

Hydrogen storage alloys for remote area power supply

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Hydrogen Storage Alloys for Remote Area Power Supply

Kean Long Lim

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Abstract

To supply electricity to a remote area community from national power grids is expensive and technically difficult. One of the possible solutions is to build a self-sustaining power generation system by harvesting the free renewable energy. However, the key issue to address in utilizing renewable energy is its intermittent nature that cannot guarantee a non-interruptible power supply at all time. Hence, this work proposed to store the energy in the form of hydrogen because of its superior energy density. The excess energy from renewable energy source is converted to hydrogen energy via electrolysis. The hydrogen is stored and used by the fuel cells to generate electricity. Nevertheless, hydrogen has a very low density at ambient pressure and temperature, which increases the complexity to store it in safe and economical manner.

Metal hydrides can be used to address this issue because of its extremely high volumetric hydrogen storage capacity. The aim of this work was to develop a new type of alloy that can be used in Remote Area Power Supply (RAPS). The designed alloys should have a hydrogen storage capacity of more than 1.00 wt% and have a capability to store and reverse the hydrogen within the pressure range of 0.10 to 1.00 MPa at room temperature. In addition to the fast absorption kinetics (less than 100 s for 1 g of sample), the alloy should also have the capability to retain at least 50% of hydrogen storage efficiency with at least 1.00 wt% of hydrogen storage capacity after 500 charge-discharge cycles. It is expected that the newly designed alloys can save at least 10% of raw materials cost as compared to the AB₅ type alloys.

In this work, La-Mg-Ni based AB₃ type Hydrogen Storage Alloy (HSA) was selected as the candidate. It was found that the hydrogen storage capacity was 1.67 wt%. An AB₅ HSA has also been chosen for comparison. The hydrogen storage capacity of the La-Mg-Ni based AB₃ was approximately 40% higher than the conventional AB₅ type alloys. The effects of partial substitutions of both Ce and Al on the hydrogenation properties of La_(0.65-x)Ce_xCa_{1.03}Mg_{1.32}Ni_(9-y)Al_y were investigated simultaneously using factorial design. Both Ce and Al additions greatly improve the reversibility of hydrogen storage capacity. However, the maximum hydrogen storage

capacity and absorption kinetics can be affected by the additions. As Ce and Al give opposite effects on the absorption and desorption plateaus, response surface methodology can be used to tune and optimize the properties of the HSA to the desired operating conditions for fuel cell applications.

The Johnson-Mehl-Avrami-Kolmogorov model was used to understand the kinetics and hydrogen absorption mechanisms of La-Mg-Ni based HSA. Nonetheless, the experimental data cannot fit into the model with a single slope line, demonstrating that there was more than one mechanism operating. Hence the results were split into two regions according to their slopes. The results showed that the dominant rate-limiting step of samples with Al addition were interface-controlled absorption. On the other hand, a diffusion-controlled reaction is applicable to all other fast absorbing samples, as well as the second region of the absorption where hydrides formation are closed to saturation.

The effects of Ce and Al on the cycle stability of the La-Mg-Ni based HSA have also been investigated. The cycle stability was mainly enhanced by Al additions; unfortunately excessive addition of Al deteriorated the hydrogen storage capacity unanimously. Hence, even though La-Mg-Ni based HSA is more price-competitive than AB₅ type HSA, its commercial readiness is limited by its efficiency. A hybrid system between AB₅ type and La-Mg-Ni based HSA could be a solution. This work indicated that a composite with 50 wt% of each type of HSA had a superior cycle stability with a reasonable capacity retention and operating pressure plateaus, as well as, a 10% cost saving in raw materials. This work has successfully demonstrated the viability of HSA as the energy storage medium for RAPS application.

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Chapter 1 Introduction

1.1 Background

The provision of an energy supply to remote areas distant from a central electricity grid is usually practically difficult and economically infeasible by extending the connections from the existing national power grids, for instance, Gray et al. [1] has pointed out that to supply a community in Australia that is close to the existing electricity grid can be \$AUD 1 million per kilometre. Low-income consumers and less dense populations as well as natural barriers are also among the reasons that inhibit these communities to access to the electricity from the power grids. Hence, it is essential to find a solution to improve the quality of life in remote villages, as well as, to power the critical facilities such as tourist facilities, telecommunication towers, military bases, agricultural and mining industries. Conventionally, diesel generators are the main source of supplying electricity to these communities. While this type of generator has a relatively low capital cost, they are economically and environmentally inefficient in the long term, because they consume expensive diesel fuel and emit a considerable amount of pollutants.

A remote area power supply (RAPS) system that integrates with renewable energy is a promising alternative to traditional fossil-fuel dependent technologies. For example, today's electrical energy demand can be supplied by solar radiation falling on just 1% of the earth's desert area [2]. Unfortunately, history has shown that the development of these sustainable technologies is inhibited by their installation cost, low efficiency, in addition to the low dispatchability and intermittent nature of renewable energy resources particularly solar and wind energy. However, the advance in materials research and technologies over the past few decades has significantly improved the energy harvesting efficiency, making solar power competitive against fossil fuel. As mentioned in the European Commission energy roadmap 2050 report [3], energy storage still remains as the major technical challenge in maximizing the potential of renewable energy power generation. Hence, a reliable energy storage system or a backup power supply that can guarantee an uninterrupted supply of electricity is the key to further enhancing the economic viability of these technologies.

A few of experimental solar-hydrogen systems have been reported in the literature [4-6]. However, a majority of them stored the hydrogen as compressed gas, which has a very low mass and volumetric capacity. Furthermore, there is also a safety concern to store compressed explosive hydrogen in a tank in a residential community. Solid state hydrogen storage such as metal hydrides would be advantage in this application. Metal hydrides are able to store 3 times the volume of hydrogen that is stored at 800 bar and room temperature [7]. Nevertheless, commercially available metal hydrides especially rare earth based alloys are costly. A more affordable AB₅ type alloy (CaNi₅) however suffered from a significant capacity upon cycling. Therefore, there is a strong urge to develop a new type of hydrogen storage alloy (HSA) that is more cost competitive. In this work, a more affordable and high hydrogen storage capacity AB₃ type La-Mg-Ni based alloys was proposed as the candidate. La_{0.65}Ca_{1.03}Mg_{1.32}Ni₉ which is an alloy that was claimed to have the capability of storing 1.87 wt% of hydrogen was used as the base materials [8]. In addition, the practicability of HSA is highly depended on their cycle stability. La-Mg-Ni based alloys have been found to be particularly poor in their cycle stabilities. Most of the cycle stability studies on this type of La-Mg-Ni based alloys were based on electrochemical cycle test which could not represent the actual degradation in a gas-solid reaction. Although corrosion caused by oxidation is one of the reasons that degrades the hydrogen storage properties of alloys, this process is not significant in a gas-solid storage system, especially when the hydrogen is produced directly from water by electrolysis. Hence, the degradation of HSA caused by this factor is beyond the scope of this thesis. Here, it is targeted that the designed hydrogen storage alloys should meet the following requirements, which is modified from the USDOE hydrogen storage target for light-duty vehicles listed in Table 2.2 and criteria listed by Grey et al. [1]:

- i. Hydrogen storage capacity higher than 1 wt%, which is equivalent to a volumetric energy density of approximately 2 kWh/L.
- ii. Capable to store and reverse the hydrogen within the pressure range of 0.1 MPa to 1 MPa at room temperature, which are the operating conditions of PEM electrolyzers and PEM fuel cells.
- iii. Absorption kinetic that is less than 100 s for a gram of materials.

- iv. Capable to maintain at least 50% of hydrogen storage efficiency and retain more than 1.00 wt% of hydrogen storage capacity after 500 charge-discharge cycles.
- v. At least 10% cost reduction as compared to the AB₅ type alloys.

1.2 Aim and Objectives

The overall aim of this thesis was to design a cost-effective hydrogen storage alloy that has a competitive performance to be used in RAPS, by partial elemental substitutions and composite methods. The project was divided into five main parts with the following objectives:

- i. To investigate the hydrogen storage properties of La_{0.65}Ca_{1.03}Mg_{1.32}Ni₉ hydrogen storage alloy and its derivatives.
- ii. To optimize the compositions of the La-Mg-Ni based hydrogen storage alloys by response surface method to meet the operating conditions of a PEM electrolyser and PEM fuel cells.
- iii. To predict the underlying absorption mechanism of La-Mg-Ni based alloys by Johnson-Mehl-Avrami-Kolmogorov (JMAK) empirical model
- iv. To investigate the effects of partial element substitutions on the cycle life of La-Mg-Ni based alloys in a gas-solid reaction.
- v. To investigate to the effects of the addition of AB₅ on the cycle life of La-Mg-Ni based alloys in a gas-solid reaction.

The main research questions to be addressed in this thesis are as follows:

- i. What are the effects of partial element substitution on the hydrogen storage properties of La_{0.65}Ca_{1.03}Mg_{1.32}Ni₉ alloy?
- ii. What are the optimal compositions of La-Mg-Ni based alloys that meet the specified requirements.
- iii. Which factor (diffusion or surface reaction) is dominant during absorption?
- iv. Can element substitution improve the cycle stability of La-Mg-Ni based alloys?
- v. Is composite method a better option than partial element substitution method in improving the cycle stability of La-Mg-Ni based alloys, as well as reducing the overall material cost?

Chapter 2 Literature Review

2.1 Energy Storage System

There are several common energy storage options available in the market depending on the area of applications. These options include batteries, pumped hydro, compressed air, hydrogen-fuel cells system, thermal energy, flywheel energy and so forth, where they are commonly categorized according to the form of energy stored, as shown in Figure 2.1 [9]. The criteria to consider among these options include the operational cost, technology availability, environmental impact, energy storage capacity, geological location and accessibility of the storage medium. In addition, Ragone plots (in Figure 2.2) which integrate the energy density, power density and discharge times into a chart could be used to evaluate the suitability of the system.

Figure 2.1 has been removed due to Copyright restrictions

Figure 2.1 Classification of energy storage systems [9]

Figure 2.2 has been removed due to Copyright restrictions

Figure 2.2 Mapping of different types of energy storage systems in a Ragone plot [10]

2.1.1 Pumped Hydro Energy Storage System

Pumped hydro energy storage system is the most common and mature energy storage technology. In these systems, water is pumped from a lower reservoir to another elevated reservoir during off peak periods. Electricity is regenerated by flowing down the reservoir water through a hydroelectric turbine (Figure 2.3). This type of energy storage has a fast response time, high efficiency of 75–80% and long lifespan. However, the pumped hydro system can only be built if the site is topographically suitable, because it is necessary to construct a dam at a certain height depending on the storage capacity [11].

Figure 2.3 has been removed due to Copyright restrictions

Figure 2.3 Pumped hydro system [12]

2.1.2 Compressed Air Energy Storage System

Compressed air energy storage (CAES) system could also be used to store energy over a long period of times. However these system are costly and dangerous to be stored in a cylinder pressure vessel [13], hence large scale storage in an underground salt cavern is more common, which indicates that these systems are very site specific. A recent report by Sandia National Laboratories [14] has shown that a USD\$ 400 million CAES project in Iowa Stored Energy Park was terminated after eight years of development because of site geological limitations. The project was intended to store the renewable wind energy during off-peak period. During the air testing on the selected site, the geologist found that the double dome structure was unable to support a 135 MW power plant, and further air injection test consumed additional cost with no guarantee of success, thus, the project was ceased. Nevertheless, this project has highlighted the importance of site selection for a CAES system. On the other hand, there are another two well-known and successful commercial CAES systems in the world that were built since the 20th century, one at Huntorf in Germany with a capacity of 321 MW and the other at McIntosh in Alabama, USA with a capacity of 110 MW.

Figure 2.4 has been removed due to Copyright restrictions

Figure 2.4 An underground salt caverns created by solution mining of salt dome [13].

2.1.3 Flywheel Energy Storage and Electromagnetic Storage System

Another option for mechanical storage technologies is flywheel technology. While it is possible that flywheel is able to release a significant amount of power almost instantaneously, its discharge time is relatively short. At standby mode or long period of storage, flywheel system also experienced energy loss as a certain amount of power is used to maintain a high level of charge [15]. Electromagnetic storage systems such as super capacitors and superconducting magnetic electricity storage (SMES) also posse a very similar problem, where both have significantly high self-discharge rate over long periods. In fact, SMES system required cryogenic temperature to maintain its superconducting properties, which required additional power to operate the cryogenic refrigerator system.

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Figure 2.5 A flywheel energy storage system by Boeing [16]

2.1.4 Batteries

Batteries are one of the most flexible and geological independent energy storage technologies which are commercially ready to be applied into RAPS. A wide range of rechargeable secondary batteries based on different electrochemical reactions is available or under development. Lead acid (PbA) and nickel cadmium (NiCd) batteries

are the main existing technology for RAPS. Other new type of batteries such as lithium-ion (Li-ion), nickel metal hydride (NiMH) and sodium sulphur (NaS) batteries are not commonly employed in RAPS. A single battery cell is made up of two electrodes that are different in galvanic potential, and an electrolyte that allows the mobility of ions between these electrodes. Electricity is generated through the flow of electrons from the external circuit that connected to a load. The desired capacity and voltage are modified according to the arrangement of battery cells either in series or in parallel. Batteries are able to respond very rapidly to load changes and have high energy efficiency. Even though batteries offer wide range of benefits, large scale utility setup involves high maintenance cost because batteries have a shorter cycle life and limited discharge capability [12]. In addition, the most common batteries for RAPS i.e. NiCd and lead acid batteries, contain heavy metals that have negative impacts on the environment. A summary of different types of batteries with their respective characteristics is presented in Table 2.1.

Lead acid batteries which are less costly also suffer from capacity loss due to self-discharge issue [17]. Two major types of lead-acid batteries can be found: flooded batteries, which is the most typical configuration topology, and valve-regulated lead acid (VRLA) batteries, which represent subjects of ongoing research and development. The flooded type battery has been the preferred battery technology for RAPS systems, however this type of battery requires regular topping up with distilled water, and failure to do so can contribute towards reduced battery performance. In addition, it has to be ensured that the impurities in the top up water must be kept minimum as severe corrosion of the positive grids may occur. The requirement for water maintenance regularity accounts for the high maintenance cost of the flooded battery. Hence, the flooded type battery has encountered a gradual shift in choice towards its VRLA counterpart which required lower maintenance requirement [18]. However, the design of VRLA with limited amount of electrolyte makes it more susceptible to thermal runaway, which happens when heat generated within the battery rises quicker with temperature than heat dissipated from the battery. Thus, additional thermal management system is needed.

The NiCd battery has good cycle life with better mechanical and thermal stability [19]. A typical NiCd battery can achieve greater than 2000 cycles. Low maintenance is required for NiCd battery because the electrolyte is not consumed during the recharging and the vented-type is also safe to withstand overcharging. In comparison to lead-based technologies, NiCd batteries have better thermal resistance, hence they are viable storage system candidates for RAPS where a high-temperature environment is present [20]. However, the Ni-Cd batteries have not experienced much commercial success because they cost 10 times more than the lead acid, in addition to their highly toxic heavy metal, which raises environmental concerns [21].

The Ni-MH battery is an environmental friendly variant of the Ni-Cd system, which also use nickel oxyhydroxide (NiOOH) as the active material of positive plates and aqueous potassium hydroxide electrolyte. However, in NiMH batteries, the active material in the negative plate is a hydrogen-absorbing intermetallic alloy, the same type of hydrogen storage alloys that will be discussed in Section Overview of Metal hydrides 2.4. The NiMH battery stores the energy in the form of hydrogen but electrochemically. The commercial available metal alloys for NiMH batteries fall mainly into two classes: AB_2 and AB_5 alloys. While AB_2 alloys yield higher energy storage densities, AB_5 alloys can hold hydrogen better, thus lowering the self-discharge rate of the battery. Nevertheless, they still suffer significant high self-discharge ($\sim 30\%$ per month) rate compare to other type of batteries which reduce their efficiency for long term energy storage [22, 23].

A NaS battery consists of molten sulphur at the positive electrode and molten sodium at the negative electrode, separated by a sodium ion-conducting solid beta alumina ceramic electrolyte. To facilitate the ion mobility in solid electrolyte, the battery is kept at a working temperature of 300°C to 350°C to allow this [24]. NaS batteries have a high energy density, long cycle life (~ 2500 cycles) and excellent coulombic efficiency (no self-discharge) [25], due to beta alumina being a very poor conductor of electrons. Nevertheless, its high operating temperature of about 300°C makes them more appropriate as an energy storage system for large-scale, non-mobile applications [26]. A sodium-sulphur battery plant developed and installed by American Electric Power at Charleston, West Virginia, USA was used to supply power to off the

grid remote communities, providing 1.2 MW of electricity for seven hours [26]. However, installations of such NaS batteries have shown to be quite expensive, and can cost approximately \$350/kWh [12]. There is also an issue with safety, especially after the fire incident at Tsukuba Plant, Japan in September 2011, caused by the malfunction of a cell contained in one of the modular NaS batteries. This forced NGK Insulators Ltd., the battery manufacturer, to recall their NaS product to devise safety enhancement measures and design modifications.

Comparing the characteristics of each type of batteries in Table 2.1, Li-ion battery no doubt has the highest energy density and high storage efficiency (close to 100%) among other type of batteries [24]. Li-ion batteries also have excellent cycle life, low self-discharge and do not suffer from memory effect. However, Li-ion battery is very costly, ranges from USD\$250/kWh to USD\$2500/kWh depending on the technologies and applications. Li-ion battery also required special circuitry for battery protection to protect the battery against over-charging or over-discharging applied through an electronic control circuit to open the circuit. The protection circuit helps limit the cell peak voltage during charging and prevents it from falling too low during discharging. During over-charge, excessive currents will result in temperature increased due to heat accumulation. The rapid rise in temperature can accelerate the Li dendrites formation, resulting in short circuit and thermal runaway. While during over-discharge, part of the copper anode is dissolved into electrolyte. Upon the attempted recharge, the metallic copper will precipitate at wherever they happen to be, not necessary back on the anode, which can eventually result in a dangerous short circuit situation [27, 28]. The results of failure batteries could be disastrous, especially in a large scale operation [29]. For instance, in 2010, a prototype self-sufficient (SELF) home unit, which was built by EMPA, Switzerland and storing its excess energy in Li-ion battery, was destroyed by fire because of a technical fault [30]. In short, the safety issues regarding Li-ion battery is the utmost importance to be addressed before it can be introduced into RAPS.

Table 2.1 Economic and environmental characteristics of selected battery systems [31-34]

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2.1.5 Hydrogen Energy Storage System

One of the other possible energy storage is to store in hydrogen form. The hydrogen can be generated by electrolysis of water using an electrolyzer powered by the excess electricity from the renewable sources. The hydrogen is then stored in a tank and converted back to electricity via fuel cells when needed. In 2004, a self-sustained solar hydrogen eco-house (Figure 2.6) was built in the University Kebangsaan Malaysia to showcase the viability of this concept. The house was powered with a 5 kW solar panel and was installed with an electrolyzer that has a hydrogen production capacity of 0.54 m³ per hour. The produced hydrogen was compressed and stored in a 1500 L vertical tank at 13.8 bar (approximately 1 kg of hydrogen), which was then used to operate a fuel cell, cooking stove and boiler for the absorption air-conditioning system. The hydrogen storage system is relatively small and simple and does not require thermal management, except during compression. However, we estimated that with the same

volume of storage tank that is filled with three quarters of metal hydrides, it could store up to approximately 100 kg of hydrogen at the same abovementioned pressure. Another example of storing hydrogen in the form of compressed gas in large quantity has been demonstrated by Germany. Germany has commissioned its first 2 MW wind-hydrogen facility where the hydrogen generated is compressed and stored in an underground salt cavern [35, 36]. Nonetheless, storing hydrogen underground is very site-specific; hence it is only viable to large power plant production scale in particular locations.

The concept of using metal hydrides as the hydrogen storage medium to power a building was demonstrated by the Griffith University, Australia. In 2013, the first teaching and research facility powered completely by solar PV, batteries and hydrogen-metal hydrides storage technologies. This \$40 million worth Sir Samuel Griffith building (Figure 2.7) was covered by 1124 solar panels which converted the solar energy to electricity: 85% was used to power the building and the excess 15% was stored in both batteries and hydrogen-metal hydrides tank.

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Figure 2.6 The solar hydrogen eco-house in Universiti Kebangsaan Malaysia

Figure 2.7 has been removed due to Copyright restrictions

Figure 2.7 Sir Samuel Griffith Center in the Griffith University (Nathan Campus) [37]

Although the cost of these technologies is still high and the overall hydrogen storage systems efficiency is rather low, storing energy in hydrogen is yet considered to be one of the cleanest and most promising alternatives. Its high energy density property is highly suitable for seasonal storage and to electrify a small community in remote area.

2.2 Overview of Remote Power Areas Supply (RAPS)

The cost of reaching the electricity grid to a community that is not in a remote area could be expensive. Hence, depending on the electricity demand and grid construction cost, a stand-alone off-grid power generator might be a better trade off. Traditionally, diesel generators are the common used technology to supply electricity in such area. The RAPS based on clean renewable energy could be a better solution to further reduce the carbon footprint. Coupling solar photovoltaic (PV) with fuel cells system in RAPS systems are potentially the pioneer zero-emission technology where in such systems, excess solar energy is used to produce hydrogen through water electrolysis and stored for night, dull weather or even season to season used. Figure 2.8 shows the basic setup of a solar-electrolyser-fuel cells coupling system.

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Figure 2.8 A standalone RAPS system that couples photovoltaic with hydrogen storage system [1].

A typical RAPS system consists of a power generation unit, an energy storage unit, a power inverter, a controller system and a backup generator. The selection of power generation from renewable resources is very site-specific, with solar photovoltaic (PV) panels being suitable for most sites. Hence, for ease of discussion, this thesis will focus on a solar-basis RAPS system only. The electricity generated from the solar PV is supplied directly to the loads where possible; any excess electricity is then stored in an energy storage system and fed back to the loads when the energy input is low. While both solar PV and batteries produce direct current (DC), most house appliances use alternating current (AC) to operate. In other words, a high efficiency, reliable and safe inverter that provides good voltage regulation is necessary. Another essential component of a RAPS system is a controller system which functions as an intelligent system to record, monitor, regulate and optimise the supply, demand and storage of energy.

A fundamental concept of supply-demand in economics can be used in designing a RAPS system. A new system design should move away from the paradigm of the conventional power generation where the electricity generated has to be consumed and the supply-demand gap is normally filled with a combustion engine. The system designers should start with the evaluation of the energy demand of the load where the new system should be designed to reduce the energy waste by utilising energy

efficiency appliances and a better insulation system. For an existing system, an energy audit should be carried out to improve the energy usage efficiency. With that in mind, the size of the power generator or solar panels is estimated according to the load demand and the size of the energy storage system that could last for months or years depending on the usage. A typical household is normally designed to meet the requirements of approximately 5kW.

Apart from the two abovementioned solar-hydrogen projects, many experimental and demonstration projects have been reported in Europe since the last century. In 1993, a standalone solar-hydrogen demonstration plant, known as the PHOEBUS project [38], was built to power part of the Central Library in Forschungszentrum Jülich, Germany. The objective was to identify the shortcomings from the operation and to collect operational data for system optimization. The project has successfully demonstrated the feasibility of powering a building purely on renewable energy without connecting to the public grid [39]. Another solar-hydrogen project – SAPHYS (Stand Alone Photovoltaic Hydrogen System) – funded by the European Commission within the framework of the Non-Nuclear Energy Program Joule-II was launched in 1994 [40]. The project was developed by three institutions: ENEA (Ente per le Nuove Tecnologie, l'Energia e l'Ambiente; Italy), IFE (Institut for Energiteknikk; Norway) and KFA (Forschungszentrum Jülich; Germany). The objectives were to design an unattended operation system and to assess the efficiency of hydrogen as an energy storage option. The 3 kW plant was operated for 1200 hour without fault and produced 123 Nm³ of hydrogen with a production efficiency of 55% [38].

