-1.717
Ni-Mo	5.007	3.996	-1.591
Ni-Nb	5.027	4.003	-1.680
Ni-Nd	5.051	4.021	-1.601
Ni-Pb	5.042	4.007	-1.618
Ni-Pd	5.007	4.008	-1.772
Ni-Sb	5.040	3.988	-1.764
Ni-Sc	5.025	4.004	-1.781
Ni-Si	5.015	3.963	-1.899
Ni-Sm	5.038	4.015	-1.631
Ni-Sn	5.033	3.999	-1.761
Ni-Ta	5.032	4.006	-1.700
Ni-Th	5.057	4.011	-1.695
Ni-Ti	5.022	3.990	-1.784
Ni-V	5.004	3.980	-1.675
Ni-W	5.011	3.995	-1.584
Ni-Y	5.045	4.021	-1.661
Ni-Yb	5.024	4.008	-1.680
Ni-Zn	5.019	3.994	-1.796
Ni-Zr	5.032	4.010	-1.748
Ni-Ca	5.033	4.022	-1.570
Ni-Se	5.037	3.961	-1.836
Ni-Na	5.017	4.014	-1.515
Ni-Ac	5.064	4.008	-1.487
Ni-Au	5.017	4.007	-1.750
Ni-Hg	5.025	4.013	-1.663
Ni-In	5.029	4.001	-1.715
Ni-Ge	5.020	3.975	-1.852
Ni-P	5.027	3.939	-1.929

Table 20. Lattice parameters, total energies and formation energies of Ni-2 site substitution alloys.

Alloy	**Lattice Parameters (Å)**		**ΔE (La$_8$N$_{39}$M) (eV/cell)**
	a	**c**	
LaNi$_5$ (8)	5.000	3.998	-1.754
Ni-Ag	5.035	4.009	-1.674
Ni-Al	4.997	3.995	-1.884
Ni-B	4.962	3.967	-1.701
Ni-Ba	5.092	4.040	-1.308
Ni-Bi	5.042	4.010	-1.676
Ni-Cd	5.033	4.011	-1.683
Ni-Ce	5.070	4.029	-1.513
Ni-Co	4.991	3.991	-1.710
Ni-Cr	4.998	3.993	-1.645
Ni-Cu	4.998	3.998	-1.739
Ni-Dy	5.056	4.016	-1.646
Ni-Er	5.034	4.016	-1.661
Ni-Fe	4.989	3.999	-1.714
Ni-Gd	5.044	4.015	-1.623
Ni-Hf	5.013	4.007	-1.753
Ni-K	5.095	4.018	-1.207
Ni-La	5.049	4.025	-1.591
Ni-Li	5.000	3.999	-1.692
Ni-Mg	5.014	4.001	-1.715
Ni-Mn	5.001	3.997	-1.718
Ni-Mo	5.011	3.998	-1.619
Ni-Nb	5.012	4.002	-1.676
Ni-Nd	5.056	4.020	-1.556
Ni-Pb	5.039	4.020	-1.654
Ni-Pd	5.024	4.001	-1.789
Ni-Sb	5.019	4.011	-1.834
Ni-Sc	5.019	4.004	-1.752
Ni-Si	4.985	3.994	-1.944
Ni-Sm	5.065	4.026	-1.590
Ni-Sn	5.019	4.010	-1.801
Ni-Ta	5.006	4.002	-1.709
Ni-Th	5.039	4.021	-1.674
Ni-Ti	5.010	4.008	-1.780
Ni-V	4.986	3.986	-1.704
Ni-W	5.008	3.999	-1.622
Ni-Y	5.055	4.019	-1.628
Ni-Yb	5.043	4.015	-1.641
Ni-Zn	5.000	3.993	-1.793
Ni-Zr	5.025	4.013	-1.716
Ni-Ca	5.061	4.020	-1.544
Ni-Ni	5.010	3.996	-1.861
Ni-Na	5.051	4.016	-1.494
Ni-Ac	5.065	4.026	-1.494
Ni-Au	5.026	4.007	-1.777
Ni-Hg	5.037	4.013	-1.687
Ni-In	5.026	4.019	-1.735
Ni-Ge	5.004	4.002	-1.886
Ni-P	4.970	3.981	-1.965

Table 21. Percent change in the formation energy of $LaNi_5$ due to alloying at La, Ni-1 and Ni-2 sites.