In 1995, an energy self-sufficient solar house which was built by Fraunhofer Institute, was coupled with an electrolyser, a fuel cell and pressurized hydrogen and oxygen storage tanks to store the excessive energy [41]. The house was also equipped with a catalytic hydrogen cooking stove. The demands for electricity, heating, domestic hot water and cooking was delivered by this standalone power system with no significant issue [42]. The Solar Hydrogen Pilot Plant project in Finland was started since 1990 [40, 43, 44]. The project consisted of two phases: the first phase was to demonstrate the technical feasibility of the integrated system, while the second phase was to improve the round-trip efficiency of the seasonal hydrogen storage system. The

project has suggested that PEM fuel cell is a better option than the phosphoric acid fuel cell used in this system because the PEM fuel cell does not require a pre-heating process. An industrial demonstration scale project in Germany was operated from 1989 to 1996 [45]. The Solar-Wasserstoff-Bayern (SWB) project was intended to convert as much excess solar energy as possible into hydrogen for uninterrupted power supply to power a small hospital on an island. In 1994, the alkaline fuel cell used in this system was decommissioned and replaced with phosphoric acid fuel cell because of its complexity in maintenance.

In 21st century, the FIRST project was installed in Madrid, Spain, to power remote telecommunication stations [38]. Instead of using a diesel engine generator, the solar-hydrogen system in this project was used to provide an alternative backup power solution when the power level of the batteries reached low. The hydrogen was produced by the electrolyzer during sunny period and was stored in a metal hydride tank. In the United Kingdom, the Hydrogen and Renewables Integration (HARI) project was initiated at West Beacon Farm (WBF) since 2002 [46]. The HARI project generated its power from three renewable sources i.e. wind, solar and hydro as the power sources. The excess energy was stored in battery for shorter-term and in the form of hydrogen for longer-term. The total amount of stored hydrogen was 2856 Nm³ which has the capability to provide 3 weeks of electricity with no energy input. An autonomous laboratory scale standalone solar/wind-hydrogen system was successfully installed and developed by the Hydrogen Research Institute (HRI), Canada, in 2001 [47]. Again, the research institute has demonstrated the safeness and reliability of a standalone power system based on renewable energy and hydrogen storage system. Apart from the European countries, Algeria have also shown the feasibility to produce hydrogen on site. They have built several solar-hydrogen plants that have successfully produced approximately 0.09 kg H₂/m²·day to 0.20 kg H₂/m²·day depending on the season [48].

In short, it can be seen from all projects mentioned above, solar-hydrogen power generation system have a significant potential to be used in RAPS. While batteries are favorable for short-term storage in terms of their high overall round-trip energy efficiency (above 80%), their overall round-trip efficiency in longer-term storage (particularly season to season) is considerably low due to self-discharged [49]. On the

other hand, solar-hydrogen system has an efficiency of approximately 50% if it is used for power generation only. Nonetheless, Shabani et al. [50] have suggested that the efficiency of a 500 W solar-hydrogen system, that used metal hydrides tank as the hydrogen storage medium, can be increased to approximately 70% when the system is used in combined heat power (CHP) system. Battery and hydrogen as energy storage are not competitive technologies but complementary.

2.3 Hydrogen as the Energy Carrier

Hydrogen is the most abundant chemical element on earth. It is well known as the green energy carrier. Naturally, hydrogen elements are stored in three different compounds: gas, liquid and solid, where only traces exist in a pure gas forms. More often, the hydrogen element is chemically bonded with other elements to form stable compounds in gas, liquid and solid states. Nonetheless, not all compounds are easily reversible. Therefore, to capture sensible and a usable amount of hydrogen in a container is technologically challenging. In order for hydrogen to be widely used as the energy carrier, the storage method must be practical, reversible, safe and price competitive.

2.3.1 Gas Phase Storage

Currently, the most common practice of storing hydrogen gas is by pressurized tanks. There are four main types of hydrogen storage tank based on the fabricating materials and designed storage pressure. The body material of Type I and Type II tanks is made of metal, with Type II tank is wrapped with additional filament. Both Type I and Type II tanks are able to withhold a maximum pressure of 20 MPa and 30 MPa depending on the body materials. On the other hand, the body of Type III and Type IV is made of composite materials reinforced with metal liners (aluminium) and composite liners, respectively. Both of these tanks are specially designed for automotive application which can contain the storage pressure of up to 45 MPa and 80 MPa, respectively. The weight and volume distributions of a Type IV compressed hydrogen storage tank are shown in Figure 2.9. The weight of the system is mainly contributed by the carbon fiber composite body and body-of-plant (BOP) including valves, pressure transducer, tubes and regulators. While in the system volume distribution, the stored hydrogen and carbon fiber are the main contributors.

Figure 2.9 has been removed due to Copyright restrictions

Figure 2.9 The weight and volume distribution of a Type IV compressed hydrogen storage tank at 35 MPa and 70 MPa [51].

Both Type I and Type II tanks are usually used in stationary applications because they are cheaper and heavier as compared to both Type III and Type IV tanks. The gravimetric and volumetric energy densities of Type III and Type IV tanks are higher than that of Type I and Type II, owing to their ability to store the compressed hydrogen gas at a higher pressure, as well as they are made of lightweight composite materials. We choose Type IV as the best compressed hydrogen storage option to compare with the Li-ion batteries. Typically, high pressure tank systems that store 35 MPa and 70 MPa of compressed hydrogen have a gravimetric capacity of 5.5 wt% and 5.2 wt%, respectively, and a volumetric capacity of 17.6 g H₂/L and 26.3 g H₂/L, respectively [51]. In short, the highest volumetric energy density that can be stored in a Type IV tank is approximately 875 Wh/L at 70 MPa, relatively higher than that of Li-ion batteries, which is approximately 160 Wh/L [52]. The volumetric energy density of compressed hydrogen tank will be compared with the metal hydrides system in Section 2.4.

In view of the explosive characteristic of hydrogen gas, thermal management during compression is critical to reducing any heat accumulation. Therefore, hydrogen gas has to be pressurized in multiple stages and oxygen free environment. Apart from the soaring compressors maintenance expenses, compressing hydrogen at room temperature requires approximately 2.21 kWh/kg to reach 80 MPa [7]. Although volumetric density may not be a major issue in RAPS, the gas storage tanks may still need to maintain a level of base gas (or cushion gas) to provide sufficient pressure and flow rates in facilitating the withdrawal period; this gas contributes to a significant waste of space in large vessels. Cost and safety issues remain as the major challenges of this technology.

2.3.2 Liquid Phase Storage

Hydrogen molecules are favorably to exist in gas form. Despite the fact that liquefied hydrogen has a higher volumetric density compared to compressed hydrogen; it has extremely low boiling point (20 K) has contributed to the complexity of liquefying process. Hydrogen gas can only be liquefied under cryogenic temperature. Such low temperature hydrogen must be stored in a thermal insulated tank; an unavoidable amount of heat is still leaks into the system, which resulting in the boiling off of hydrogen. This will subsequently build up the pressure of storage vessel; hence a vent valve must be installed. This venting process results in a significant loss of hydrogen over a long period of time. Hence, it is the least feasible method to be used for seasonal energy storage.

2.3.3 Solid-state Storage

Both pressurized and liquefied hydrogen are carried out in extreme conditions, which is costly and hazardous. Hence, the development of solid state hydrogen storage method is gaining momentum rapidly which has a greater potential with a number of candidates that are able to store and release hydrogen in near ambient conditions. Solid-state hydrogen storage by either physical adsorption (physisorption) or chemical absorption (chemisorption) has the advantage over gas phase storage and liquid storage from safety, gravimetric and volumetric density perspectives. Physisorption is superior in its

fast kinetics characteristic whereas chemisorption is better in absorbing huge amounts of hydrogen but may require higher temperature to desorb the gas [53]. Over the years, there are considerable amount of research carried out on hydrogen storage materials, particularly, for automotive application. This could be used as a good starting-point to explore the possible applications of solid-state hydrogen storage in RAPS. New storage materials that based on physisorption, such as, metal organic frameworks (MOF), zeolites, carbon nanotubes, clathrate hydrates, etc., are great potential candidates for automotive application mainly because of their light-weighted property. However, physisorption methods required cryogenic temperature to achieve a substantial usable capacity. In RAPS, gravimetric density property may not be as critical as other properties i.e. the hydrogen storage capacity, kinetics and cycle life of the storage materials. Further research and improving of these characteristics in metal hydrides to be utilized in RAPS could be promising.

2.4 Overview of Metal hydrides

To date, metal hydrides show the most promising and consistent results in solid-state hydrogen storage when compared to other solid-state storage methods. Generally, the metal hydrides consist of three major groups: elements, alloys and complexes; as shown in Figure 2.10. Elementary metals that are alkali or alkaline earth metals usually react with hydrogen to form hydrides that are thermodynamically unfavorable in general. They are either too stable or too unstable at near ambient state [54]. Similarly, complex hydrides decomposed through reaction and easily generate a large amount of hydrogen. However the regeneration of used-hydrides that are relatively stable remains the key issues to be solved [55].

In 2009, the United State Department of Energy has revised the hydrogen storage capacity targets for light-duty vehicles [56], as shown in Table 2.2. Due to the heavy characteristic of metal hydrides, no metal hydrides to date is able to meet the gravimetric capacity target. Although alloys may seem to be low in gravimetric capacity for on-board application, they have better volumetric density storage, hence have great potential for stationary usage. This can be seen from Figure 2.11, where the volumetric energy density of hydrogen stored in metal hydrides (in this case, LaNi_5) is approximately 1.5 kWh/L, 1.25 times more than the corresponding energy density of

compressed hydrogen gas at 70 MPa but 1.33 times less than the energy density of liquefied hydrogen. Metal hydrides that have a volumetric energy density between the other two hydrogen storage technologies, can be easily stored at room temperature and relatively low pressure, i.e. less than 2 MPa.

Table 2.2 The United State Department of Energy hydrogen storage systems targets for light-duty vehicles [56]

Table 2.2 has been removed due to Copyright restrictions

Figure 2.5 has been removed due to Copyright restrictions

* TM – transition metals

Figure 2.10 Metal hydride family tree [57].

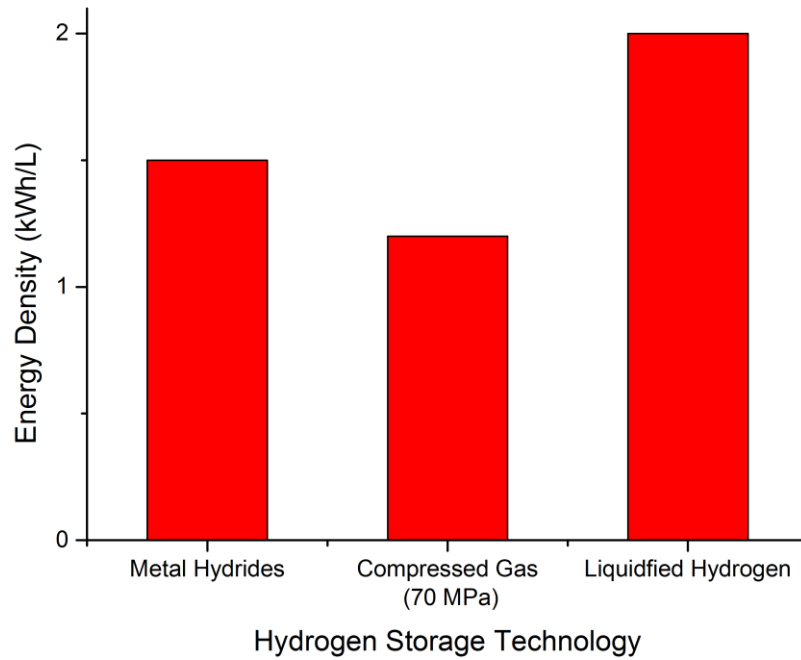


Figure 2.11 Comparison of the volumetric energy densities of various hydrogen storage technologies.

Ozaki et al. [58, 59] have conducted a feasibility study comparing the cost of different types of hydrogen storage technologies for a 600 metric tonne of hydrogen storage facility, as shown in Figure 2.12. It is undeniable that in their analysis, they have concluded that the liquefied hydrogen is the most cost saving method to store hydrogen, while the cost of storing hydrogen in metal hydrides is the highest among other options. Notably, the amount of stored hydrogen is targeted for industrial facilities, thus the analysis is not applicable to a small scale systems such as in the RAPS application. Nevertheless, the analysis has provided important information, whereby the cost of hydrogen storage in metal hydrides is mainly contributed by the capital cost of metal hydrides (i.e. LaNi_5). On the other hand, in a 100 kg hydrogen storage system, Amos [60] has shown that the cost of hydrogen stored in metal hydrides is \$0.38/kg H_2 , comparable to compressed gas system which is \$0.36/kg H_2 , whereas the cost of liquefied hydrogen is drastically increased to \$1.75/kg H_2 , approximately four time more costly than metal hydrides system. Taking safety and cost of maintenance into consideration, metal hydrides are no doubt one of the highly potential hydrogen storage methods for RAPS application.

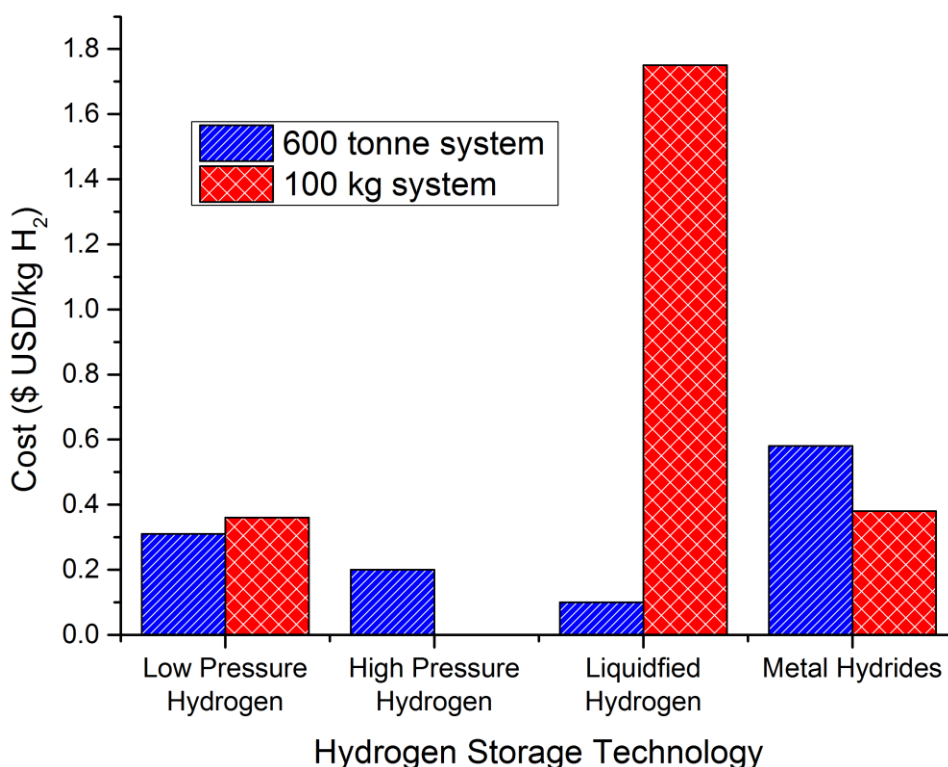


Figure 2.12 Cost of hydrogen for different hydrogen-storage technologies at different hydrogen storage capacity (blue: 600 tonne [58, 59] and red: 100 kg [60] of hydrogen)

One of the most widely used alloys for hydrogen storage is intermetallic compounds. Intermetallic compounds are generally represented by the molecular formula of A_nB_m , where A sites are elements of rare earth or alkaline earth that form stable hydrides, while B sites are transition metals that have weak hydride forming characteristics [61]. Hydrogen molecules are dissociated into atoms at the alloy surface and diffused into the interstitial spaces between the metal elements. The ratio of elements A to B influences the hydrogen storage properties of the alloys. Two major groups of intermetallic compounds (AB_5 and AB_2) and the product of the combination of both groups (AB_3) will be further discussed in the following sections [62-64].

2.4.1 AB_5 Alloys

AB_5 alloys are one of the most commonly known hydrogen storage alloys. In fact, AB_5 alloys have been successfully commercialized in the battery industries particularly in NiMH batteries, because their suitable electrochemical hydrogen storage characteristics. These alloys have a $CaCu_5$ -type hexagonal crystal structure [57]. AB_5 alloys, in particular $LaNi_5$, have been widely researched during the last decades because of their

favorable operating temperature and pressure, and reasonable surface poisoning resistance [65]. The gaseous reversible hydrogen storage capacity of LaNi_5 can reach approximately 1.28 wt% [66]; unfortunately, this is too low for transportation applications. However, when mass is not a major concern, particularly in stationary applications, the amount of hydrogen stored in these alloys is superior to any other conventional storage methods. The physical and chemical properties of these intermetallic alloys can be tuned by substituting or partially substituting the A site atom with rare earth metal like cerium (Ce), praseodymium (Pr), neodymium (Nd), calcium (Ca) or mixture of mischmetal (Mm), and/or the B site atom with transition metals, i.e. aluminum (Al), cobalt (Co), manganese (Mn), iron (Fe), tin (Sn), copper (Cu) and titanium (Ti) [57, 65, 67]. This characteristic offers the flexibility to design the alloys to operate in a desired pressure and temperature range. AB_5 alloys can be easily activated by simply exposing the sample to hydrogen pressure of approximately 3 to 5 MPa at room or elevated temperature for certain period of time [68]. This activation process barely requires any heating, but it is an essential step to remove the oxide layer (specifically nickel oxide) that retards the alloys [69, 70]. As this type of alloys can be easily activated, AB_5 alloys are able to withstand small amounts of oxygen and humidity in hydrogen. In other word, they have better tolerance to the impurities, which is an important feature for RAPS application. Their hydrogen storage capacities in terms of weight percent are the lowest among other alloys family because of excessive content of Ni. The raw materials cost of the alloys is slightly higher than AB_2 and AB_3 alloys, as the ratio of B to A atoms is the highest among the other two [57]. The low-cost CaNi_5 has a great potential to be used in RAPS, unfortunately the cycle durability is unfavorable caused by the disproportionation of Ca from the alloy [71].

2.4.2 AB_2 Alloys

In 2001, Sandia National Laboratories online databases [66] funded by United State Department of Energy (US DoE) included 625 entries of AB_2 alloys, which signified the importance of the alloys as hydrogen storage materials at that time. Many of the original metal hydride candidates identified by the US DoE have now been remove as prospective candidates in automotive applications but not in other applications. AB_2 alloys are generally based on two types of Laves phase crystal structures which are the hexagonal crystal structure (C14) [72] and face-centered-cubic structure (C15) [73].

Similar to AB₅ alloys, a broad range of elements can be used to replace elements in both A and B sites to fine tune the thermodynamic properties [57]. Ti and Zr based AB₂ alloys are among the well-known candidates that offer substantial advantages over the AB₅ alloys in hydrogen storage capacity and cost [57, 74], for example TiCr_{1.2}V_{0.8} alloy is able to store up to 3.4 wt% [75]. Generally, the range of the storage capacity is around 1.5 – 3 wt% [66]. In terms of storage cost, less AB₂ alloys are required to store the same amount of hydrogen as AB₅. Wang et al. [74] have given a very comprehensive of summary on the effect of side B substitution with Ni, Cr, V and Al in improving the overall performance of Ti based AB₂ alloys. They concluded that Ni, V and Cr have the highest influence on the overall hydrogen storage performance of the alloys. Even though AB₂ alloys have higher hydrogen storage capacity, they are sensitive with impurity, i.e. oxygen and humidity. Their usable hydrogen storage capacity was reduced by the amount of hydrogen that is trapped in a considerably low plateau pressure, as shown in Figure 2.13 [76].

Figure 2.13 has been removed due to Copyright restrictions

Figure 2.13 PCI of the Ti-V-Cr alloys after cycle tests and reactivation treatment [76].

2.4.3 AB₃ Alloys

In the recent years, AB₃ alloys (PuNi₃ or CeNi₃ type) have emerged as another promising hydrogen storing candidate because the hydrogen storage capacity of AB₅ alloys are low and the catalytic activity of AB₂ alloys are low [77]. Takeshita et al. [78] claimed that the hydrogen storage capacity of RT₃ alloys (R = Dy, Ho, Er, Tb, Gd; T = Fe or Co) surpassed RCo₅ alloys and even the well-known AB₅ alloys, LaNi₅. Dunlap et al. [79] suggested that AB₃ alloys were produced by the long range stacking of one third of AB₂ alloys and two third of AB₅ alloys. Taking into considerations of these combinations, the theoretical maximum hydrogen capacity for AB₃ alloys should be AB₃H_{4.7} [77]. A few previous studies also have shown that LaNi₃ and CaNi₃ alloys were able to form hydrides instantly under ambient conditions, although LaNi₃ alloys did not show any pressure plateau at the temperature range of 20 – 40 °C under 3.3 MPa pressure [80, 81]. According to Kadir et al. [82], element substitutions of RMg₂Ni₉ (R = Y, Ca or rare earths) alloys could reversibly store up to 1.87 wt% of hydrogen. Since AB₃ alloys are the result of the stacking of both AB₅ and AB₂ subunits, they are expected to inherit the characteristics of both materials. Hypothetically, the AB₂ subunit should retain the capacity of AB₃ alloys, while the AB₅ subunit should prolong the cycle life and improve the kinetics of AB₃ alloys. The cycle durability of AB₃ alloys, however, is less impressive [37, 83-98].

2.4.4 Other Alloys

Other types of common hydrogen storage alloy include AB, A₂B and A₂B₇ type alloys. The main representative of AB alloys is TiFe, which has a body-centered cubic CsCl-type structure. It is lighter and more affordable than the LaNi₅ alloy, but activation is slow and difficult, which is also its main drawback [99, 100]. A₂B type alloys also have high hydrogen storage capacity however their applications were limited by other properties. For instance, Mg₂Ni alloy which has a hydrogen storage capacity up to 3.6 wt% [101], but the reaction temperature of 325 °C is unacceptably high and impractical [102]. Ti₂Ni alloy could also absorb 1.85 wt% of hydrogen [103], but has poor cycle stability and reversibility issue [104]. A₂B₇ type alloys are another type of alloys that have a superstructure with different stacking order of AB₂ and AB₅ subunits from AB₃ alloys [105]. Hence, they always co-exist with the AB₃ phases and its subunits phases

[106], depending on their annealing temperature [107]. A summary of the properties of different types of hydrogen storage alloys is presented in Table 2.3.

Table 2.3 Hydrogen storage characteristics of selected metal alloys

Types of hydrides	AB ₅	AB ₂	AB ₃	A ₂ B	AB
Example	LaNi ₅	TiCrV	LaMg ₂ Ni ₉	Mg ₂ Ni	TiFe
Crystal structure	CaCu ₅	C15	PuNi ₃	P6222	CsCl
Hydrogen storage capacity (wt%)	1.28	3.40	1.87	3.59	1.89
Activation	Easy	Difficult	Moderate	Difficult	Difficult
Impurity tolerance	Good	Poor	Moderate	Poor	Poor
Cycle stability	Good	Moderate	Moderate	Poor	Poor

2.5 Thermodynamic Properties of Metal Hydrides

In general, hydrogen reacts with metals (M) or intermetallic alloys to form metal hydrides (MH_x) compound. The formation of metal hydrides is an exothermic reaction, while its reverse reaction is an endothermic reaction. The reaction equation is as following:



The reversible reaction equation is controlled by two driving parameters: pressure and temperature of the system. A pressure-composition-isotherm (PCI) diagram as shown in Figure 2.14 is the best way to represent the interactions between the alloys and hydrogen. This diagram illustrates the relationships between the changes of equilibrium pressure with the amount of hydrogen content in the alloys at a constant temperature. In Figure 2.14, the increased amount of hydrogen dissolved in the alloys changes the α phase to β phase at a constant temperature.