Alloying Element	La Site	Ni-1 Site	Ni-2 Site	Alloying Element	La Site	Ni-1 Site	Ni-2 Site
Ac	3.10	15.23	14.81	**Mn**	19.98	2.09	2.06
Ag	21.76	5.38	4.57	**Mo**	24.36	9.29	7.70
Al	12.00	-6.41	-7.41	**Na**	20.97	13.64	14.79
Au	20.16	0.24	-1.34	**Nb**	12.10	4.19	4.46
B	38.76	2.53	3.00	**Nd**	0.59	8.73	11.28
Ba	16.82	24.48	25.42	**Ni**	2.54	0.00	0.00
Bi	18.03	10.10	4.46	**P**	23.39	-9.97	-12.01
Ca	7.04	10.51	11.98	**Pb**	18.79	7.77	5.69
Cd	16.91	4.90	4.03	**Pd**	20.54	-1.02	-2.02
Ce	2.04	12.87	13.76	**Sb**	15.91	-0.56	-4.59
Co	27.45	3.66	2.51	**Sc**	0.84	-1.55	0.14
Cr	23.12	6.87	6.22	**Se**	23.75	-4.70	-6.13
Cu	23.81	0.32	0.85	**Si**	18.15	-8.29	-10.87
Dy	-1.65	4.07	6.12	**Sm**	-0.40	7.02	9.37
Er	-1.74	3.04	5.29	**Sn**	13.37	-0.40	-2.69
Fe	34.04	3.28	2.28	**Ta**	11.81	3.10	2.54
Gd	-1.32	5.23	7.46	**Th**	-5.23	3.36	4.56
Ge	17.61	-5.61	-7.54	**Ti**	9.06	-1.73	-1.50
Hf	0.99	-1.11	0.06	**V**	21.08	4.47	2.86
Hg	20.04	5.19	3.81	**W**	25.04	9.71	7.50
In	13.83	2.20	1.06	**Y**	-1.26	5.27	7.20
K	29.31	30.58	31.21	**Yb**	3.36	4.23	6.42
La	0	7.10	9.32	**Zn**	17.83	-2.40	-2.22
Li	17.28	1.16	3.51	**Zr**	1.00	0.35	2.14
Mg	11.64	1.56	2.20				

Some agreements can be seen between these results and results found in literature. For example, according to studies, Al, Ge, Si, Sn and Ti improves cycle life if they are replaced with Ni atom [30, 39-41] and it was found in this study that these elements decrease formation energy of system and they prefer Ni site substitution. However, in literature, it was stated that, these elements improve cycle life by formation of stable oxide layer on alloy surface and lowering the lattice expansion during hydriding. Therefore, it is hard to say which mechanism is dominant in order to improve cycle life of $LaNi_5$. A similar agreement can be seen in Fe added alloys. In literature, it was stated that Fe adversely effects the cycle life of $LaNi_5$ [37] and as can be seen on Table 21, Fe increases formation energy of system. In addition, in literature, it was found that, Ce, Pr, Co and Zr improves cycle life by formation of stable oxide layer on surface [30, 34, 42, 60]. On the other hand, in this study, it was found that they have no noticeable effect on formation energy of $LaNi_5$. Therefore, it can be said that instead of thermodynamic stability, formation of stable oxide layer on surface would be dominant mechanism for improvement of cycle life.

In addition, it is known from literature that [30], lattice distortions enhance mobility of La atom and which leads to corrosion of $LaNi_5$. Therefore, effect of alloying on lattice parameters were investigated. According to Table 18, 19 and 20, it is seen that, for La site substitution rare earth elements and some early transition metals has no considerable effect on lattice parameters. For Ni site substitution, except Sb, Si and Se, alloying elements which decrease formation energy of $LaNi_5$ has no considerable effect on lattice parameters.

4.2.2 NEB Calculations

As mentioned above, activation energies of diffusion of La atom in crystal structure were calculated for different alloying elements and different substitution sites by NEB method and tabulated on Table 22 - 24. Elements were selected for NEB calculations, according to their effect on formation energy of $LaNi_5$. Generally, elements which decrease formation energy of $LaNi_5$ were selected. In this manner, for La site substitution, Ca, Dy, Er, Gd, Sm, Y and Zr were selected and for Ni site substitution, Al, Co, Cu, P, Sb, Si and Ti were selected for NEB calculations. It was found that, activation energy for diffusion of La atom on pure $LaNi_5$ structure is 1,02 eV. In addition graphs of these activation energies are given on following Fig 12 - 14.

As mentioned before, formation energy of pure $CaNi_5$ was found as -30.547 eV and activation energy for diffusion of Ca atom in pure $CaNi_5$ structure was found as 0.89191 eV. On the other hand, formation energy of pure $LaNi_5$ was found as -34.53 eV and activation energy for diffusion of La atom on pure $LaNi_5$ structure was found as 1,02 eV. According to these results, $LaNi_5$ is more stable than $CaNi_5$ because of the lower energy state. Therefore, it may be more difficult to improve cycle life of $CaNi_5$ than the $LaNi_5$. In addition, as can be seen, energy barrier for diffusion of La atom in $LaNi_5$ is higher than the that for Ca in $CaNi_5$. This is the another reason for difficulty of improvement of cycle life of $CaNi_5$.

As can be seen on Table 22, alloying $LaNi_5$ with Ca leads not only to increase in formation energy but also decreases activation energy for diffusion of La atom. On the other hand, rare earth elements (Dy, Er, Gd and Sm) and Y decreases slightly formation energy of system and increases activation energy for diffusion of La atom. In this manner, it can be concluded that, these rare earth elements and Y would have positive effect on cyclic stability of $LaNi_5$. In addition, although Zr increases formation energy of system slightly , it has increased activation energy for diffusion of La atom sharply. In this manner, agreements can be seen with the results found in this study and literature. For example, positive effects of rare earth elements on cyclic durability of $LaNi_5$ were detected by Chen et al. [42] and in this study, it was found that rare earth elements substituted with La atom decrease formation energy of system and increase activation energy for diffusion of La atom in the structure. In addition, Chan et al. has determined the positive effect of Zr on cyclic durability of $LaNi_5$ [41]. In this study, it was found that, although Zr substitution has no any positive effect on formation energy, Zr substitution with La atom increases activation energy for diffusion of La atom about 10 %.

Table 22. Activation energies and change in the activation energy for La site substitution.

Element	Activation Energy (eV)	% Change in Activation Energy	% Change in Formation Energy	Activation Energy of Pure $LaNi_5$ (eV)
Ca	1.012	-0.732	7.041	1.020
Dy	1.041	2.081	-1.654	1.020
Er	1.047	2.662	-1.744	1.020
Gd	1.038	1.744	-1.318	1.020
Sm	1.028	0.772	-0.398	1.020
Y	1.039	1.888	-1.261	1.020
Zr	1.131	10.848	1.004	1.020

Table 23. Activation energies and change in the activation energy for Ni-1 site substitution

Element	Activation Energy (eV)	% Change in Activation Energy	% Change in Formation Energy	Activation Energy of Pure $LaNi_5$ (eV)
Al	1.35372	32.66578	-6.412220	1.020
Co	1.13503	11.23447	3.662937	1.020
Cu	0.98734	-3.23924	0.318381	1.020
Sb	1.60833	57.61857	-0.559162	1.020
Si	1.27463	24.91535	-8.288358	1.020

Table 24. Activation energies and change in the activation energy for Ni-2 site substitution.

Element	Activation Energy (eV)	% Change in Activation Energy	% Change in Formation Energy	Activation Energy of Pure $LaNi_5$ (eV)
Al	0.774	-24.12556	-7.414073	1.020
Co	0.957	-6.14311	2.514626	1.020
Cu	0.964	-5.47582	0.845078	1.020
P	0.835	-18.15885	-12.014775	1.020
Sb	0.655	-35.73371	-4.594572	1.020
Si	0.852	-16.45912	-10.866261	1.020
Ti	0.503	-50.67302	-1.496663	1.020

As can be seen on Table 23 and 24, change in activation energy and formation energy are tabulated for Ni-1 site and Ni-2 site substitutions. From these tables, it can be concluded that, for Ni-1 site substitution, Al, Co, Sb and Si increase activation energy for diffusion of La atom sharply. Except Co, these elements also decrease formation energy of the system. However, when formation energies for Ni-1 site and Ni-2 site are compared, it can be seen that, all of these elements prefer Ni-2 site on crystal structure because of the lower energy state. On the other hand, as can be seen on the Table 24, although Al, P, Sb, Si and Ti decreases formation energy of these system, all of the elements decrease also activation energy for diffusion of La atom which make diffusion of La atom easier.