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Figure 2.14 A general PCI diagram for hydrogen absorption in metal alloys. The van't Hoff plot is presented on the right hand side [108]

There are three main regions in the system that describe the behavior of hydrogen adsorbed into the metal lattice. The first region shows a steep increment of pressure at very low hydrogen content. This region is indicated as the α phase where hydrogen gas begins to dissolve into the single phased solid solution. In this α phase, hydrogen atoms are randomly dispersed in the lattice structure. The pressure increases until a point where α phase is saturated, the slope reduces suddenly forming a relatively flat plateau (second region). From this point onwards, the α phase is slowly transformed to β hydride phase, of which the plateau pressure stays almost constant. The system pressure begins to climb at the last region, as soon as all α phase transforms to β phase completely [57, 109]. The length of the plateau represents the reversible storage capacity of the metal hydrides and it is temperature dependent. The higher the temperature, the higher the plateau pressure is but the shorter the length is [110]. This is because at higher temperature the hydrogen gas molecules have more energy to move around. Therefore, it requires higher driving force (in this case, higher pressure) to force the gas molecules to contact with the metal surface and shift the reaction towards the formation of a stable metal hydride. That also implies that the affinity of the metal atoms to hydrogen is weaker thus results in lower hydrogen storage capacity.

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Figure 2.15 A PCI diagram with absorption (top) and desorption (bottom) pressure plateaus [57].

The plateau region provides most of the important information regarding the characteristics of the alloys in addition to the reversibly hydrogen storage capacity. This is also the region where the formation of desorption pressure plateau (in Figure 2.15) is observed, and the desorption pressure plateau is usually lower than the absorption plateau pressure – a phenomenon known as hysteresis. The hysteresis is caused by the plastic deformation and production of entropy, which is an irreversible process [111]. The enthalpy and entropy of formation and decomposition of metal hydrides could also be derived from the plateau region via Van't Hoff plot. The plot is presented on the right side the PCI curve in Figure 2.14, which relates the plateau pressure (P), absolute temperature (T), change of enthalpy (ΔH) and entropy (ΔS) as well as gas constant (R). The Van't Hoff equation is presented as below:

$$\ln P = \frac{\Delta H}{RT} - \frac{\Delta S}{R} \quad (2.2)$$

As mentioned above, the hydrogen storage capacity of alloys is highly depended on the binding energy; thus temperature and pressure of the system influences the

hydrogen storage capacity of the alloys. As a rule of thumb, the higher the system temperature and/or the lower the system pressure, the lower the storage capacity is, since hydrogen molecules acquires sufficient energy and have less barrier to dissociate from metal surface. In the report of Gross et al. [112], one of the commonly used units in reporting the property of hydride is hydrogen per formula unit ($H/f.u.$). However, such reporting unit is only suitable for single phase hydride compounds. Nowadays, due to the fact that the research on hydrogen storage materials usually involves multi-phases compounds, this reporting unit is not less appropriate. Hence, the hydrogen storage capacity in the recent research is typically presented in the following units either by mass or by volume basis:

The weight ratio (wt. ratio) is defined as Mass (M) of hydrogen per mass sample [g/g]:

$$\frac{M_{hydrogen}}{M_{solid}} \quad (2.3)$$

The weight percent hydrogen (wt%) [g/g] is defined as:

$$\frac{M_{hydrogen}}{M_{solid} + M_{hydrogen}} \times 100\% \quad (2.4)$$

Moles of hydrogen per unit mass of sample (mole H) [Moles H/g] is defined as:

$$\frac{moles_{hydrogen}}{M_{solid}} \quad (2.5)$$

Volume of hydrogen per unit mass of sample (STP Vol H₂) [litres/g] is defined as:

$$\frac{Litres_{hydrogen}}{M_{solid}} \quad (2.6)$$

Among these units, the weight ratio term would be the handiest when quantitatively comparing and correlating with specific surface area (m^2/g), specific volume (ml/g) and other concentrations (mol/g). However, for engineering design, the performance of materials is better to compare in the terms of weight percent hydrogen (wt%).

2.6 Cycle stability of hydrogen storage alloys

The viability of metal hydrides in practical applications is also strongly affected by their cycle life performance. The cycle life is highly dependent on the ability of metal hydrides to resist decrepitation (or also known as self-pulverization), disproportionation, oxidation (including corrosion) and poisoning. In a gas-solid reaction, the decrepitation and disproportionation are related to the materials itself while the oxidation and poisoning are related to the source of hydrogen supply. Degradation of metal hydrides caused by a poisoning process in a RAPS system that is obtaining the source of hydrogen from with an electrolyser is very unlikely, because hydrogen production from electrolyser has a very high purity, unlike those that is produced from steam reforming of hydrocarbon source [113-115]. Oxidation would be a factor unless the hydrogen source has high content of moisture or there is a leak in the system, which both could be minimized with a good engineering system design, otherwise oxidation is not a serious issue in a gas-solid reaction. Oxygen contaminated alloys can be regenerated by heat treatment under reduce atmosphere [116-118]. Oxidation is more serious in an electrochemical test where corrosion is more likely to occur in alkaline environment [119-125]. Alloys that consist of La, Fe, Zr, Ti, Mg and so forth have high affinity to oxygen could easily form oxide layer and corrode. The oxidation layer of these elements is loose and permeable to oxygen, thus could not prevent further corrosion. Liu et al. [126] asserted that the addition of Al element in the alloys reduces the oxidation progress. Aluminum forms an oxide layer that is dense and protective; hence further inhibits the corrosion process. However, the degradation caused by corrosion process is beyond the scope of this project.

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Figure 2.16 A schematic model of disintegration and surface oxidation of $\text{La}_{0.7}\text{Mg}_{0.3}\text{Ni}_{2.35}\text{Co}_{0.75}\text{Mn}_{0.1}\text{Al}_{0.3}$ alloy upon cycling [127].

Two main factors that contribute to the degradation of metal hydrides in a gas-solid reaction are pulverization and disproportionation. Pulverization is caused by the lattice expansion and contraction as shown in Figure 2.16. For example, LaNi_5 alloys could have a volume expansion ratio of up to 24% upon hydrogenation [128]. The hydrogen atoms that are inserted into the interstitial sites of LaNi_5 cause the unit cell volume to expand [129]. The drastic changes of cell volume leads to the formation of cracks as well as disintegration of large particles into smaller ones. The smaller particle size increases the packing density leading to the formation of internal gas impedance, hence reducing the absorption capability [57]. Figure 2.17 shows the microstructure of the pulverized alloys after up to 80 cycles of charged and discharged. The X-ray diffraction technique could also tell the change of lattice length through the peaks shift of the spectrum. At higher high pressure, more hydrogen atoms are packed into the lattice resulting the lattice cell unit to expand and shift the diffraction peaks to a lower angle as shown in Figure 2.18 [130]. Lattice expansion can also be explained from a PCI study where the gap between adsorption and desorption curves (hysteresis) that

indicates the magnitude of volume expansion [131-134]. Partial substitution with a costly metal element such as Co, is excellent in suppressing the volume expansion in AB₅ type metal hydrides [118, 129, 135]. For instance, Hagström et al. [136] reported that the replacement of Mn with Co in AB₂-type metal hydrides effectively reduces lattice volume, contracts the unit cell in both lattice parameters and reduces the hysteresis effects. Other elements like Cr [137] and V [136] also provide positive effects in the minimization of hysteresis loops, but the drawback is the increment of pressure plateau slope and decrement of plateau length. Zhang et al. [138] identified the need of replacing the expensive Co by other more economical elements that still retain the anti-pulverization capability. They discovered that a certain ratio of substitution of Co with Fe preserved the anti-pulverization characteristic.

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Figure 2.17 Microstructure changes of La_{0.7}Mg_{0.3}Ni_{2.65-x}Co_{0.75}Mn_{0.1}Al_x (x = 0, 0.3) after cycle test (x = 0: (a) as cast, (b) after 10 cycles, (c) after 30 cycles, (d) after 80 cycles; x = 0.03, (e) as cast, (f) after 10 cycles, (g) after 25 cycles and (h) after 80 cycles) [127].

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Figure 2.18 Peak shift to the left due to high hydrogen loading at higher pressure [130].

The degradation of the cycle stability of metal hydrides in a gas-solid reaction is often related to disproportionation. The occurrence of disproportionation is due to the significantly high pressure above the plateau pressure or the presence of high temperature [139, 140]. The temperature effect is more significant because this mechanism involves short-range diffusion of metallic atoms [141]. During disproportionation, the elements that have a higher affinity to hydrogen disproportionate into stable elemental hydride and lose their crystallinity, forming an amorphous phase that does not absorb hydrogen [78]. AB₃-type alloys have a significant disproportionation issue as compared to AB₅-type alloys. As an example, Xie et al. [142] has observed that the degradation of ErNi₃ during cycle tests was caused by the collapse of the superstructure into AB₂ and AB₅ subunits, as shown in Figure 2.19. This AB₂ subunit is prone to amorphize easily[143]. In a CaNi₃ system, the alloy was found to be disproportionated into CaH₂ and Ni upon cycling [78]. Again, heat treatment is able to reverse the alloys back to a higher storage capacity (as shown in Figure 2.20) but not to its original hydrogen storage capacity.

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Figure 2.19 Decomposition of ErNi_3 superstructure into ErNi_2 subunit and ErNi_5 subunit during cycle test [142].

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Figure 2.20 Reactivation treatment of Ti-V-Cr alloy at 500 °C for 30 min [76].

Regardless the factors that contribute to the degradation of hydrogen storage capacity, partial element substitution technique is always one of the options that can improve the cycle stability. Partial element substitutions, particularly in AB_3 type alloys change the distributions of phases, and hence modify the hydrogen storage capacity and cycle stability [144]. For instance, Figure 2.21 shows the variation of cycle stability

upon partial element substitution of La with different rare earth elements in La-Mg-Ni based alloys. Some researchers [83, 84, 89, 145] also found that hybridizing two different types of hydrogen storage alloys could possibly improve the cycle stability properties. For example, the cycle stability performance of La-Mg-Ni based alloys was found to have improved with a 40 wt% of Ti-V based alloys addition [83, 85]. Both Hu et al. [145] and Huang et al. [89] added AB₅ alloys into La-Mg-Ni based alloys successfully prolonged cycle stability of AB₃ alloys but with a reduction of hydrogen storage capacity. Lu et al. [90] ball milled Zr based AB₂ type alloys with La-Mg-Ni based alloys, also showed great enhancement of cycle life.

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Figure 2.21 Electrochemical cycle stability curves of La_{0.63}R_{0.2}Mg_{0.17}Ni_{3.1}Co_{0.3}Al_{0.1} alloy electrodes at 293 K under 300 mA g⁻¹ of current density [88].

2.7 Kinetic Study

Kinetic study is important to improve the rate of adsorption and desorption of hydrogen gas by the metal hydrides. Both mechanisms, adsorption and desorption, are influenced by the temperature, pressure, surface area of absorbent, bonding energy and catalytic effects. For practical applications, it is favorable that the operating temperature and pressure are near ambient conditions. Therefore, most of the research activities focus on the improvement of surface area or substitution and additional elements in absorbent.

Ball milling, for instance, is a common technique used to modify the microstructure by reducing the particles size to increase the overall surface area per volume unit, which leads to a better gas-solid interaction. A few groups of researchers have improved the hydrogenation properties of magnesium type alloys as compared to their as-cast alloys [146-149]. Some other research groups [70, 150] have proposed that ball milling has either reduced the diffusion path length or increased the particle surface area and thus reducing the time for hydrogen to release from the alloys. In Figure 2.22, Zaluska et al. [149] has shown that at 300 °C, nanosized magnesium powder has significantly enhanced the adsorption rate by 20 – 80 times faster. The performance enhancement was due to the shorter hydrogen diffusion path in nanosize particles. Nevertheless, the hydrogen absorption still required approximately 2 hours, operating at 300 °C, to achieve its maximum capacity (6 wt%).

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Figure 2.22 Effect of particle size on hydrogen absorption after ball milling magnesium powder at 300 °C [149].

Other effort of enhancing the kinetic property is by co-milling metal, metal oxide or carbon nanotube that has catalytic effects over hydrogen gas, i.e. nickel, iron, cobalt, aluminum, palladium, platinum, titanium, niobium, vanadium, etc [151-158]. The addition of these elements or oxides creates a spill-over effect that reduces the activation energy for hydrogen recombination and dissociation [149]. Although ball

milling is an excellent option for kinetic improvement, long duration milling may cause amorphization, change of the crystal lattice or formation of oxide layer. In some case, even after heat treatment, the hydrogen capacity is irreversible [98]. There is also literature [159] that has mentioned Fe is able to reduce the pressure plateau and increased the desorption rate.

Chapter 3 The Design of a Sievert-type Instrument

3.1 Introduction

One of the main tasks of this thesis is to evaluate the hydrogen storage properties of different alloys using Sievert's instrument. A significant amount of time has been devoted to custom design of such an instrument with the capability to characterize the hydrogen storage alloys' properties for RAPS applications. These properties include Pressure-Composition-Isotherm (PCI) relationships (including hydrogen storage capacity, hydrogen absorption and desorption plateaus, storage reversibility) and kinetic properties, as well as their cycle stability. This chapter will cover the background theory on Sievert's method, and design and construction of the instrument used in the present study. Other standard characterization techniques will be mentioned in the respective chapter.

There are two major methods that could be used to measure the pressure-composition-temperature relations: the thermogravimetric method and the volumetric method (also known as the Sieverts method). The thermogravimetric method measures the change of the sample mass with a microbalance after exposure to a hydrogen atmosphere and taking into account the buoyancy effects. Due to the sensitivity of the microbalance, the instrument is limited by the sample size and it must be leveled and positioned on the anti-vibration supports to minimize the mechanical disturbance effects. Another challenge is to position a thermocouple so that it measures the sample temperature directly and accurately without interfering with the weight measurement.

The other method is the volumetric method, also known as Sieverts method. This method determines the amount of hydrogen taken up indirectly through pressure-volume-temperature correlations. The volumetric technique is believed to be potentially more accurate and versatile than the gravimetric method since significant changes in pressure are measured rather than a small increment in mass by thermogravimetric method. An instrument based on volumetric technique can be easily constructed from the off-the-shelf gas handling components [160]. Hence, this chapter will concentrate on the design and construction of a Sievert's instrument in School of Materials Science and

Engineering, University of New South Wales. The instrument was specially designed based on our need to study hydrogen storage alloys for RAPS applications. Not only it has the capability to perform PCI characterization, but it also able to study multiple cycle charging and discharging test.

3.2 Instrument Design and Measurement

3.2.1 Layout and Volume Measurement

A schematic diagram of the basic Sieverts apparatus is shown in Figure 3.1. The apparatus consists of two major parts which is separated by a valve (V3): the measuring system (E1 chamber or reservoir chamber) and the sample system (E2 chamber). The volume of the E2 chamber was measured according to the procedure suggested in Japanese Industrial Standard (JIS H 7201:2007 [161]) with some modifications. The chamber together with the valve was first vacuumed, sealed, weighted and filled with distilled water at room temperature. The mass difference between the filled and the empty chamber was divided by the specific gravity of water at room temperature to obtain the standard volume of sample system. The volume of measuring system was estimated by Boyle's law using helium gas with reference to the standard volume of sample system.

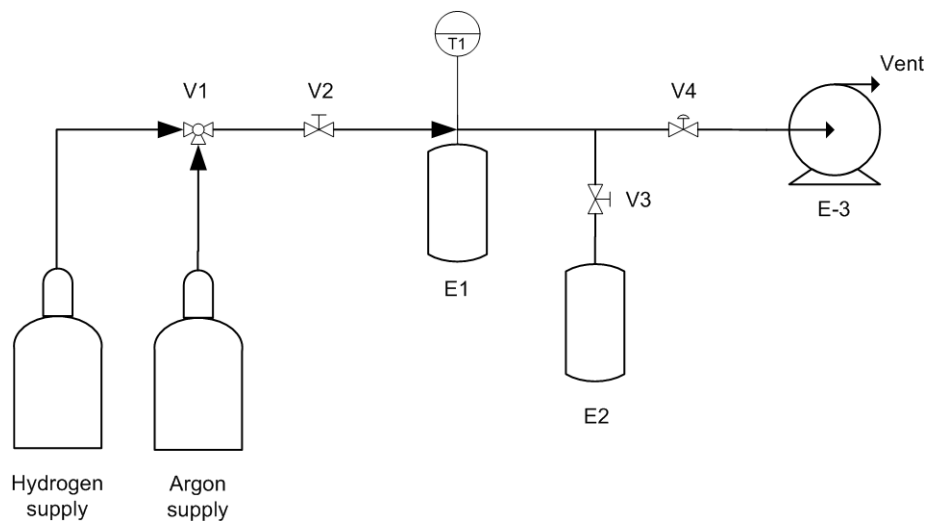


Figure 3.1 Schematic diagram of a basic volumetric (Sieverts') setup; E1 and E2 are chambers, V1 to V4 are valves and E-3 is a vacuum pump.

3.2.2 Absorption and desorption measurement

This section will discuss the general steps to perform a measurement as well as the principle to calculate the amount of hydrogen absorbed in a sample. The activation and measurement conditions will be detailed in the respective chapters.

To perform a measurement, the sample is loaded into sample chamber, vacuumed and activated accordingly. The volume of the sample can be measured via Archimedes' method and should be deducted from that of sample chamber. First, a known amount of hydrogen, calculated from the pressure, temperature and volume, is fed into the reservoir chamber. Next, the valve between the reservoir and sample chamber is opened to allow the hydrogen to be charged onto the sample. The first pressure drop observed is due to the volume expansion; a subsequent pressure drop with a noticeable temperature increase indicates the absorption of hydrogen into the sample. When an equilibrium state is achieved (with no significant change of pressure and temperature reading), the final pressure and temperature measurements are taken to calculate the amount of hydrogen absorbed. To obtain reasonable data points to plot a PCI curve, the charging step is repeated by reintroducing a small aliquot of fresh hydrogen at a higher pressure than the previous equilibrium state. Similar steps are used during desorption measurements, where a known amount of hydrogen is released and the same equation is used to calculate the remaining hydrogen in the sample. The amount of hydrogen gas absorbed is calculated using the corrected ideal gas law:

$$PV = zNRT \quad (3.1)$$

Where, z is the hydrogen compressibility factor at a defined pressure and temperature.

The compressibility factor is calculated based on the JIS H 7201:2007 [161]:

$$z = 1 + p[A + BT^{-1} + CT^{-2} + DT^{-3} + ET^{-4}] \quad (3.2)$$

where,

$$\begin{aligned} A &= 4.93482 \times 10^{-5} \\ B &= 2.04036 \\ C &= 8.15334 \times 10^1 \\ D &= -6.5561 \times 10^4 \\ E &= 4.56516 \times 10^6 \end{aligned}$$

The amount of hydrogen absorbed, n_{abs} , is calculated using the following equation:

$$n_{abs} = n_i - n_{eq} = \left(\frac{P_i V_1}{z_i R T_1} + \frac{P_{eq,i-1} V_2}{z_{eq,i-1} R T_2} \right) - \left(\frac{P_{eq,i} V_1}{z_{eq,i} R T_1} + \frac{P_{eq,i} V_2}{z_{eq,i} R T_2} \right) \quad (3.3)$$

Where,

- n_{abs} : amount of hydrogen absorbed
- P_i : initial pressure in reservoir chamber
- V_1 : volume of reservoir chamber
- T_1 : temperature of reservoir chamber
- $P_{eq,i}$: equilibrium pressure
- $P_{eq,i-1}$: previous equilibrium pressure
- V_2 : volume of sample chamber (after deducted the volume of sample)
- T_2 : temperature of sample
- R : gas constant

3.3 Construction of Sieverts instrument

The Sieverts instrument used in the present study was constructed by JNP Tech Co. Ltd in Taiwan. The instrument shown in Figure 3.2 (a) was designed with two independent channels (Channel 1 at the right and Channel 2 at the left) and with different reservoir and sample chamber volumes. Both channels were installed with a pressure transducer and each chamber is connected to a K-type thermocouple. The volumes of each chamber are tabulated in Table 3.1.

Table 3.1 Volumes of different parts of the instrument

Channel 1	Volume (cm ³)
Sample Chamber	19.370
Reservoir	58.650
Channel 2	
Sample Chamber	9.190
Reservoir 1	18.060
Reservoir 1 + 2	44.630

**The volumes have included tubes that connected to the valves*

Unlike the conventional design, this instrument was designed with two systems that can be operated independently. All chamber volumes, including the reservoirs and sample holders, are interchangeable. The different chamber sizes enable the user to modify the sensitivity of the measurement according to the sample size and hydrogen storage capacity. A smaller volume increases the resolution of a PCI curve, however prolong the experimental time. In a kinetic measurement, a bigger reservoir chamber could provide sufficient pressure driving force and amount of hydrogen, ensuring complete hydrogenation. Hence, in Channel 2, a diaphragm valve was installed between two reservoirs as shown in Figure 3.2 (b), offering the flexibility to modify the hydrogen charging and discharging dosage. A furnace that has a maximum temperature of 600 °C is used for activation and heat treatment.

A detailed piping and instrumentation diagram (P&ID) of one of the channels (Channel 2) is presented in Figure 3.3, because both channels have the same setup except that Channel 2 has an additional reservoir as abovementioned. The charging and discharging of gas was controlled by the pneumatic diaphragm valves (PDVs) and a needle valve before the inlet was used to control the flow rate. The compressed-air-operated PDVs were controlled by the solenoid valves, as shown in Figure 3.4. To minimize the contamination from the samples to undesirable parts like valve seats, a 0.5 μm Swagelok® inline filter was installed between the sample chamber and the measuring system. Two high-pressure ball valves were placed before and after the system to isolate the system from the pressure source during service and emergency. Two check valves were positioned before and after the system to ensure unidirectional flow of gas.

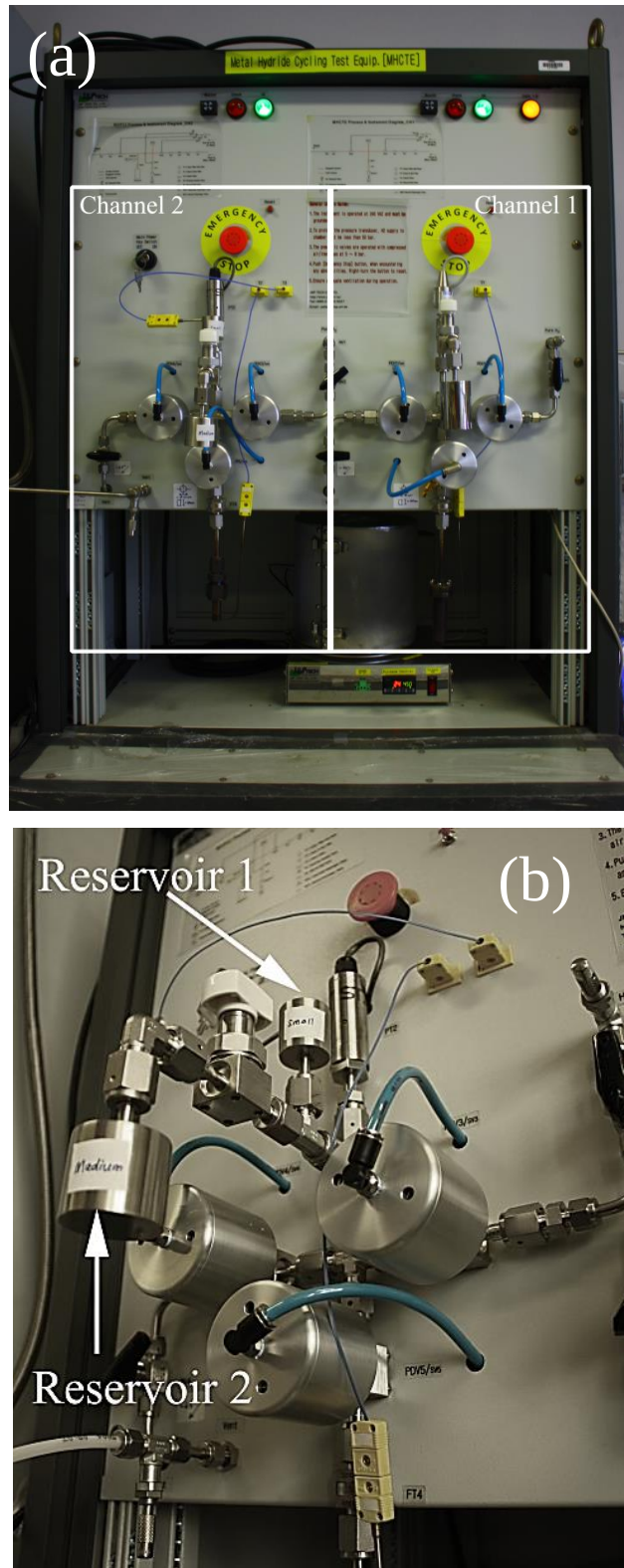


Figure 3.2 (a) Two channels Sieverts instrument and (b) reservoirs of channel 2

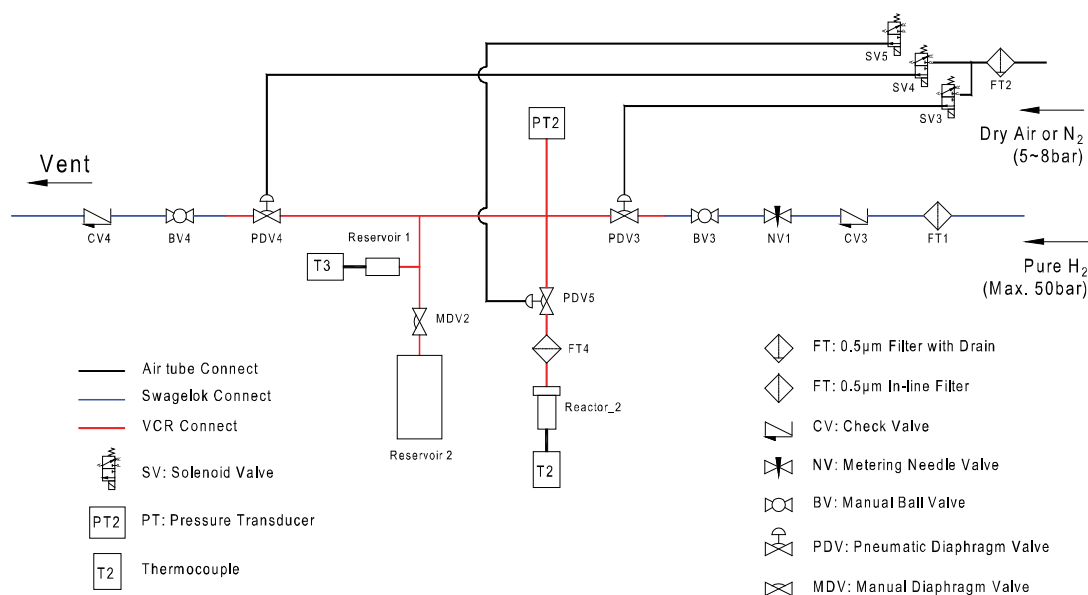


Figure 3.3 Piping and instrumentation diagram of Channel 2

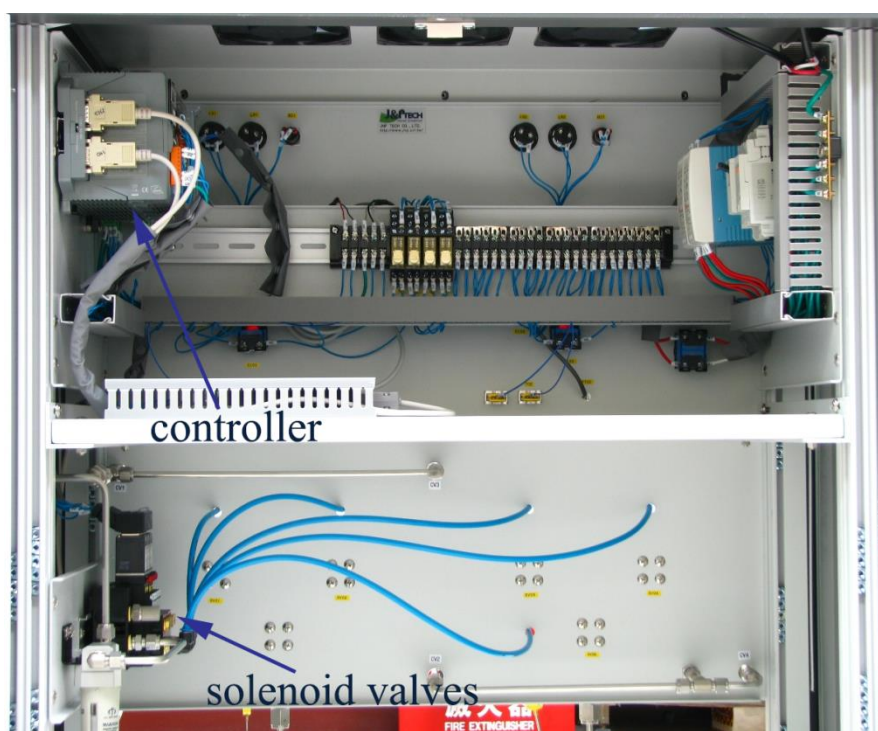
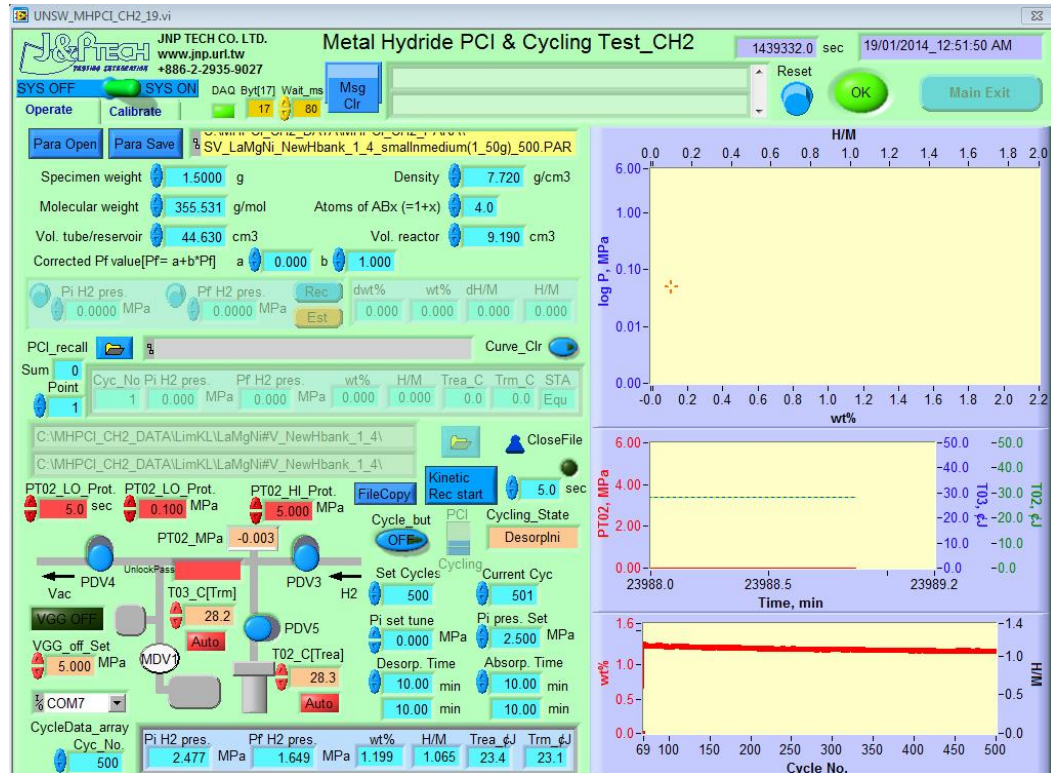


Figure 3.4 Back view of Sieverts instrument

3.3.1 Control Interface

The control interface was developed with the commercial graphical object oriented programming software, LabVIEW®. The interface (Figure 3.5) is divided into four

parts: parameter inputs, data recording, control and display. All parameters are preset before running the experiment. The real-time data are recorded, calculated and presented in the three displays, where the top one is to plot a PCI curve, the middle one is the real-time pressure and temperature, and the bottom one is the cycle test.



room temperature of approximately 20 °C, which was lower than their room temperatures in Taiwan, which were at approximately 30 °C. Although there is a possibility to adjust the pressure plateaus via temperature correction, the overall hydrogen storage capacity is not predictable. Hence, in this case, it is best to present the PCI curve at the measured equilibrium pressure and temperature. Nonetheless, the overall absorption capacities were not seriously distorted by the 10 °C temperature difference. Hence, taking into consideration of the sensitivity of pressure transducers and thermocouples, it can be concluded that the instrument has the capability to provide reliable PCI results with a maximum uncertainty of $\pm 3.5\%$.

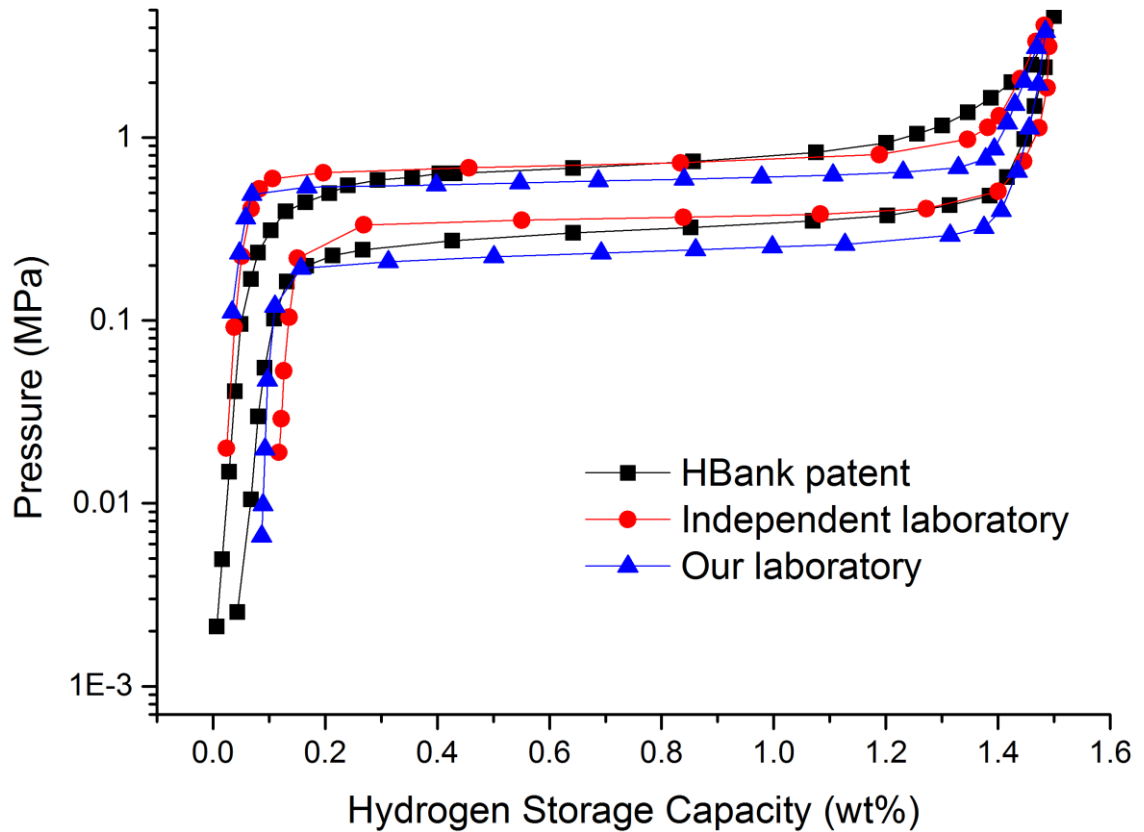


Figure 3.6 Comparing PCI curves of HBank hydrogen storage alloys by different laboratories.

3.3.3 Safety Considerations

The aim to design the instrument with four prevention layers (Figure 3.7) is to protect the safety of the user and instrument.

i) Choosing the right parts and fittings

All parts including chambers, valves, tubes and fittings were designed to withstand at least 20 MPa, approximately four times of the maximum operating pressure. The VCR® fittings with a maximum leak rate of 4×10^{-9} std cm³/s were used to ensure leak-tight from vacuum to high positive pressure.

ii) Setting the operation limits

All PDVs were set to fail-close; hence during an emergency all PDVs will shut-off automatically, protecting the system from the high pressure inlet feed, as well as, preventing the released of explosive gas uncontrollably. The automatic emergency shut-off will be triggered and alarmed under the following conditions:

- a) over pressure (> 5 MPa), and
- b) under pressure (< 0.1 MPa) upon charging more than 5 sec.

To over-ride the system in the case of software failure, the instrument was equipped with two emergency stop buttons, controlling two channels independently. When the emergency stop button is pushed, all PDVs will shut-off.

iii) Interlock system

An interlock system was created to prevent the inlet valve and vent valve (refer to Figure 3.3, PDV3 and PDV4, respectively) from opening at the same time, inhibiting the high pressure source to feed the gas directly to the rotary vacuum pump. Two ball valves before PDV3 and after PDV4 can be used to manually shut off the system.

iv) Hydrogen monitoring system

A fixed-point hydrogen gas monitor was installed above the instrument because hydrogen is lighter than the air.

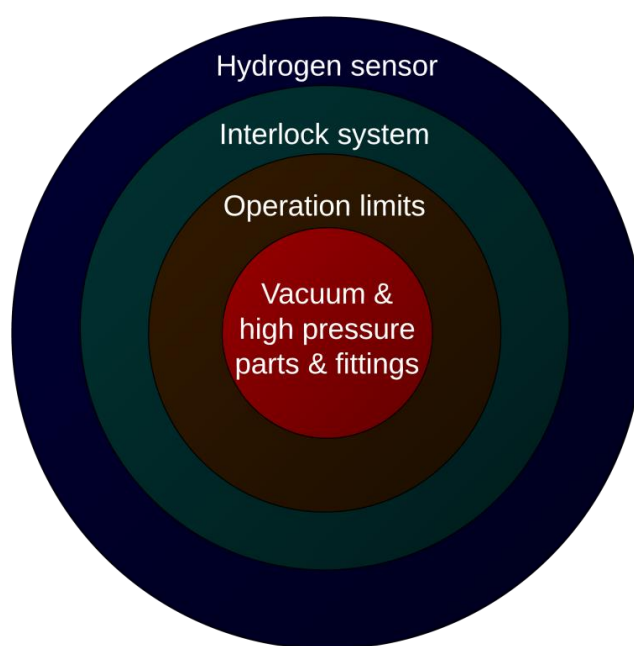


Figure 3.7 Multi-layers of protection measurements

3.3.4 Leak Test

Before further proceeding further to any measurement, a leak test on the apparatus is necessary. The leak test is performed by pressurizing the system with helium higher than atmospheric pressure, isolating from the feed in source (close valves) and maintaining it for a period of time. Helium is used in a leak test because it is monoatomic and prone to leak more easily compared to the diatomic hydrogen molecules. During the leak test, the instrument is pressurized with 4 MPa of helium and isolated from the source and vent by the ball valves. The pressure and temperature changes over time are recorded for 24 hours or more. The test could also be conducted at a higher temperature if the leak rate is slow but significant enough to affect the end result. If the leak is obvious, it can be detected by Snoop® liquid leak detector with bubbles forming vigorously. Otherwise, a leak-proof system will show a typical trend as presented in Figure 3.8, which corresponding to the Amonton's Law, where the 4 MPa pressure in the system is fluctuates proportionately to the changes of ambient temperature in Kelvin. The data per time step was recorded every 0.5 s. Hence, the data plotted in Figure 3.8 seem to have overlapping pressure and temperature readings for the same time. Nevertheless, the fast recording time is necessary to confirm if the variation of readings were caused by the sensitivity of the instrumentation itself and the laboratory environment instead of a leak. In addition, the recorded trends also indicated

that the pressure readings have an uncertainty of ± 0.0025 MPa and temperature readings have an uncertainty of ± 0.1 K.

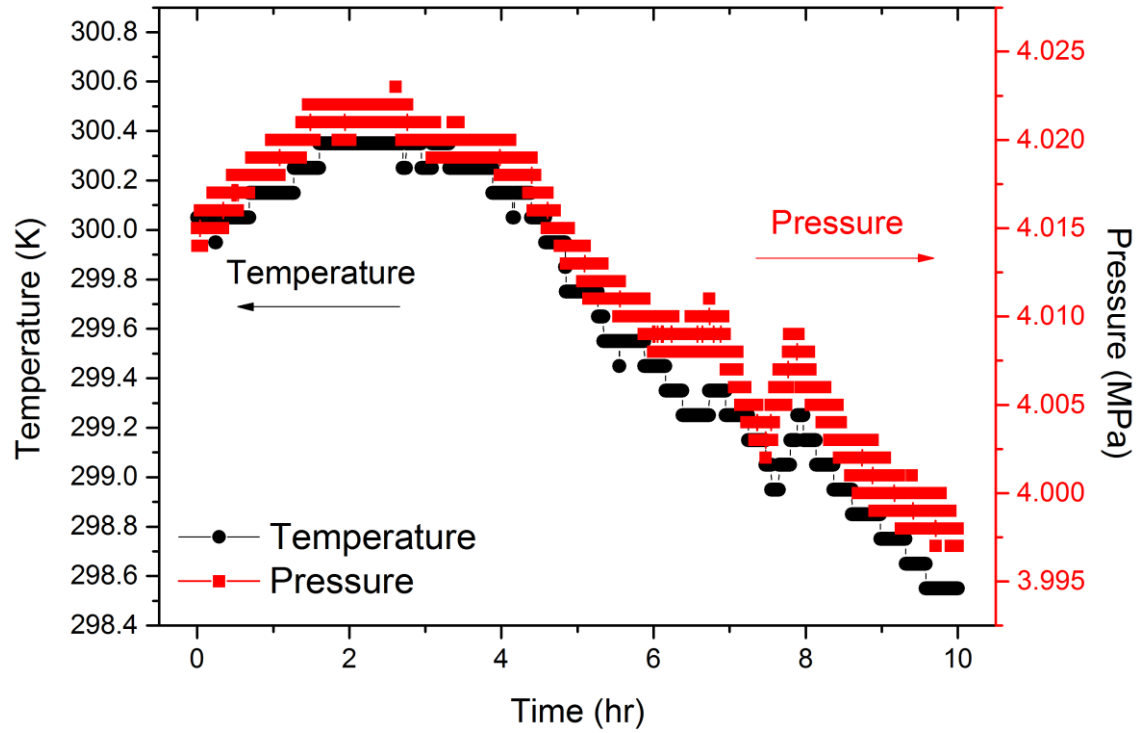


Figure 3.8 The changes of pressure (in red square) and temperature (in black circle) with time of a leak-proof system.

Chapter 4 Effects of Partial Substitutions of Cerium and Aluminum on the Hydrogenation Properties of $\text{La}_{(0.65-x)}\text{Ce}_x\text{Ca}_{1.03}\text{Mg}_{1.32}\text{Ni}_{(9-y)}\text{Al}_y$

4.1 Introduction

The AB_3 based hydrogen storage alloys (HSA), such as LaNi_3 , CeNi_3 and CaNi_3 , have mainly been studied for their uses in the Ni-MH batteries [163-166]. The unit cell of AB_3 is formed by a long-range stacking of one third of AB_5 unit and two thirds of AB_2 unit, which has a crystal structure of PuNi_3 -type rhombohedral structure [8, 79, 143]. By reducing the amount of rare earth elements as well as by adding Mg and Ca, Kadir et al. [8] have successfully synthesized an AB_3 La-Mg-Ni based hydrogen storage alloy with a storage capacity higher than that of the AB_5 type HSAs. A cost competitive La-Mg-Ni based AB_3 -type of HSA is proposed here. In this study, we choose $\text{La}_{0.65}\text{Ca}_{1.03}\text{Mg}_{1.32}\text{Ni}_9$, which has the same composition as that reported by Kadir et al. [8], as the starting HSA; the effects of element substitutions have been studied here using the combination of statistical approach.

Element substitutions are commonly used to modify the properties and performance of HSA, however most studies were concentrating on the effects of partial substitutions either at the A-side or B-side [167-172], which usually did not take into consideration of possible interactions by the substitutions at both sides. In this work, we have chosen Ce and Al as the elements to partially substitute the A-side and B-side respectively and simultaneously. Both Pan et al. and Zhang et al. have reported that Ce substitution has the capability to improve the cycle life but over substitution of Ce reduced the overall hydrogen storage capacity and increase both absorption and desorption plateau pressures, and deteriorated the performance of the alloys [173, 174]. On the B-side, Al substitution also has the capability of improving the cycle life, but over substitution of Al significantly reduced the overall hydrogen storage capacity, as well as, lowered the absorption and desorption plateau pressures [167, 170]. Hence, it is expected that there will be synergetic or antagonist effects on the HSA hydrogen storage properties when both substitutions are made simultaneously. The designed HSA properties are targeted to meet on the operating conditions of a typical Proton-Exchange membrane (PEM) fuel cells. It is expected that this work could provide an overall

picture on the combined effects of these substitutions, and a faster screening solution in estimating, designing and tuning HSA properties.

4.2 Factorial Design of Experiment

The design of $\text{La}_{(0.65-x)}\text{Ce}_x\text{Ca}_{1.03}\text{Mg}_{1.32}\text{Ni}_{(9-y)}\text{Al}_y$ alloys was set as a 2-factorial design where x denotes the partial substitution of A-side, ranging from 0.00 to 0.50; y denotes the partial substitution of B-side, ranging from 0.00 to 2.50. The label of each combination is tabulated in Table 4.1. The range of A-side was chosen to identify the changes of properties from La dominant to Ce dominant, while for the B-side, the maximum of Al substitution was limited to approximately one-third of Ni to ensure the hydrogen absorption process is not seriously affected. The importance of Ni as the catalyst for hydrogen absorption will be discussed in the next section.

4.3 Materials and Experimental Procedures

4.3.1 Fabrication of Alloys

The fabrication of La-Mg-Ni based alloy was similar to Wang et al. [37, 175]. The La-Mg-Ni based alloys were prepared by arc and induction melting methods. To achieve compositions closer to the designed values, elements with low vapour pressure (i.e. La, Ce, Al and Ni) were melted in a copper crucible by an arc furnace to produce an ingot. The ingot was turned over and remelted a few times to achieve homogeneity. Next, the ingot together with Ca and Mg (both weights in excess of 20% of the designed values) were melted in a quartz crucible in an induction furnace. The samples were then mechanically crushed into smaller pieces and ground into finer powder for further characterization.

4.3.2 Alloy Characterization

All samples were ground to powder before X-ray diffraction measurement. The crystal structure and phase compositions of the alloys were measured with a PANalytical Xpert Pro MPD X-ray diffractometer with Cu $K\alpha$ radiation that operated at 45 kV and 40 mA. The powder diffraction patterns were then analyzed and refined with X'pert HighScore Plus software. Next, the alloys were activated with the procedures listed in the next paragraph before performing the surface morphology characterization. The surface

morphology of the alloys was observed using a Hitachi 3400X scanning electron microscope (SEM) coupled with an energy dispersive X-ray spectrometer (EDS) and a backscattered electron (BSE) detector.

The pressure-composition-isotherm (PCI) and kinetic properties of the samples were measured with the custom-made Sieverts instrument discussed in Chapter 3 at room temperature, using 99.999% ultra-high purity hydrogen. Before the measurements, all alloys were activated with 0.50 MPa of hydrogen at 300 °C for 1 h, degassed at 450 °C for an hour and cooled to room temperature. This activation process was conducted to remove the surface oxide that retarded the alloys' surface, as well as to create new active surfaces by forming cracks. A decreased in pressure was the first indication that the samples had begun to absorb hydrogen, followed by an increase in temperature due to the exothermic reaction during hydrogen absorption. The samples were considered fully activated when the maximum hydrogen storage capacity remained constant after successive cycles. To ensure that the samples were fully activated, the activation process was repeated for three times and the last degassing step was extended to 2 h.

4.3.3 Data Analysis

The statistical analysis was performed by using the Design Expert software, where the data tabulated in Table 4.1 were extracted from the PCI curves with the following criteria: hydrogen absorption capacities at 1.00 MPa, hydrogen retained at 0.10 MPa, and absorption and desorption pressure plateaus. A logarithm (log) transformation was applied to the retained hydrogen, kinetics and absorption plateau data to fit the statistical model. However, part of the desorption plateau were undetectable due to the limitation of the measurement; hence these data were not logarithm transformed. Another data set on absorption kinetic times was taken from the kinetic curves at the time taken to achieve 80% of the alloys' maximum absorption capacity. The significant differences between the variables were assessed with ANalysis Of VAriance (ANOVA) using F-test, while the mean differences were assessed with Fisher's least significant difference (LSD) test. Both confidence levels were set at 95%.