From Table 23 and 24, it can be concluded that, effect of alloying on formation energy is more important than the effect on activation energy for diffusion of one La atom in the structure or certain elements are effective through the formation of a protective oxide layer, because it was known that some of the these elements such as Al, Si, Co and Ti increase cycle life of $LaNi_5$ [30, 34, 36], although they don’t seem to be effective in diffusivity. They either form a protective oxide layer or decrease the formation energy of $LaNi_5$. In this manner, these elements actually prefer Ni-2 site substitution and decreases formation energy. Therefore, cycle life of $LaNi_5$ would be increased.

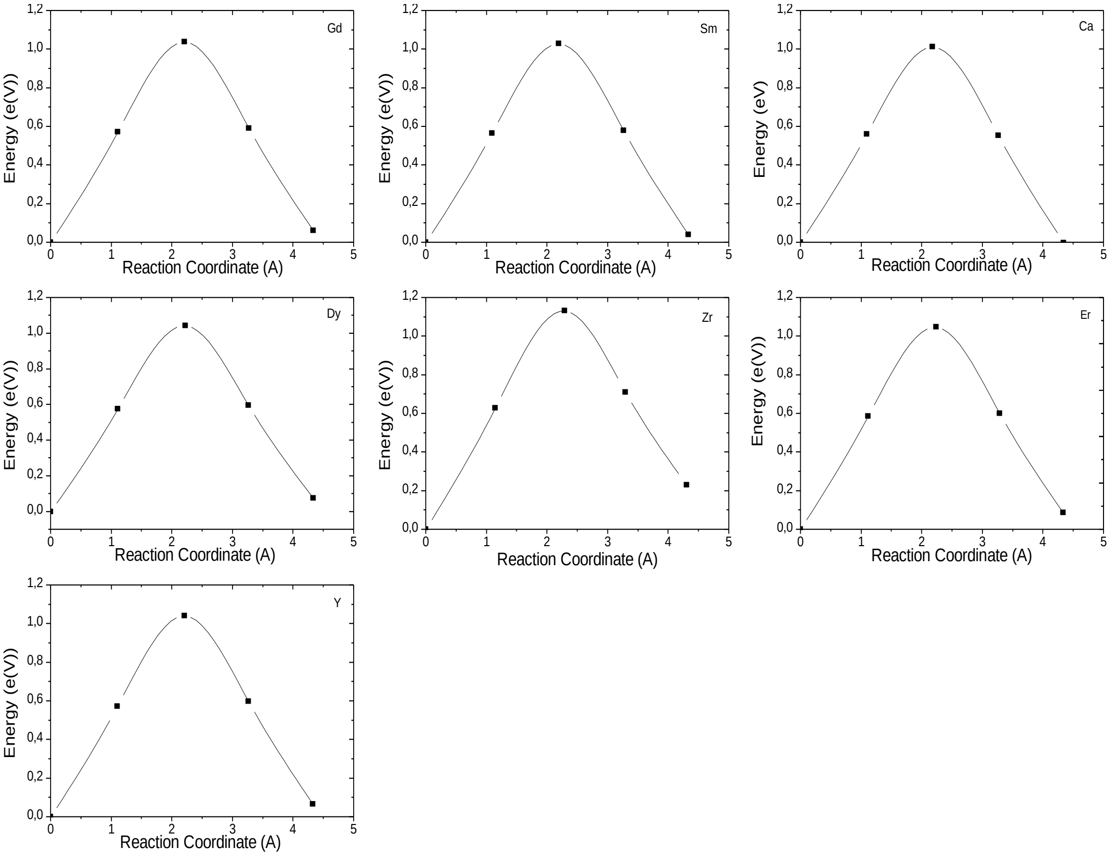

Figure 12. Activation energies for diffusion of La atom for La site substitution for Ca, Dy, Er, Gd, Sm, Y and Zr alloying elements.