Table 4.1 Response data with different substitutions with Ce ranging from 0.00 to 0.50 and Al ranging from 1.00 to 2.50.

	Hydrogen Absorption at 1.00 MPa, wt%		Entrapped Hydrogen at 0.10 MPa, wt%		Absorption Plateau, MPa		Desorption Plateau, MPa		Absorption time at 80%, s	
	<i>y</i>		<i>Y</i>		<i>y</i>		<i>Y</i>		<i>y</i>	
<i>x</i>	0.00	2.50	0.00	2.50	0.00	2.50	0.00	2.50	0.00	2.50
0.00	1.49	0.45	1.16	0.56	0.10	0.0008	0.04	0.00	38	210
0.25	1.40	0.58	0.62	0.48	0.34	0.005	0.18	0.00	56	416
0.50	1.04	0.45	0.40	0.46	0.78	0.02	0.48	0.00	70	446

4.4 Results and Discussion

4.4.1 Phase structure and Morphology of Alloys

Figure 4.1 shows the X-ray Diffraction (XRD) patterns of $\text{La}_{(0.65-x)}\text{Ce}_x\text{Ca}_{1.03}\text{Mg}_{1.32}\text{Ni}_{(9-y)}\text{Al}_y$. The diffraction patterns indicate that all alloys were multi-phases. By comparing with the peak positions with the International Centre for Diffraction Data (ICDD) crystallography library, the alloy with no additional Ce ($x=0$) and Al ($y=0$) consisted of two main phases: AB_5 phase with a CaCu_5 -type hexagonal structure and AB_3 phase with a PuNi_3 -type rhombohedral structure. This observation is inconsistent with the results obtained by Kadir et al. [8] and Chen et al. [163], where only a single main phase was detected. This inconsistency can be attributed to the fabrication methods employed: both groups used powder-sintering method to fabricate the alloys, while this study employed both arc- and induction-melting methods to synthesize the samples. Casting or melting methods tend to form multi phases during cooling and solidification processes. The coexistence of multi phases is also observed in other works [169, 172, 176-178] on La-Mg-Ni based alloys that employed similar synthesis procedures as in this work.

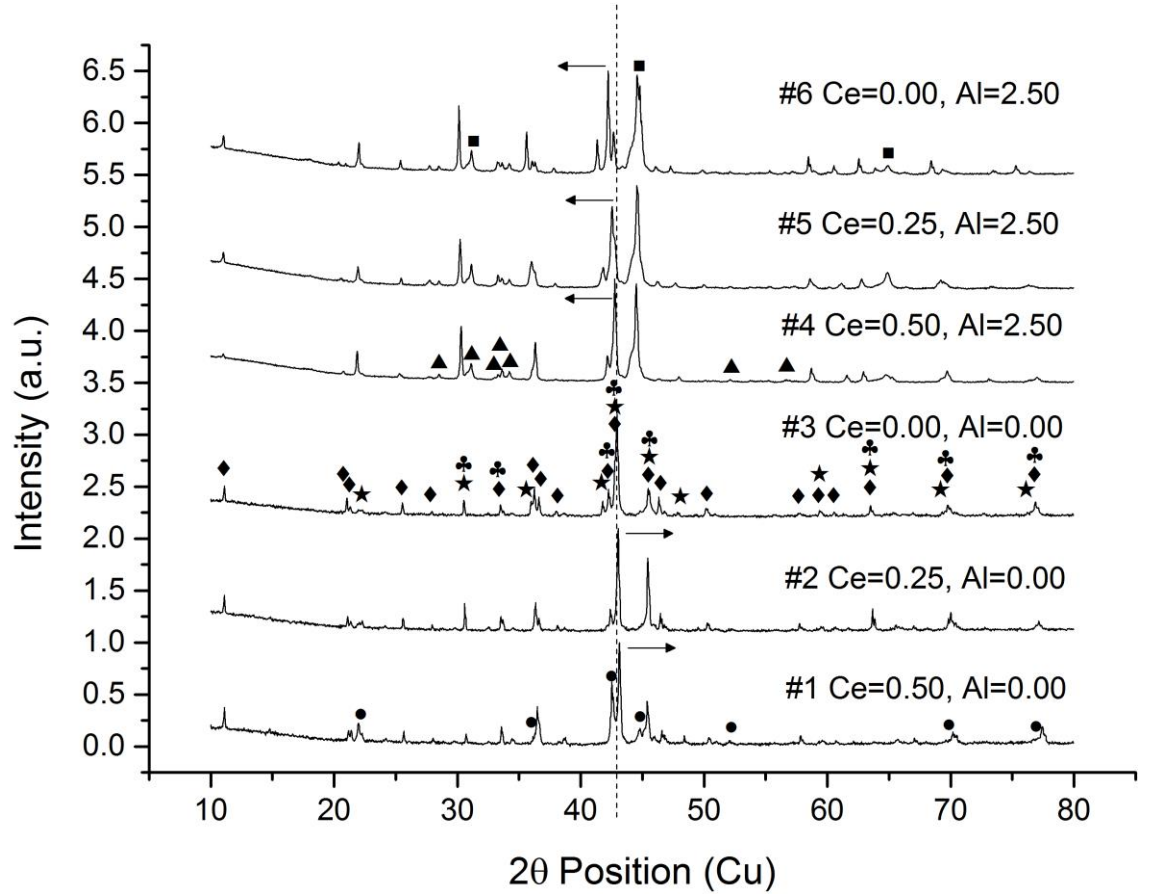


Figure 4.1 XRD patterns of $\text{La}_{(0.65-x)}\text{Ce}_x\text{Ca}_{1.03}\text{Mg}_{1.32}\text{Ni}_{(9-y)}\text{Al}_y$ with x ranging from 0.00 to 0.50 and y ranging from 0.00 to 2.50, showing phases of $(\text{La,Ce,Ca,Mg})_3(\text{Ni,Al})_9$ (◆), $(\text{La,Ce,Ca})\text{Ni}_5$ (★), $(\text{La,Ce,Ca,Mg})\text{Ni}_2$ (●), $(\text{La,Ce,Ca,Mg})_2\text{Ni}_7$ (♣), CaMg_2 (▲) and AlNi (■).

Without elemental substitution, the Rietveld refinement indicated that the basic alloy mainly consisted of 83 wt% of AB_3 phase and 15 wt% of AB_5 phase. A small amount of A_2B_7 phase (approximately 2 wt%) with a Ce_2Ni_7 -type hexagonal structure was also detected. It was found that the addition of Ce to replace La inhibited the formation of AB_3 phase and encouraged the formation of AB_5 phase. As can be seen in Figure 4.2, the amount of AB_5 increased to 22 wt% for an addition of Ce up to $x = 0.25$. However, the stacking of the AB_3 super lattice seems to be disrupted at a very high substitution of La by Ce ($x = 0.50$), where a significant amount of AB_2 phase in the form of $(\text{La,Ce,Ca,Mg})\text{Ni}_2$ was detected; but the formation of AB_5 phase was not increased as predicted. Even though in the study of Zhang et al. [174], no AB_2 formation was observed at the same Ce content but with a lower La content ($x = 0.20$),

the phase abundance of AB₃ (57 wt%) is very closed to this work, which is about 51 wt%. Therefore, it could be inferred that Ce substitution of La is unfavorable to the formation of AB₃ phase.

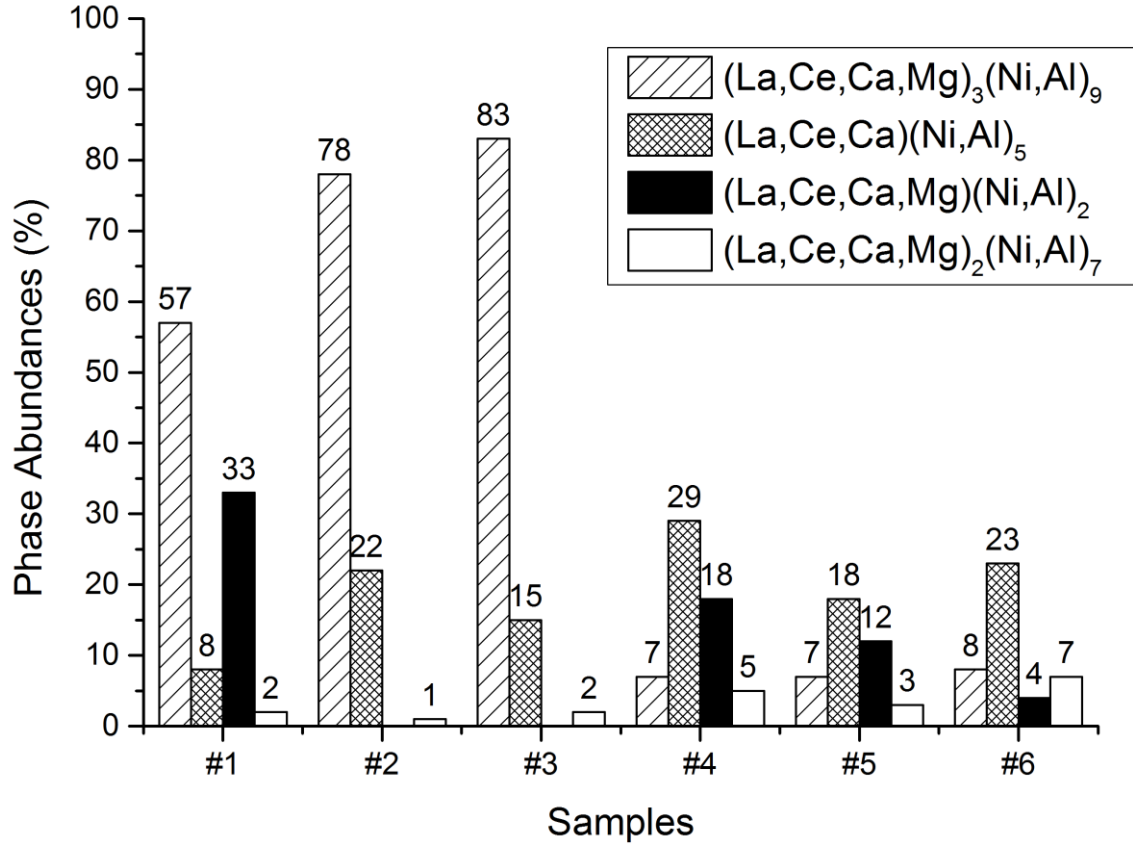


Figure 4.2 Main hydrogen absorption phases of $\text{La}_{(0.65-x)}\text{Ce}_x\text{Ca}_{1.03}\text{Mg}_{1.32}\text{Ni}_{(9-y)}\text{Al}_y$ consists of AB₃ (diagonal), AB₅ (crisscross), AB₂ (black) and A₂B₇ (blank) phases. Non-hydrogen absorbing phases (CaMg₂ and AlNi) are not included here.

The addition of Al has been used here to partially substitute the Ni. It formed additional AlNi and CaMg₂ phases, apart from the common phases (i.e. aforementioned AB₃, AB₂, AB₅ and A₂B₇) that were present in the alloys with Ce additions. This additional AlNi phase has also been noticed in the work of Chen et al. [163]. It should be noted that this AlNi phase was not playing a role in the storage of hydrogen [179], and thus the formation of the AlNi phase should be reduced in designing the optimum compositions of the alloys. Other researchers [170-172] also found that Al addition hindered the formation of AB₃ and increased the formation of AB₅, which is consistent

with our results. With high content of Ce and Al (Sample 4), not only AlNi phase but CaMg₂ phase (approximately 10 wt%) was detected.

Generally, one could observe that the substitution of La by Ce shifts the diffraction peaks to the right side, which indicates a reduction in cell volume; while the substitution of Ni by Al has the opposite effects. More detailed calculations were refined with Rietveld analysis and the results are presented Table 4.2. The table shows that the increased substitution of La by Ce reduced both lattice constants and cell volumes of both AB₃ and AB₅. The reduction of both lattice constants and cell volumes can be attributed to the small atomic radius of Ce (182.5 pm) than that of La (187.7 pm). It is believed that a larger cell volume could minimize the ratio of expansion to contraction of lattice during the cycling process and thereby improves the resistance to pulverization [53]. Aluminum (143.2 pm) has a larger atomic radius than Ni (124.6 pm), this increased both the cell volumes and the c/a ratio of the alloys; hence the lattice stress would expectedly be reduced, enhancing the pulverization resistivity.

Figure 4.3 (a) shows the BSE image of a Sample 3 particle (Ce=0.00, Al=0.00) after activation. The particle has faceted surfaces with cracks developed from the activation. Two separate areas with different grey levels were observed, indicating the co-existence of two main phases (i.e. AB₃ and AB₅ phases), confirming the results of XRD. The darker phase composition has a lower average atomic number and vice versa for lighter phase; corresponding to the EDS mapping which confirmed that the darker phase was rich in Mg (AB₃ phase) and the lighter phase was lack of magnesium (AB₅ phase). This observation is in agreement with the refinement results from Denys et al. [176] and Akiba et al. [180] where Mg tends not to reside in AB₅ phases. As shown in Figure 4.3 (b), Sample 1 (Ce=0.50, Al=0.00) has a similar faceted morphology as that in Sample 3, except that has more micro-cracks on the surface due to a larger volume expansion.

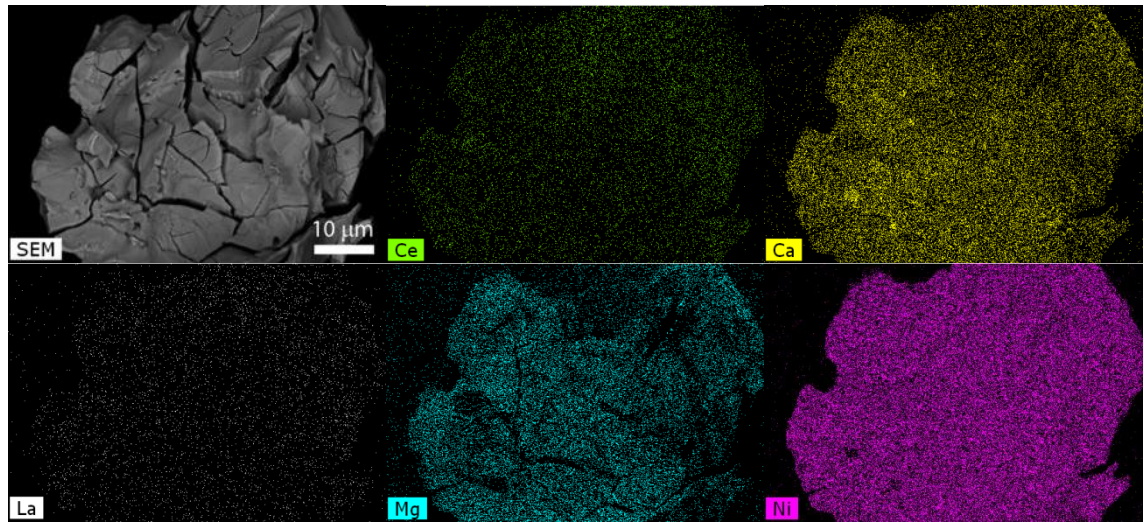
Table 4.2 Characteristics of major hydrogen absorption phases in $\text{La}_{(0.65-x)}\text{Ce}_x\text{Ca}_{1.03}\text{Mg}_{1.32}\text{Ni}_{(9-y)}\text{Al}_y$

ID	Compositions	Phases	Lattice Parameters			Cell Volume
			a/Å	c/Å	c/a	V/ Å ³
#1	x=0.50, y=0.00	(La,Ce,Ca,Mg) ₃ (Ni,Al) ₉	4.928(7)	23.966(3)	4.8625	504.1828
		(La,Ca,Ce)(Al,Ni) ₅	4.921(2)	3.996(2)	0.8121	83.7956
		(La,Ce,Ca,Mg)(Ni,Al) ₂	7.021(1)	7.021(1)	1.0000	346.1250
		(La,Ca,Ce) ₂ (Ni,Al) ₇	4.925(5)	23.956(2)	4.8636	503.3287
#2	x=0.25, y=0.00	(La,Ce,Ca,Mg) ₃ (Ni,Al) ₉	4.941(5)	23.948(3)	4.8483	506.4208
		(La,Ca,Ce)(Al,Ni) ₅	4.953(9)	3.989(0)	0.8052	84.7799
		(La,Ca,Ce) ₂ (Ni,Al) ₇	4.835(3)	24.066(4)	4.9770	487.2783
#3	x=0.00, y=0.00	(La,Ce,Ca,Mg) ₃ (Ni,Al) ₉	4.957(7)	23.932(2)	4.8273	509.3615
		(La,Ca,Ce)(Al,Ni) ₅	4.991(7)	3.978(7)	0.7971	85.6466
		(La,Ca,Ce) ₂ (Ni,Al) ₇	4.972(8)	24.768(8)	4.8721	530.4502
#4	x=0.50, y=2.50	(La,Ce,Ca,Mg) ₃ (Ni,Al) ₉	5.006(4)	23.867(3)	4.7677	517.9839
		(La,Ca,Ce)(Al,Ni) ₅	4.952(9)	4.075(0)	0.8227	86.5786
		(La,Ce,Ca,Mg)(Ni,Al) ₂	7.030(1)	7.030(1)	1	347.4568
		(La,Ca,Ce) ₂ (Ni,Al) ₇	4.851(4)	25.798(3)	5.3176	525.8497
#5	x=0.25, y=2.50	(La,Ce,Ca,Mg) ₃ (Ni,Al) ₉	4.965(6)	24.204(5)	4.8771	516.8315
		(La,Ca,Ce)(Al,Ni) ₅	4.993(0)	4.062(9)	0.8137	87.7228
		(La,Ce,Ca,Mg)(Ni,Al) ₂	7.057(6)	7.067(6)	1	351.5483
		(La,Ca,Ce) ₂ (Ni,Al) ₇	4.938(9)	24.291(7)	4.9183	513.1738
#6	x=0.00, y=2.50	(La,Ce,Ca,Mg) ₃ (Ni,Al) ₉	4.985(2)	24.189(4)	4.8521	520.6161
		(La,Ca,Ce)(Al,Ni) ₅	5.047(0)	4.046(5)	0.8018	89.26504
		(La,Ce,Ca,Mg)(Ni,Al) ₂	7.020(3)	7.020(3)	1.0000	345.9846
		(La,Ca,Ce) ₂ (Ni,Al) ₇	4.896(2)	22.86(2)	4.6689	474.6739

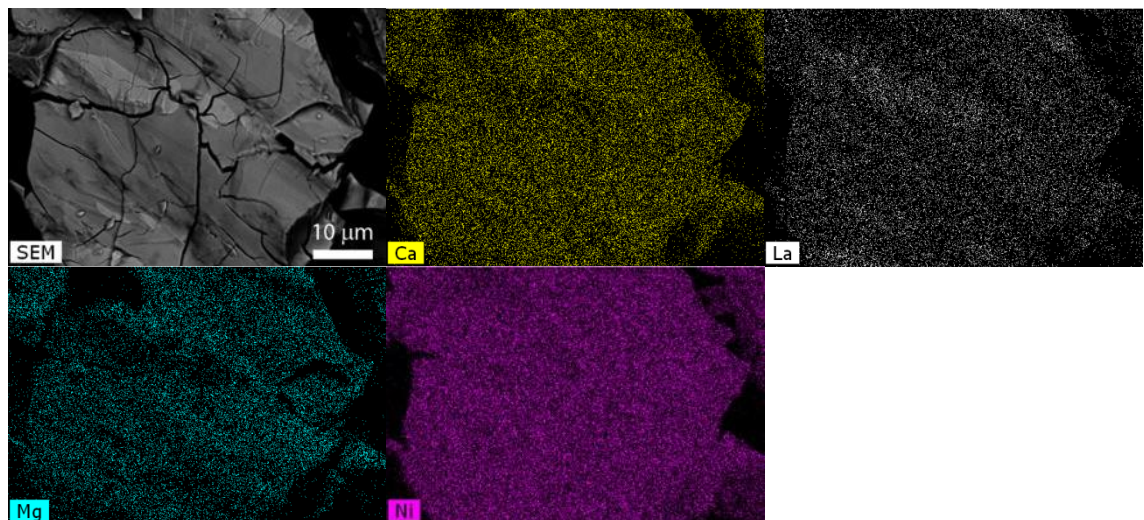
The BSE image of the activated Sample 4 (Ce=0.50, Al=2.50) in Figure 4.3 (c) shows that there are three distinctive phases: hydrogen-absorbing phase, CaMg_2 and AlNi phases. The phases with cracking surfaces were mainly the hydrogen-absorbing phase (AB_5 phase), while the darker regions with smooth surface are AlNi phase, where the EDS mapping showed that these regions were saturated with Al and Ni. The darkest regions with a granulated surface were rich in Ca and Mg. Both AlNi and CaMg_2 were not hydrogen-absorbing phases at room temperature; hence they were not susceptible to hydrogen embrittlement. However, micro cracks were found on the surface of the AB_5

phase and these cracks were more severe than that in Sample 3. This could be possibly due to the fact that AB_5 phases in Sample 4 were embedded in non-hydrogen absorbing phases. During hydrogenation in the activation process, the AB_5 phases experienced a significant volume expansion, but the neighbouring non-hydrogen absorbing phases restricted this expansion. The net result was the build-up of compressive stress which then promoting cracking in the surface. Unlike the enclosed AB_5 phase in Sample 3, both AB_5 and AB_3 phases were expanding, although at different rates, thus cracks are less severe.