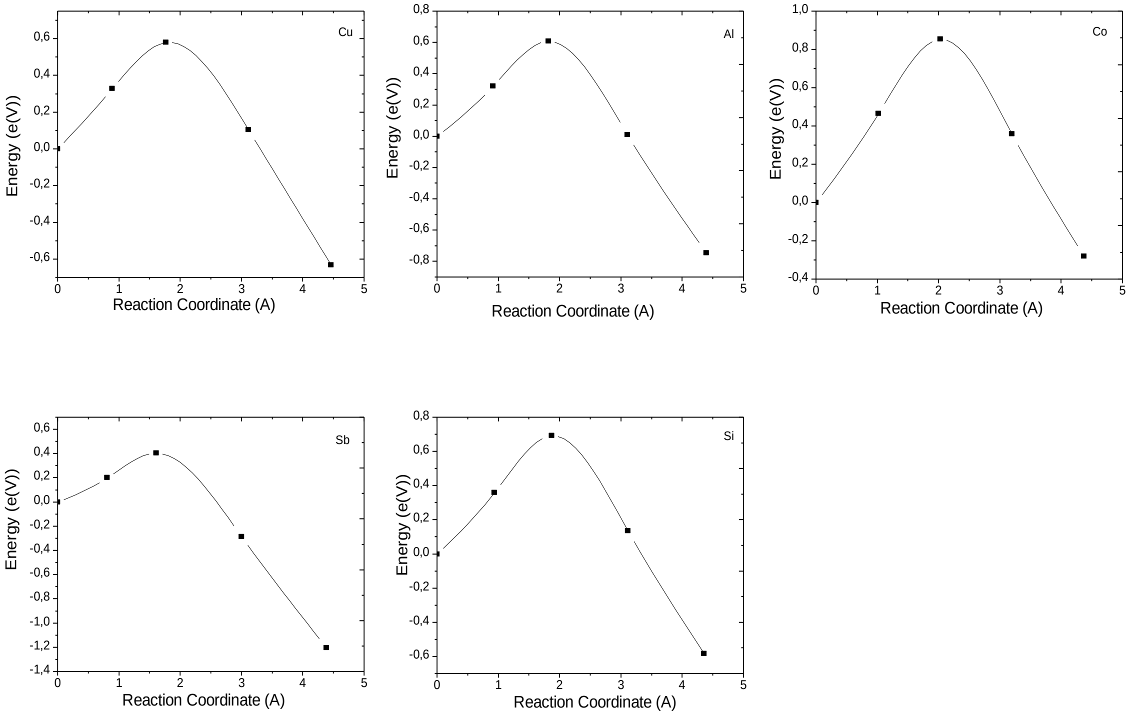

Figure 13. Activation energies for diffusion of La atom for Ni-1csite substitution for Al, Co, Cu, Sb and Si alloying elements.