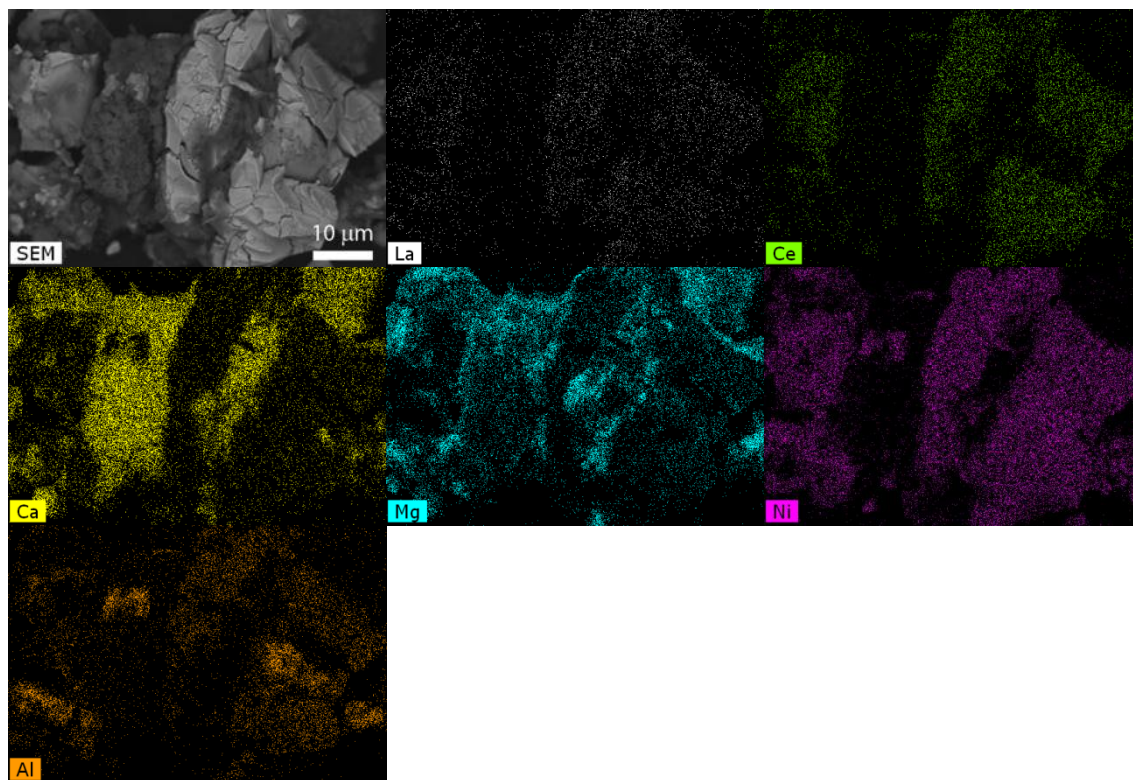
(a)



(b)



(c)



(d)

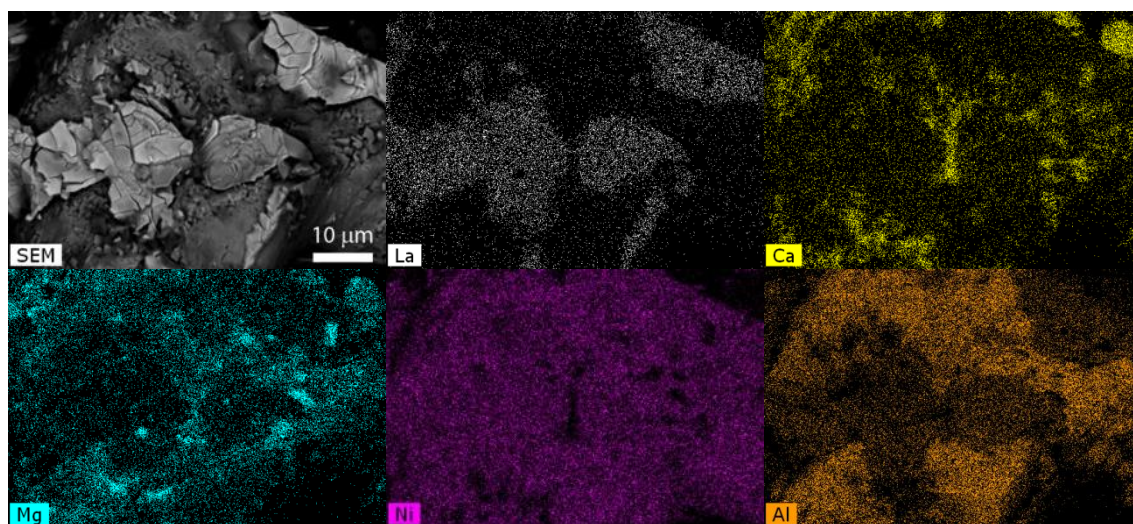


Figure 4.3 Backscattered electron image (BSE) of La_(0.65-x)Ce_xCa_{1.03}Mg_{1.32}Ni_(9-y)Al_y: (a) Sample 1 (Ce=0.50, Al=0.00), (b) Sample 3 (Ce=0.00, Al=0.00), (c) Sample 4 (Ce=0.50, Al=2.50), (d) Sample 6 (Ce=0.00, Al=2.50); with the energy dispersion spectrometer (EDS) mapping of La (white), Ce (green), Ca (yellow), Mg (aqua), Ni (pink) and Al (orange).

4.4.2 Effects on Thermodynamic Properties

Figure 4.4 shows the pressure-composition-isotherm (PCI) curves of $\text{La}_{(0.65-x)}\text{Ce}_x\text{Ca}_{1.03}\text{Mg}_{1.32}\text{Ni}_{(9-y)}\text{Al}_y$ HSAs at room temperature, where La and Ni were partially substituted with different amounts of Ce and Al, respectively. The HSA with no substitution (Sample 3) has a steep pressure plateau and two mixed phases—the AB_5 phase and AB_3 phase that have been confirmed in the XRD results. A significant part of the pressure plateau was below 0.1 MPa, which was below the lower boundary of the operating pressure of PEM fuel cells. Hence, even though the overall hydrogen storage capacity of the non-substituted alloys reached as high as 1.67 wt%, only about 25% of the stored hydrogen was released at ambient conditions, and the remaining 1.20 wt% of hydrogen was retained in the lattice. However, when substitution was made, the reversibility was greatly improved with approximately 1 wt% of hydrogen can be desorbed at ambient conditions but the improvement was accompanied with a reduction in the maximum hydrogen storage capacity. Nevertheless, the hydrogen storage characteristics of elemental substituted La-Mg-Ni based alloys are superior to that of Ti-V-Cr based alloys mentioned in Chapter 2, in addition to their significant low raw material cost. Therefore, partial elements substitution of A-side and B-side are of great interest to improve the viability of the alloys. It should be noted that Kadir et al. [8] obtained 1.87 wt% of hydrogen storage capacity with the same compositions but the measurement was conducted at 10 °C and with a different fabrication method.

The analysis of results in Figure 4.5 is based on a standard Fisher's least significant difference (LSD) test. The graphs consist of two lines (black and red) which represent the changes of measured properties with respect to the level of Ce content (from 0.00 to 0.50) at a constant Al content ($\text{Al} = 0.00$ black line and $\text{Al} = 2.50$ red line). The two lines are used to determine if the effect of Ce addition is significant at a given Al content by comparing the LSD bars. The LSD bars are set at a 95% confidence level. If the LSD bars of both end of a single line are overlapping, then the effect is not significant and vice versa. The second information that can be extracted from these graphs is the slopes of the line, where an incline slope indicates that the Ce addition gives a positive effect on the measured properties; while a decline slope indicates the other way round. If both lines gives opposite effects (positive and negative effects) at

two different levels, then there is an interaction between the two factors (Ce and Al additions). In other words, there is a possibility to find an optimum composition to achieve the desired property during optimization using Response Surface Methodology (RSM).

In Figure 4.5 (a), it can be seen that both red and black lines were almost parallel, indicating that the synergistic effect between Ce and Al contents on the hydrogen storage capacity is weak. The negative slopes of both lines also indicate that the hydrogen storage capacities were reduced with increasing Al and Ce contents. However, the effect of Al substitution was stronger than that of Ce substitution. At the end of the line for alloy with high Al content ($y=2.50$), there was an overlapping of LSD bars, showing that the influence of Ce content at this point was insignificant. The Reitveld analysis from the previous section and the PCI measurement also suggested that the hydrogen storage capacity decreased with the increasing formation of AB_5 phase.

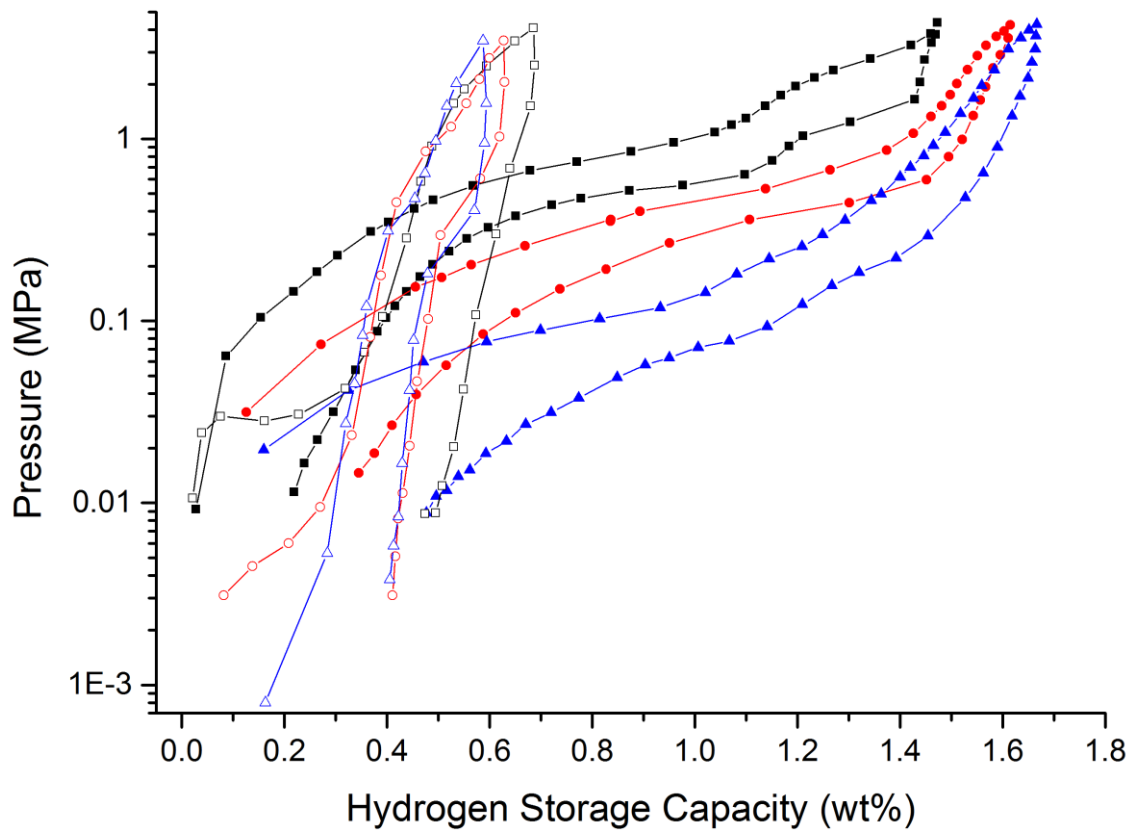
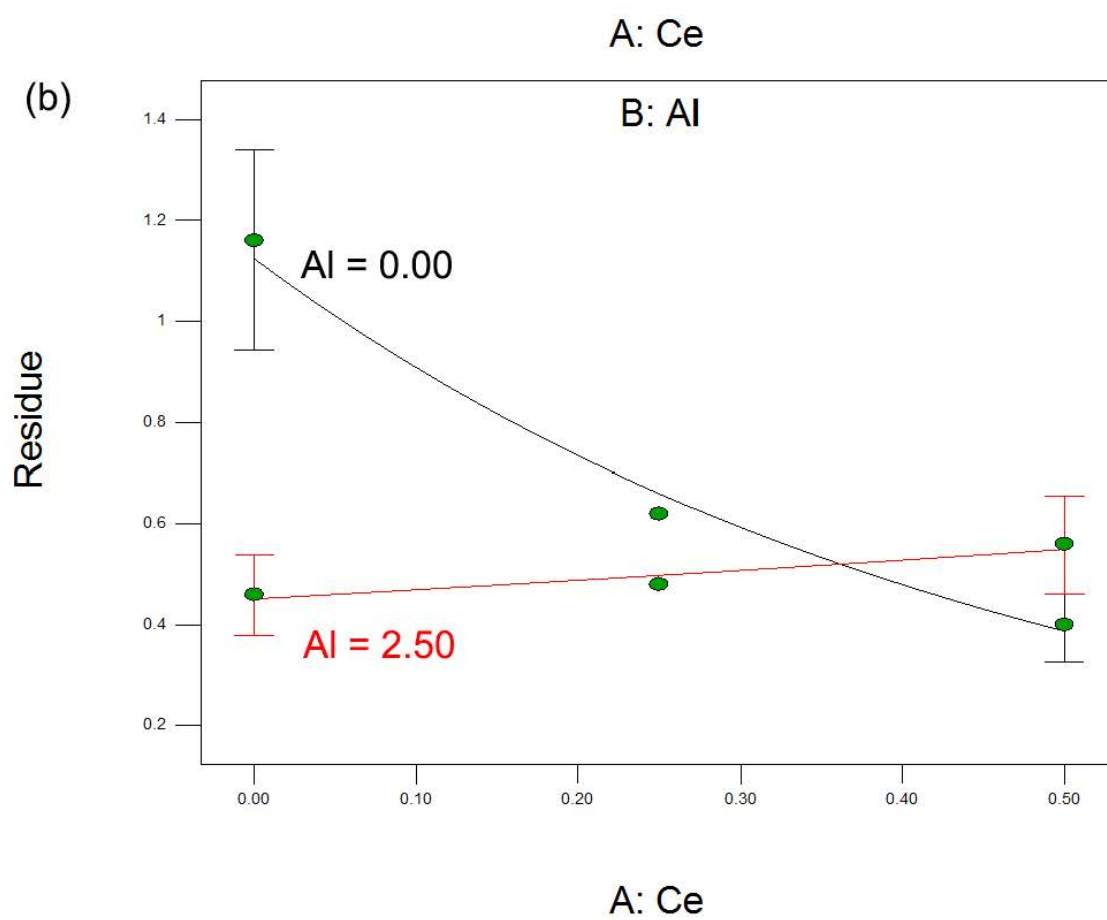
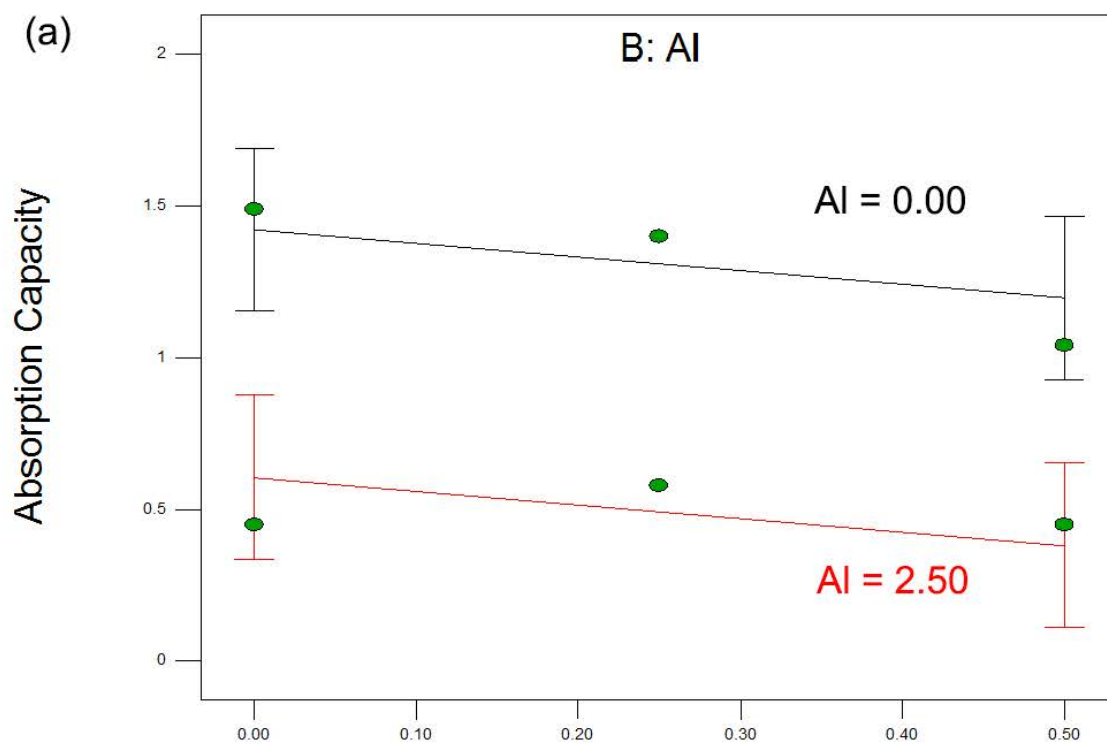
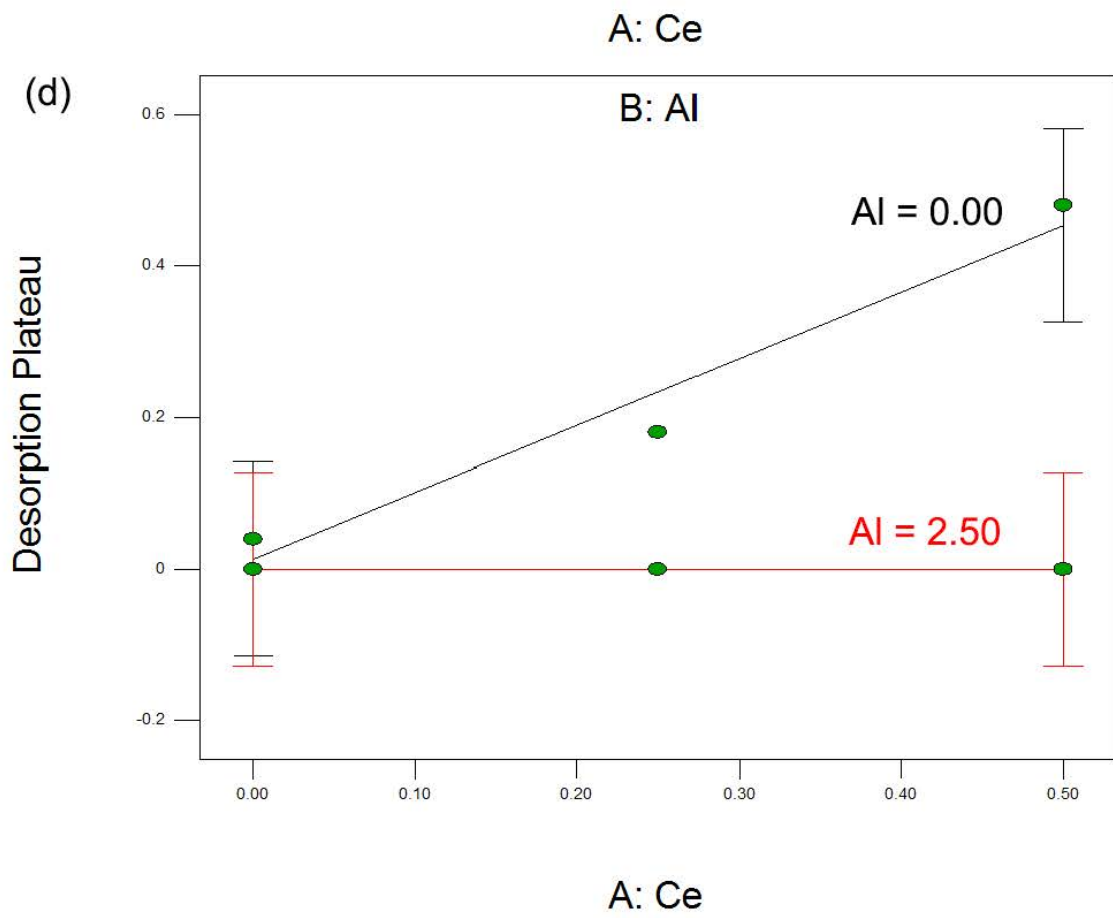
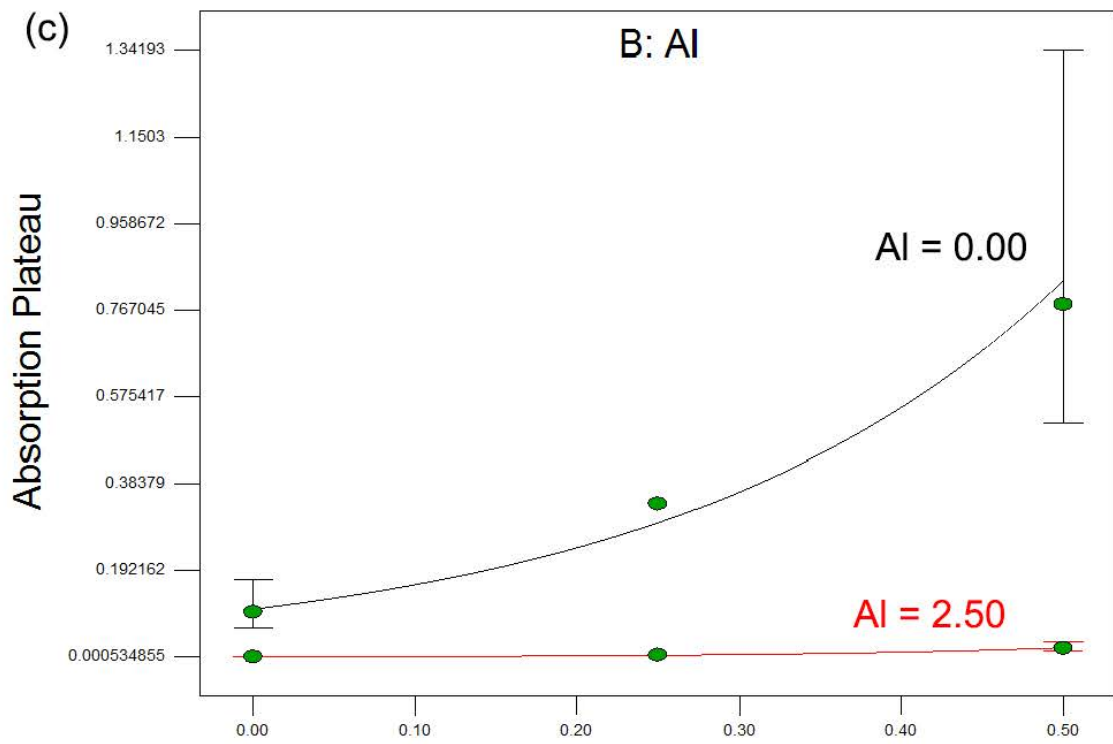


Figure 4.4 Pressure-compositions-isotherm curves of $\text{La}_{(0.65-x)}\text{Ce}_x\text{Ca}_{1.03}\text{Mg}_{1.32}\text{Ni}_{(9-y)}\text{Al}_y$ measured at room temperature with the compositions of #1 $x=0.50$, $y=0.00$ (■), #2 $x=0.25$, $y=0.00$ (●), #3 $x=0.00$, $y=0.00$ (▲), #4 $x=0.50$, $y=2.50$ (□), #5 $x=0.25$, $y=2.50$ (○) and #6 $x=0.00$, $y=2.50$ (△).

A non-monotonic interaction effect of entrapped hydrogen between the Ce and Al contents is shown in Figure 4.5 (b), because both lines were far from parallel. The influence of Al content on the amount of entrapped hydrogen depended on the Ce content. With no Ce content, Al addition was favorable in improving the reversibility of hydrogen storage. However, at high Ce content ($x=0.50$), high Al content was unfavorable. It is worth to note that, the overlapping of LSD bars at both ends of high Al content line implied that the influence of Ce was insignificant. On the other hand, with no Al substitution, the line had a very steep negative slope suggesting that higher Ce content has a significant positive effect in improving the reversibility of hydrogen storage in the alloy.

Both similar interaction effects on the hydrogen absorption and desorption plateau can be observed in Figure 4.5 (c) and (d), represented by the two lines on the graph where the effects were dominated by Ce substitution without Al. The absorption and desorption plateaus pressures increased with the Ce content, but the increment was insignificant with high Al additions. Both Ce and La at the A-side of the HSA are the stable hydride forming elements and both have very similar characteristics except in the atomic size; thus the overall hydrogen storage capacities were not significantly affected by their ratios in the composition. Due to the smaller atomic size of Ce, the cell volume of the hexagonal crystal is reducing with the increment of La substitution by Ce. This volume reduction has been discussed in the XRD results impeded the mobility of hydrogen atom from diffusing into the crystal lattice, hence resulting in higher equilibrium plateaus pressure. The overall increment of both absorption and desorption plateaus to the operating region of PEM fuel cells (0.10 MPa to 1.00 MPa) improved the reversible capability of the HSA. The substitutions of 0.25 of Ce in La and 0.50 of Ce in La increase the hydrogen reversible capability to 63% and 71% respectively.





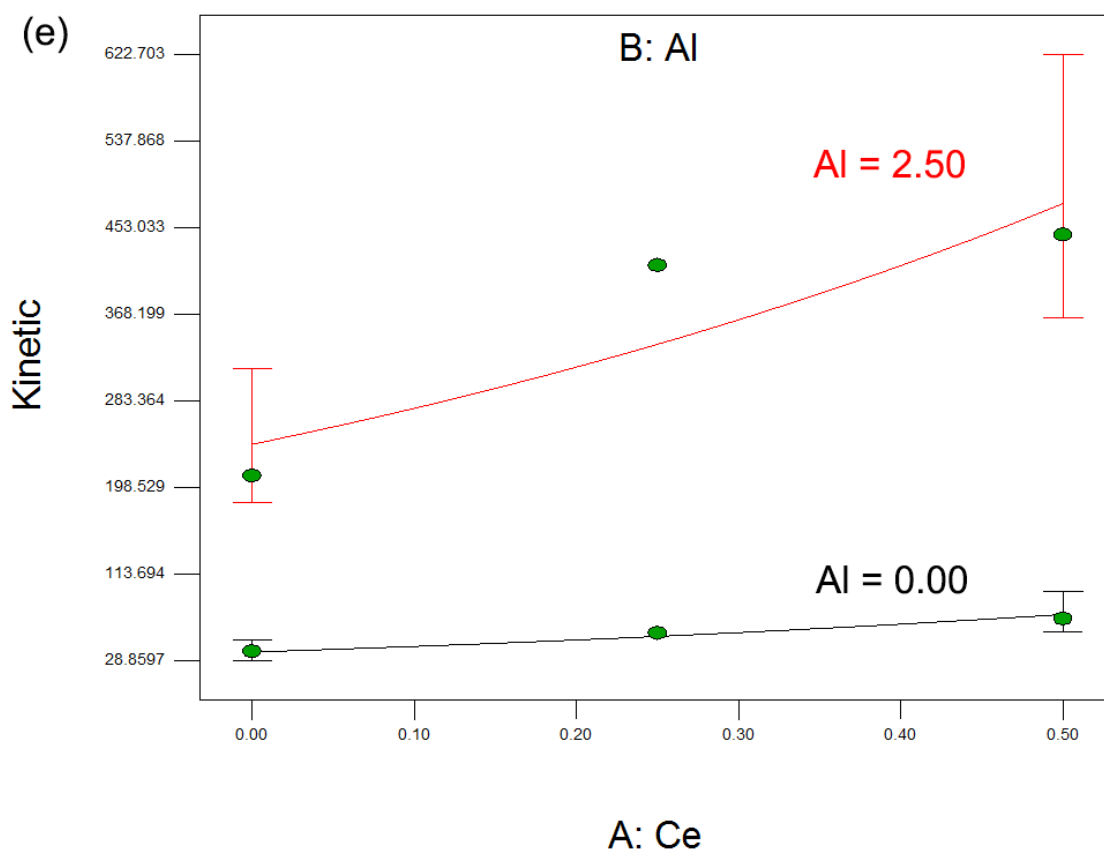


Figure 4.5 Interaction curves of different responses with 95% confidence level of Fisher's least significant difference (LSD) bars: (a) hydrogen storage capacity, (b) residue hydrogen, (c) hydrogen absorption plateau, (d) hydrogen desorption plateau and (e) hydrogen absorption kinetics.

The effect of the B-side substitution on the overall hydrogen storage capacity in HSAs was more pronounced where two groups of curves and responses (i.e. $y = 0.00$ and $y = 0.25$) are distinctively observed from both statistical analysis and PCI curves. With increase in the Ni substitution by Al, the overall hydrogen storage capacity reduced drastically from around 1.60 wt% to 0.70 wt% while the overall reversible hydrogen capacity dropped from 71% to 25%. Although the hydrogen retained was not greatly influenced by the Al substitution, over-substitution of Ni by Al ($y = 2.50$) still increased the hydrogen residue from about 0.40 wt% to 0.60 wt%. It has generally accepted that Ni plays an important role as a catalyst in separating the hydrogen molecules into atomic form, and recombining the atoms back to their molecular form during desorption [181]. On the other hand Al, with a large atomic radius of 143.2 pm,

is essential to stabilize the crystal structure and improve the cycle stability of HSAs [170], but it does not possess the catalytic effect of Ni [167]. Thus, as observed in this work, the replacement of Ni by Al reduced the probability of surface reaction between Ni and hydrogen gas. The HSAs with Al addition had a larger cell volume and a lower equilibrium pressure plateau, is contrary to their low hydrogen storage capacity. A first principle calculation done by Zhang et al. [182] has shown that the hydrogen atom has a tendency to move away from an Al atom, leaving the interstitial sites around Al atoms unoccupied. The unavoidable CaMg_2 phase that formed in Samples 4, 5 and 6 are also the culprit in the reduction of hydrogen storage capacity. This phase as indicated by Terashita et al. [183] does not show the capability of absorbing hydrogen at room temperature. All these are believed to have contributed to the significant deterioration of the hydrogen storage capacity observed for Al-bearing alloys in this work.

4.4.3 Effects on Absorption Kinetics

Figure 4.6 shows the absorption kinetics curve of $\text{La}_{(0.65-x)}\text{Ce}_x\text{Ca}_{1.03}\text{Mg}_{1.32}\text{Ni}_{(9-y)}\text{Al}_y$ alloy at room temperature. Similar to the PCI results, the absorption curves could be distinctively categorized into two groups according to the Al contents in the alloys. Ni substitution by Al substantially reduced the absorption rate. As can be seen in Figure 4.6, for alloys without Al, the time to achieve 80% of the maximum hydrogen storage capacity was less than 50s. The additions of Al up to $y = 2.50$ prolonged the time to more than 300 s to achieve the targeted capacity. One could also observe that the substitutions of La with Ce did not drastically change the absorption kinetics, even though the addition of Ce still possessed a slight adverse effect on the absorption performance. Corresponding to the interaction graph in Figure 4.5 (e), the effect of Ce addition became more pronounced at $y = 2.50$ of Al substitution.

Two main mechanisms can be used to describe hydrogen absorption. Firstly, the hydrogen molecules are chemically adsorbed on the surface of hydrogen storage alloy and split into atomic forms by Ni. Secondly, the hydrogen could only be stored effectively when hydrogen atoms are able to diffuse into the intermetallic lattice, forming solid solutions and hydride phases. This is a sequential mechanism where the second mechanism can only occur, if the hydrogen molecules are successfully dissociated in the first mechanism. However, once hydrogen molecules are split into

atoms and diffuse into the lattice, the diffusion mechanism would become the major rate determination step. In the hydrogen storage alloy, the B-side, which mostly consists of Ni, is responsible for regulating and catalyzing the hydrogen absorption, whereas the A-side, as mentioned above, is responsible for forming a stable hydride. Hence, the B-side is expected to dominate the performances of absorption kinetics. Therefore, two main possible factors – the reduction of catalytic effects and the formation of protective oxide layer, or the combination of both could contribute to a slow performance of the alloys.

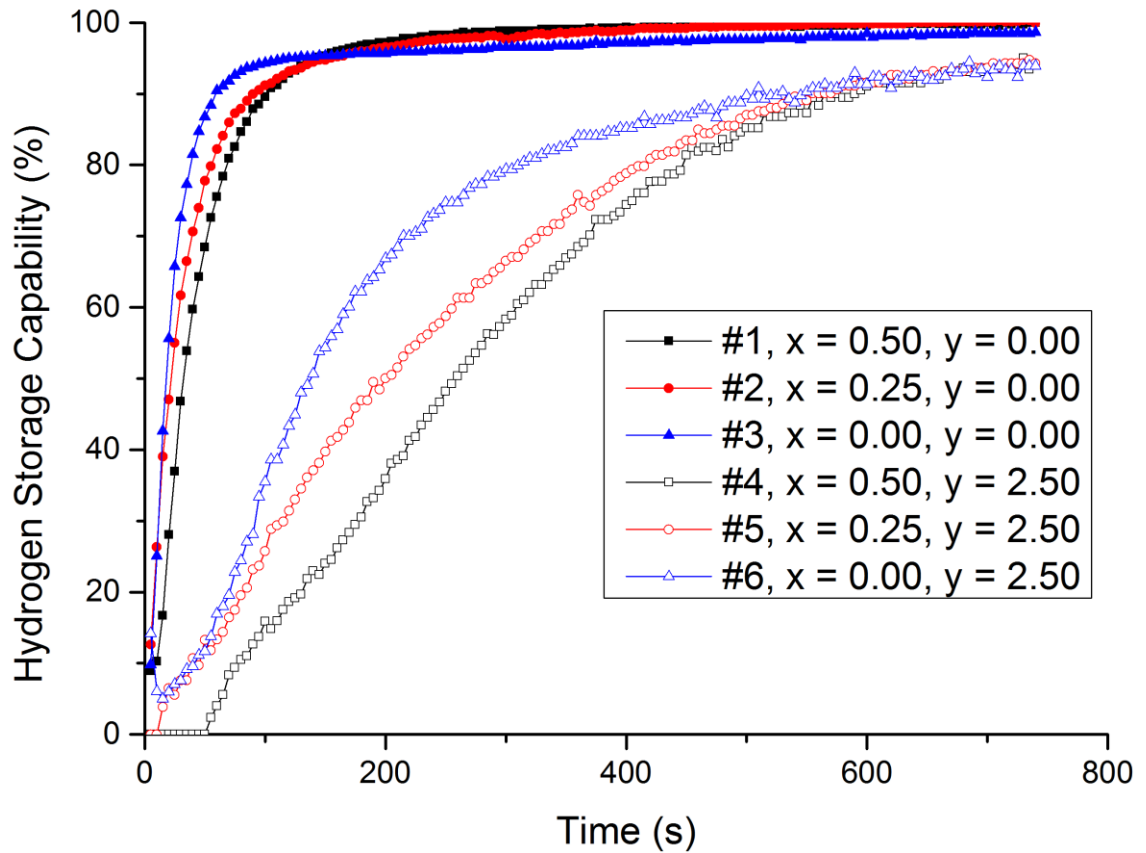


Figure 4.6 Absorption kinetic curves of $\text{La}(0.65-x)\text{Ce}_x\text{Ca}_{1.03}\text{Mg}_{1.32}\text{Ni}_{(9-y)}\text{Al}_y$ with the compositions of #1 $x=0.50$, $y=0.00$ (■), #2 $x=0.25$, $y=0.00$ (●), #3 $x=0.00$, $y=0.00$ (▲), #4 $x=0.50$, $y=2.50$ (□), #5 $x=0.25$, $y=2.50$ (○) and #6 $x=0.00$, $y=2.50$ (△).

As abovementioned, the increased substitution of Ni by Al reduces the dissociation rate of hydrogen molecules into hydrogen atoms because Al does not possess the catalytic capability of Ni. The probability of hydrogen molecules dissociating at the alloys' surface was inevitably lower. Al additions also promoted the

formation of protective oxide layers, which lowered the permeation of hydrogen molecules and lengthened the time taken for hydrogen molecules to reach active sites within the alloy. The prolonging diffusion time resulted in the tendency of forming hydrides layers that inhibited the diffusion of hydrogen atom. These could be postulated from those curves with Al additions, where an incubation period with sluggish initial absorption rates has been noticed in the first 50 s. The effect was particularly noticeable with Sample 4 ($x = 0.50$, $y = 2.50$), when both Al and Ce substitutions were at the highest. These two reasons constituted to the chemisorption mechanism as addressed above and this mechanism must take place in order to trigger the second mechanism—the diffusion mechanism.

The addition of Ce has less effect on the absorption kinetics with no addition of Al, although a slight decreased in absorption rate was still noticeable. This could be due to the smaller atomic size of Ce that has been discussed in the XRD section. A smaller atomic size contributes to a smaller cell volume, hence generating a higher diffusion barrier. In Sample 4, the aluminum oxide layer first impeded the hydrogen molecules permeation. After the hydrogen molecules dissociate on the active site, the reduced cell volume further limits the diffusion of hydrogen atom. This could be the reason that Sample 4 has an obvious and sluggish incubation period.

4.5 Conclusion

Both substitutions of A-side and B-side of the AB_3 alloys contribute to a certain degree of changes, either improving or decrementing the properties of HSA. These synergistic effects from both sides are the important factors to design the HSA compositions with optimum cost and performance. This study has identified the key effects contributed by these two element substitutions. Further improvement by response surface methodology will be used to fine-tune the HSA properties to meet the requirements of fuel cells.

Chapter 5 Performance Optimization of La-Mg-Ni Based Hydrogen Storage Alloys by Response Surface Methodology

5.1 Introduction

As mentioned in Chapter 4, the characteristics of the alloys could be optimized and fine-tuned with Response Surface Methodology (RSM) via element substitutions. An optimization process using the classical One Factor At a Time (OFAT) method in studying the effects of element substitutions is usually time consuming and normally requires a substantial number of experimental studies to identify the optimum parameters. In other words, studying the responses of elemental substitutions by varying only a single parameter while keeping other parameters at constant could be cost inefficient and might lead to false optimal conditions [184]. Additionally, the OFAT method is incapable of assessing the synergistic and antagonistic interactions among the factors; hence it is less effective for optimization. However, this constraint can be improved by employing a statistical experimental design method, i.e. response surface methodology (RSM).

RSM is a powerful statistical and mathematical tool that is useful for developing, improving and optimizing processes as well as formulation. RSM is able to evaluate and optimize multiple responses by varying the control variables collectively and simultaneously. This characteristic is important to determine the optimum alloy formulations that satisfy the operating specifications (constraints). First, a number of factors are identified and used to design the experimental space. Next, the responses with respect to the design points are collected and fitted into a mathematical model of response surface. The results of the model are able to identify the direct and indirect effects of the process parameters. In a two or three dimension plot, the interactions between the factors are illustrated as curves, where the maximum or minimum values of the response are the breakthrough optimal set of experimental parameters.

In this chapter, RSM is employed to study the responses of Ce and Al on the hydrogen storage properties of a hydrogen storage alloy $\text{La}_{(0.65-x)}\text{Ce}_x\text{Ca}_{1.03}\text{Mg}_{1.32}\text{Ni}_{(9-y)}\text{Al}_y$. These properties include hydrogen storage capacity, hydrogen residue, absorption

and desorption plateau pressures, as well as hydrogen absorption kinetics. The aim of the study is to maximize the hydrogen storage capacity of this alloy system, while improving other thermodynamic properties.

5.2 Materials and Experimental Procedures

5.2.1 Alloys characterizations

The hydrogen storage alloys were produced by arc- and induction-melting method as described in Chapter 4. The hydrogen storage alloys were analyzed by inductively coupled plasma (ICP) spectroscopy to confirm that the chemical compositions of alloys were similar to the designed compositions. Other characterization techniques were similar to those in Chapter 4, where the crystal structure and phase compositions were measured with a PANalytical Xpert Pro MPD X-ray diffractometer with Cu $K\alpha$ radiation that operated at 45 kV and 40 mA, and the results were analyzed and refined with X'pert HighScore Plus software. The measurement of pressure-composition-isotherm (PCI) and kinetic properties were carried out with the custom Sieverts instrument in 0, with the same procedures described in Chapter 4.

5.2.2 Data Analysis

The RSM approach was employed to optimize the compositions of hydrogen storage alloys that enhanced the performance of hydrogen storage properties. Two additional points were added into the combined design space in Chapter 4 (as shown in Figure 5.1). Unless specifically indicated, the sample labels henceforth are in accordance to Table 5.1. The statistical analysis of model equations including ANalysis Of Variance (ANOVA), coefficient of determination (R^2), and F-test, was performed by using the Design-Expert® software.

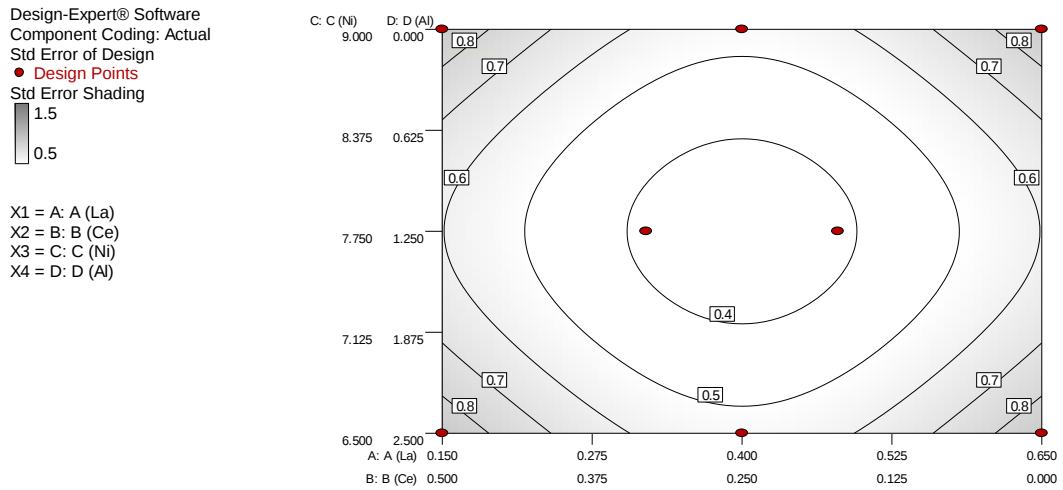


Figure 5.1 Experimental points in the design space with the compositions of La and Ce at x-axis, and Ni and Al at y-axis

5.3 Results and Discussion

5.3.1 Determination of Sample Compositions

ICP was used to confirm the chemical compositions of the alloys. The results tabulated in Table 5.2 are compared with the designed compositions in Table 5.1. There is no significant difference in the compositions between the designed and measured one, where the largest variation is approximately 8 wt%.

Table 5.1 Chemical compositions design of $\text{La}_{(0.65-x)}\text{Ce}_x\text{Ca}_{1.03}\text{Mg}_{1.32}\text{Ni}_{(9-y)}\text{Al}_y$

Sample	Element (wt%)					
	La	Ce	Ca	Mg	Ni	Al
1	3.01	10.12	5.96	4.63	76.28	0.00
2	8.03	5.06	5.96	4.63	76.31	0.00
3	13.05	0.00	5.97	4.64	76.35	0.00
4	6.81	7.08	6.33	4.92	69.70	5.17
5	10.22	3.65	6.33	4.92	69.72	5.17
6	3.40	11.42	6.73	5.23	62.21	11.00
7	9.07	5.72	6.74	5.23	62.24	11.01
8	14.74	0.00	6.74	5.24	62.28	11.01

Table 5.2 Chemical composition of $\text{La}_{(0.65-x)}\text{Ce}_x\text{Ca}_{1.03}\text{Mg}_{1.32}\text{Ni}_{(9-y)}\text{Al}_y$ obtained from ICP

<i>Sample</i>	Element (wt%)					
	La	Ce	Ca	Mg	Ni	Al
1	3.15	9.48	6.49	5.12	71.69	0.08
2	7.82	5.00	5.70	4.70	73.66	0.03
3	12.90	0.03	6.00	5.04	80.65	0.02
4	7.14	7.18	7.16	5.61	61.73	5.61
5	8.92	3.28	6.38	4.95	63.82	4.56
6	3.22	12.60	6.66	5.31	55.34	9.06
7	8.41	5.33	6.49	4.86	58.64	10.22
8	12.65	0.05	6.35	5.00	56.67	10.11

5.3.2 Phase Identifications

Sample 4 and Sample 5 consisted of the similar phases that were presented in Sample 5, 6 and 7 (labeled as Sample 4, 5 and 6 in Chapter 4). This chapter did not further discuss the phase distributions because these data were not use in the process of optimization. Nevertheless, the hydrogen storage phase distributions could be found in Figure 6.26, Chapter 6. Overall, the weight percent of hydrogen storage phases were 76% and 71% for Sample 4 and Sample 5, respectively. These results are to confirm that both Sample 4 and Sample 5 have the capability to absorb hydrogen with their hydrogen storage capacities fall between the group of Samples 1, 2 and 3, and the other group of Samples 6, 7 and 8.

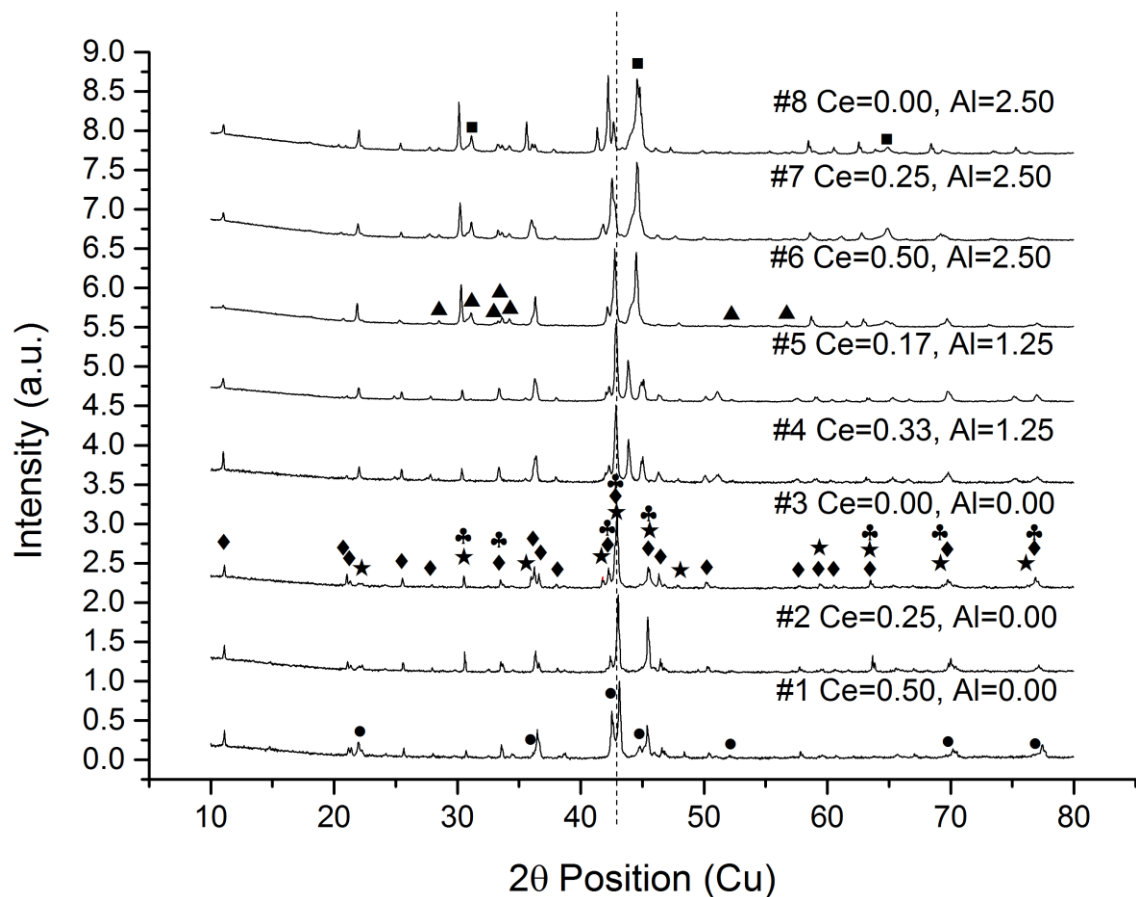


Figure 5.2 XRD patterns of $\text{La}_{(0.65-x)}\text{Ce}_x\text{Ca}_{1.03}\text{Mg}_{1.32}\text{Ni}_{(9-y)}\text{Al}_y$ with x ranging from 0.00 to 0.50 and y ranging from 0.00 to 2.50, showing phases of $(\text{La,Ce,Ca,Mg})_3(\text{Ni,Al})_9$ (◆), $(\text{La,Ce,Ca})\text{Ni}_5$ (★), $(\text{La,Ce,Ca,Mg})\text{Ni}_2$ (●), $(\text{La,Ce,Ca,Mg})_2\text{Ni}_7$ (♣), CaMg_2 (▲) and AlNi (■).

5.3.3 Pressure-Composition-Isotherm and Kinetic Properties

Figure 5.3 showed that the pressure-composition-isotherm curves of all eight samples could be distinctively separated into three groups depending on the Al content. The first group with no Al substitution had a maximum hydrogen storage capacity ranging from 1.40 wt% to 1.70 wt%. The second group which was doped with $y = 1.25$ of Al, reduced the maximum hydrogen storage capacity to the range of 0.90 wt% to 1.20 wt%. Further increased of Al substitution to $y = 2.50$ (the third group) reduced the maximum hydrogen storage capacity to less than 0.70 wt%. The two new samples (Sample 4 and Sample 5) that were synthesized in this chapter were in the second group that had a capacity in between first and third group, which was consistent with the expectation. As

mentioned in Chapter 4, the reduction of hydrogen storage capacity with the increased proportion of Al was due to the formation of non-hydrogen absorbing phases, which were agreed with the XRD results.