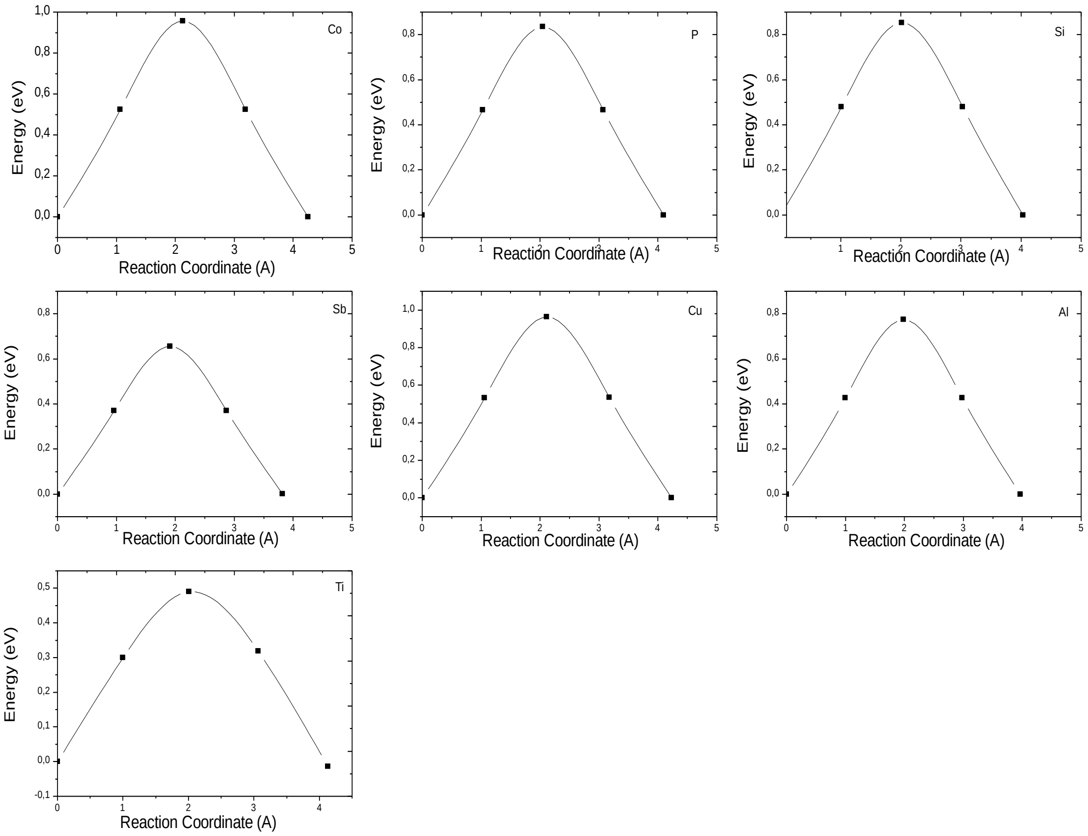

Figure 14. Activation energies for diffusion of La atom for Ni-2 site substitution for Al, Co, Cu, P, Sb, Si and Ti alloying elements.

CHAPTER 4

CONCLUSION

In this study, effects of alloying on $CaNi_5$ and $LaNi_5$ were studied using density functional theory within generalized approximation. In this regard, formation energies of the $CaNi_5$ and $LaNi_5$ compounds having different alloying elements were calculated for the understanding of the effect of the alloying element on the stability of the compound. It was found for $CaNi_5$ alloying that, all lanthanides and actinides and early transition metals (Sc, Y, Zr, Hf) replacing Ca and early transition metals (Sc, Ti, Zr, Hf) plus elements like Al, Si, P, Ge, Zn, Sn and Sb decrease the formation energy of $CaNi_{5.}$ In addition, effect of alloying on formation energy of hydride compounds of $CaNi_5$ were calculated and compared with the pure hydride compound. It was found that, although substitution of Ca with La, Ce and Yb do not change the formation energy of $CaNi_5H_6$ too much, other rare earth elements and Hf, Y and Zr decrease formation energy of $CaNi_5H_6$ between 4 % and 20 %. In addition, it was determined that, when Ni is substituted with Si, Ge and P decrease formation energy and Zr, Ti, Hf and Sn elements increase the formation energy of $CaNi_5H_6$. For $LaNi_5$ alloying, it was found that some lanthanides and actinides and early transition metals (Dy, Er, Gd, Sm, Th and Y) replacing La and for Ni replacing some early transition metals (Sc, Ti and Hf) plus elements like Al, Si, P, Ge, Zn, Sn, Pd, Au and Sb replacing Ni, decrease the formation energy of $LaNi_5$. Lower formation energy, compared to the pure compound, increases the stability which could improve the cyclic durability of $CaNi_5$ and $LaNi_5$ to be used as an anode in Ni-MH batteries. In addition, effect of alloying on volume expansion while hydrogen absorbing were investigated and it was found that some of the elements which decrease formation energy of $CaNi_5$, decrease also volume expansion while hydrogen absorbing. It can be concluded that these elements would be important to improve cycle life of $CaNi_5$

Secondly, in order to investigate effects of alloying on Ca diffusion in $CaNi_5$ and La diffusion in $LaNi_5$, activation energies of Ca and La diffusion for different alloys were calculated by Nudged Elastic Band method (NEB) method. Activation energy is important in order to investigate diffusion mechanism of Ca and La atom. According to found results for $CaNi_5$, for Ca site substitution, rare earth elements, Ti, Hf and Zr increase activation energy for diffusion of Ca atom. For Ni site substitution, Al, Fe, Si, Sn, V and Zn increase activation energy when substituted with nickel atom on Ni-1 site. For $LaNi_5$, substitution of La atom with rare earth elements, Y and Zr increase activation energy for diffusion of La atom in the structure. For Ni site substitution, Al, Co, Sb and Si increase activation energy when substituted with Ni atom on Ni-1 site.

In this regard, effects of alloying was studied using an ab initio pseudo potential method. Therefore, it was determined that, low cycle life problem of $CaNi_5$ may be solved by proper alloying.

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