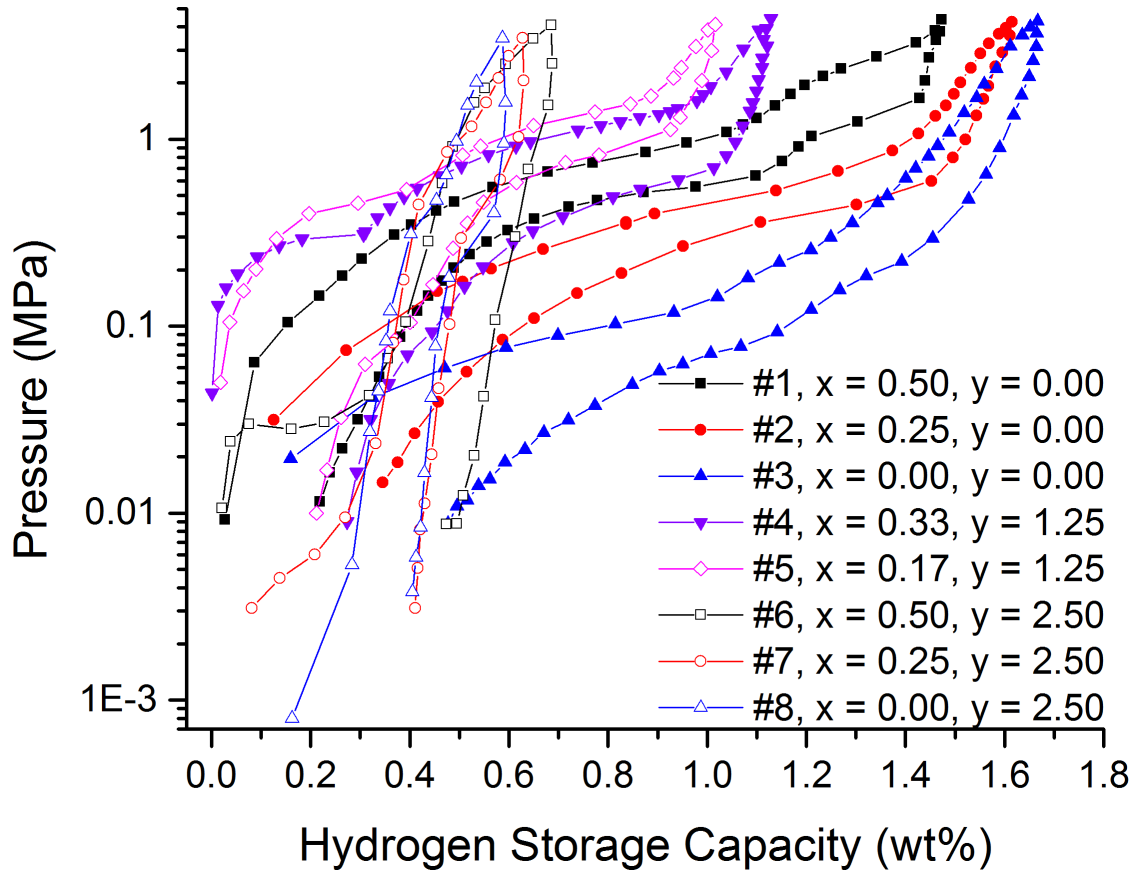


Figure 5.3 Pressure-compositions-isotherm curves of $\text{La}_{(0.65-x)}\text{Ce}_x\text{Ca}_{1.03}\text{Mg}_{1.32}\text{Ni}_{(9-y)}\text{Al}_y$ measured at room temperature: Sample 1 (■), Sample 2 (●), Sample 3 (▲), Sample 4 (▼), Sample 5 (◆), Sample 6 (□), Sample 7 (○), and Sample 8 (△).

Both absorption and desorption pressure plateaus also behaved similar to the trend of hydrogen storage capacity, where three groups of plateau pressures according to the Al content were observed. In general, the second group had higher pressure plateaus than the first and third group. Again, the changes of plateaus due to the atomic sizes of Ce and Al have been discussed in detail in Chapter 4. Importantly, these synergetic interactions provided a platform to regulate the plateaus to the desired operating conditions.

The hydrogen absorption kinetics of the hydrogen storage alloys are presented in Figure 5.4. In-depth analysis of the absorption kinetics and mechanisms will be repeated and discussed in Chapter 6.

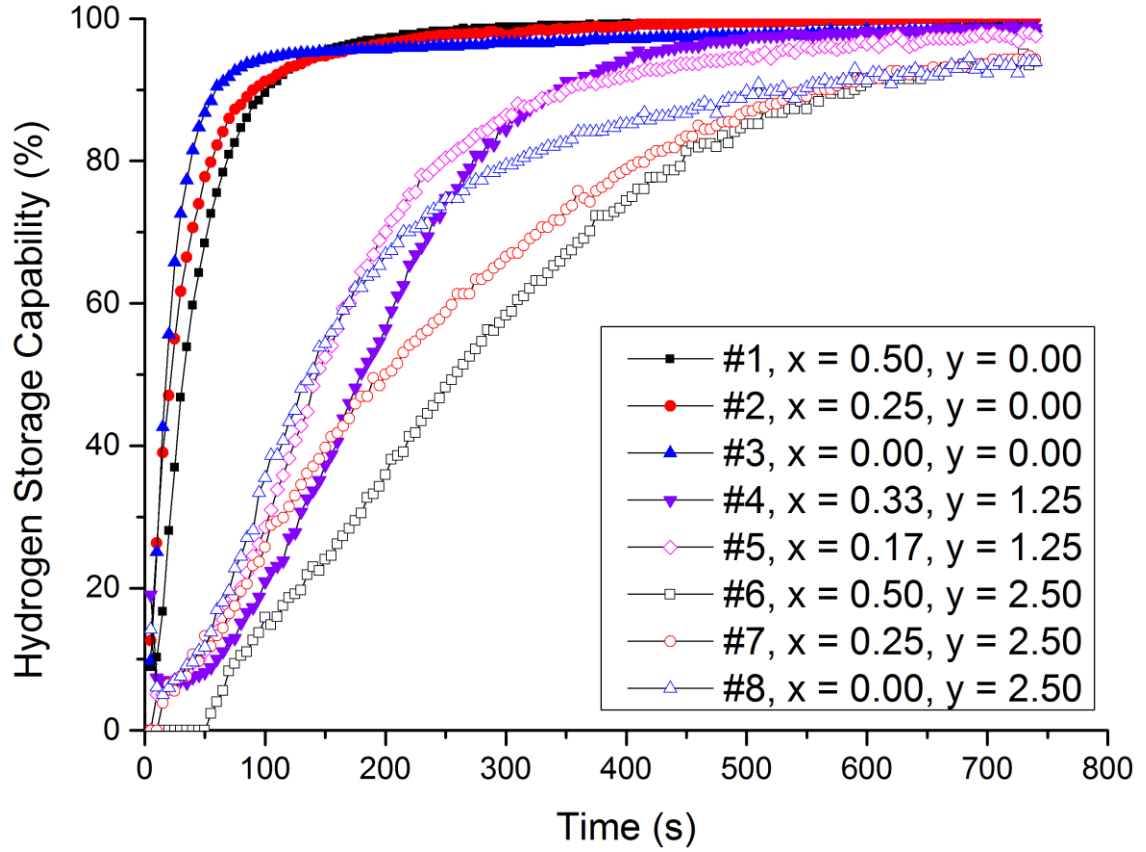


Figure 5.4 Hydrogen absorption kinetic of $\text{La}_{0.65}\text{Ce}_{(0.65-x)}\text{Mg}_{1.32}\text{Ca}_{1.03}\text{Ni}_9\text{Al}_{(9-y)}$ measured at room temperature with an approximate initial charging pressure of 4.00 MPa.

5.3.4 Analysis of response surface

The data obtained from the PCI and kinetic measurements were translated into the response surface plots in Figure 5.5 to Figure 5.9. To better illustrate the effects on the hydrogen storage properties, the corresponding contour plots were also included. The response surfaces of respective properties were fitted into model according to the following equations:

$$\ln Y_1 = 0.029C + 1.084D - 0.214CD \quad (5.1)$$

$$\ln Y_2 = 0.018AC + 3.119AD - 0.211BC + 0.043BD - 0.545ACD \quad (5.2)$$

$$\ln Y_3 = -0.382AC - 11.149AD + 0.074BC - 6.235BD + 1.716ACD + 0.692BCD \quad (5.3)$$

$$Y_4 = 0.017A^*C^* + 0.004A^*D^* + 0.43B^*C^* - 0.018B^*D^* + 1.06A^*C^*D^* \quad (5.4)$$

$$\ln Y_5 = 0.441C - 1.551D + 0.421CD \quad (5.5)$$

where, Y_1 is the hydrogen absorption capacity (wt%) at 1.00 MPa, Y_2 is the residue capacity (wt%) at 0.01MPa, Y_3 is the absorption plateau (MPa), Y_4 is the desorption plateau (MPa), Y_5 is the absorption kinetic (s), A is the element La, B is the element Ce, C is the element of Ni and D is the element of Al. Equation (5.4) is retained in pseudo components (*) form because the higher order terms in the actual equation did not give the same predictions as the pseudo equation. The pseudo components are defined as below:

$$P_i = \frac{x_i - L_i}{1 - L} \quad (5.6)$$

where, P_i is the i -th pseudo component, X_i is the i -th actual component (the elements of La, Ce, Ni and Al), L_i is the lower constraints for the i -th component and L is the sum of all lower constraints. Pseudo components are used to simplify model fittings and rescale constraints of each factor. The reason for the equation to retain in the pseudo form is because the desorption plateau pressures should be fitted in logarithm form. However, there were a few samples that had exceptionally low desorption plateau pressures, which exceed the measurement limits of the Sievert's instrument. Hence, it is assumed that those undetected desorption plateau pressures were at 0 MPa, which prohibits the results to be analyzed in logarithm form. Nonetheless, the non-logarithm pseudo model proposed in this chapter is still valid for optimization but may not give same predictions for higher order terms.

All model equations were checked with ANOVA tabulated in Table 5.3. Two indicators were used to determine the significance of the models, the p-value and coefficient of determination, R^2 . As the p-values of all model equations were less than 0.05%, the proposed models of each response were statistically significant. This is supported by the values of coefficient of determination that are more than 0.90, confirming that the models have a very high goodness of fittings and are able to give

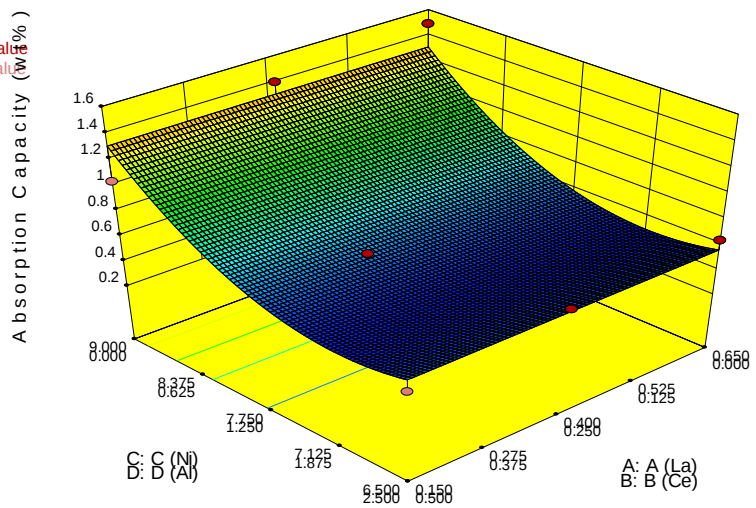
acceptable and reproducible predictions. It should be noted that the model equations were merely the empirical relationships between the factors and responses but had no theoretical justification.

The equation (5.1) shows that the hydrogen absorption capacity reduced quadratically with the addition of Al, but the effect of Ce was statistically insignificant. This indicates that Al substitution should be kept to a minimum so that the hydrogen storage capacity is not seriously lowered. As mentioned in Chapter 4, Al addition is essential to improve the cycle stability. Hence, during the optimization in the next section, the minimum Al addition was set as 0.10. The response surface of hydrogen residue in Figure 5.6 is tilted at one vertex, showing that without Ce and Al additions, the hydrogen residue was relatively high. Nonetheless, the hydrogen residue reduced drastically by the addition of either Ce or Al, or both. The response surfaces of both absorption and desorption plateaus show an interesting curvature in Figure 5.7 and Figure 5.8 respectively, where the substitution effect on the absorption plateau was more prominent. Both plots have a similar hump at the middle region, which is the resultant of the different unit cell volumes and the atomic sizes of Ce and Al, as discussed in Chapter 4. The absorption kinetic response model which is represented by equation (5.5) has a similar characteristic as the hydrogen storage capacity response model, except that the response surface of the former one is the reverse of the later one.

Table 5.3 ANOVA for the response surface model

Response		Sum of Squares	Degrees of freedom	Mean square	F-value	p-value (prob>F)	R ²	Adjusted R ²
Absorption capacity	Model	1.23	2	0.61	23.20	0.0030	0.9027	0.8638
	Residual	0.13	5	0.026				
Residue capacity	Model	0.85	4	0.21	38.37	0.0066	0.9808	0.9553
	Residual	0.017	3	5.57×10 ⁻³				
Absorption plateau	Model	5.90	5	1.18	91.18	0.0109	0.9956	0.9847
	Residual	0.026	2	0.013				
Desorption plateau	Model	0.21	4	0.049	9.40	0.0480	0.9261	0.8277
	Residual	0.016	3	5.21×10 ⁻³				
Absorption kinetic	Model	5.81	2	2.91	26.78	0.0021	0.9146	0.8805
	Residual	0.54	5	0.11				

Design-Expert® Software
 Component Coding: Actual
 Absorption Capacity (wt%)
 ● Design points above predicted value
 ● Design points below predicted value
 1.49
 0.47
 X1 = A: A (La)
 X2 = B: B (Ce)
 X3 = C: C (Ni)
 X4 = D: D (Al)



Design-Expert® Software
 Component Coding: Actual
 Absorption Capacity (wt%)
 ● Design Points
 1.49
 0.47
 X1 = A: A (La)
 X2 = B: B (Ce)
 X3 = C: C (Ni)
 X4 = D: D (Al)

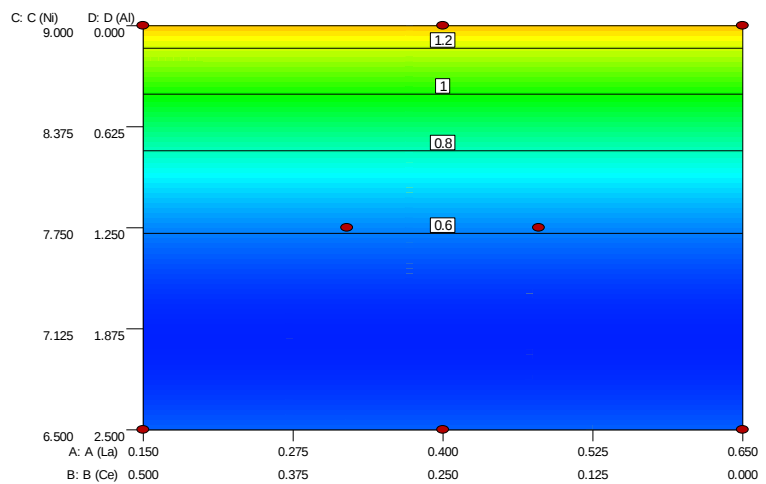
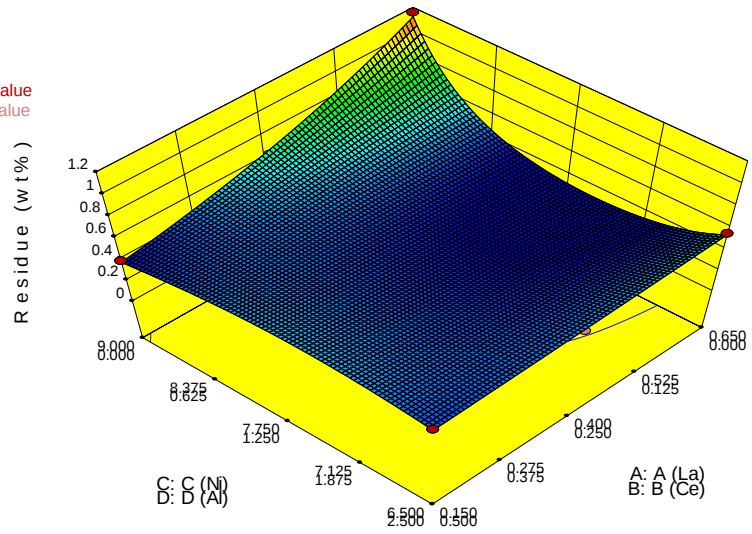


Figure 5.5 Response surface and the corresponding contour plot of absorption capacity at 1.00 MPa.

Design-Expert® Software
 Component Coding: Actual
 Original Scale
 Residue (wt%)
 ● Design points above predicted value
 ○ Design points below predicted value
 1.16
 0.39
 X1 = A: A (La)
 X2 = B: B (Ce)
 X3 = C: C (Ni)
 X4 = D: D (Al)



Design-Expert® Software
 Component Coding: Actual
 Original Scale
 Residue (wt%)
 ● Design Points
 1.16
 0.39
 X1 = A: A (La)
 X2 = B: B (Ce)
 X3 = C: C (Ni)
 X4 = D: D (Al)

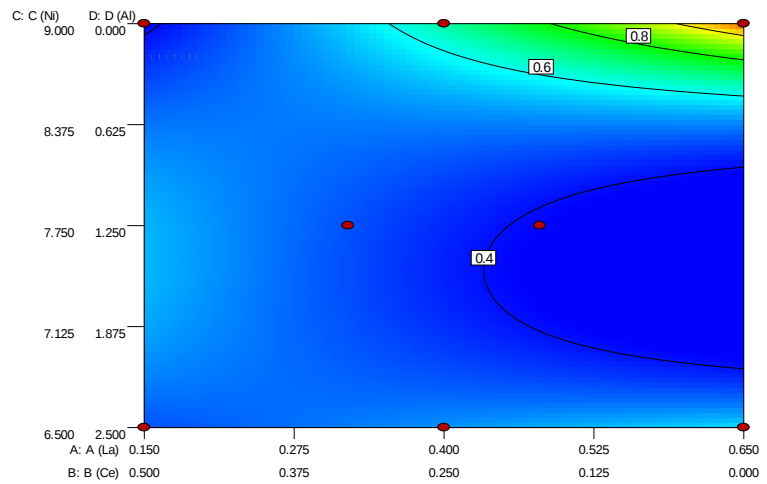
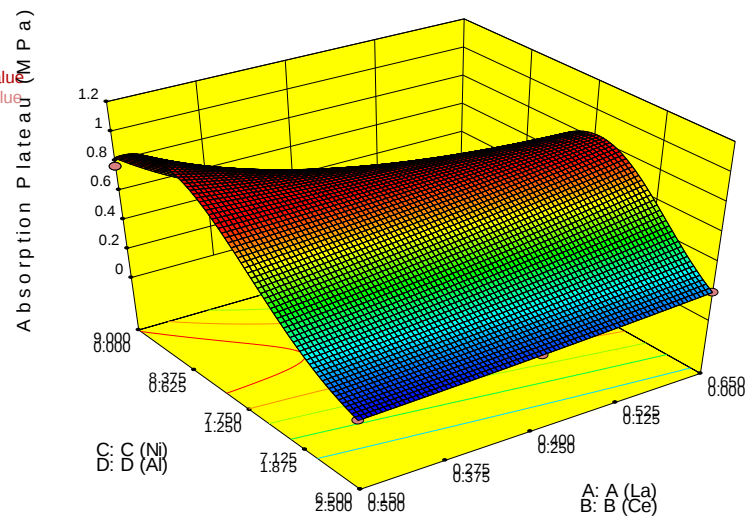


Figure 5.6 Response surface and the corresponding contour plot of residue capacity at 0.01 MPa.

Design-Expert® Software
 Component Coding: Actual
 Original Scale
 Absorption Plateau (MPa)
 ● Design points above predicted value
 ○ Design points below predicted value
 0.8
 0.1
 X1 = A: A (La)
 X2 = B: B (Ce)
 X3 = C: C (Ni)
 X4 = D: D (Al)



Design-Expert® Software
 Component Coding: Actual
 Original Scale
 Absorption Plateau (MPa)
 ● Design Points
 0.8
 0.1
 X1 = A: A (La)
 X2 = B: B (Ce)
 X3 = C: C (Ni)
 X4 = D: D (Al)

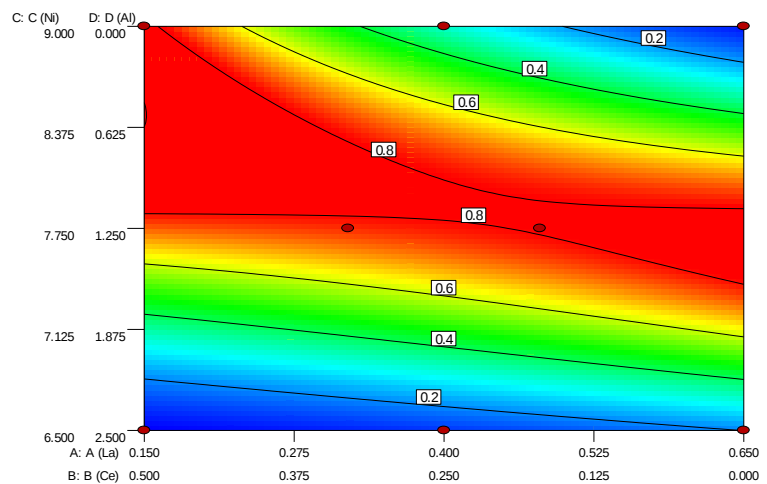
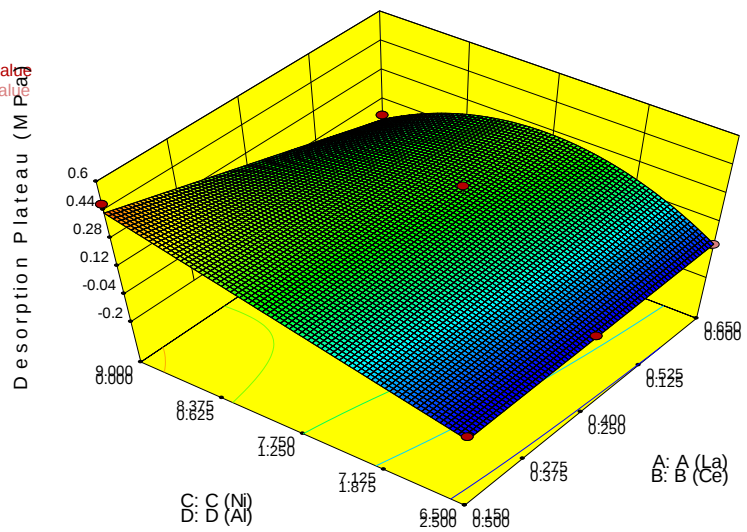


Figure 5.7 Response surface and the corresponding contour plot of absorption pressure plateau.

Design-Expert® Software
 Component Coding: Actual
 Desorption Plateau (MPa)
 ● Design points above predicted value
 ● Design points below predicted value
 0.48
 0
 X1 = A: A (La)
 X2 = B: B (Ce)
 X3 = C: C (Ni)
 X4 = D: D (Al)



Design-Expert® Software
 Component Coding: Actual
 Desorption Plateau (MPa)
 ● Design Points
 0.48
 0
 X1 = A: A (La)
 X2 = B: B (Ce)
 X3 = C: C (Ni)
 X4 = D: D (Al)

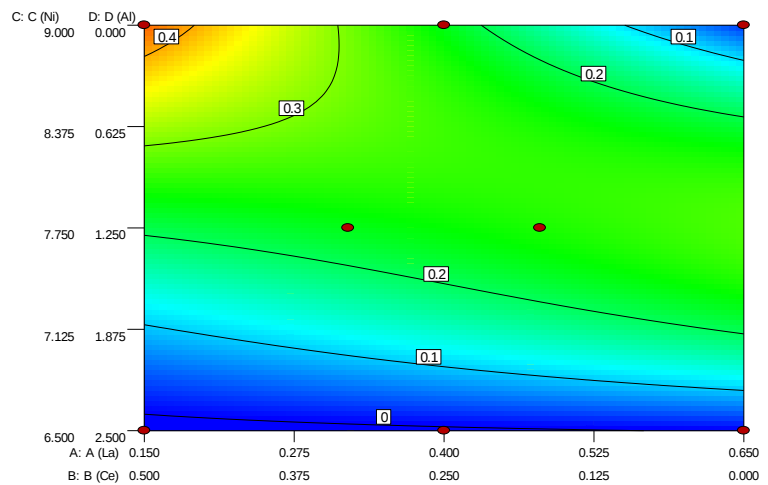


Figure 5.8 Response surface and the corresponding contour plot of desorption pressure plateaus.

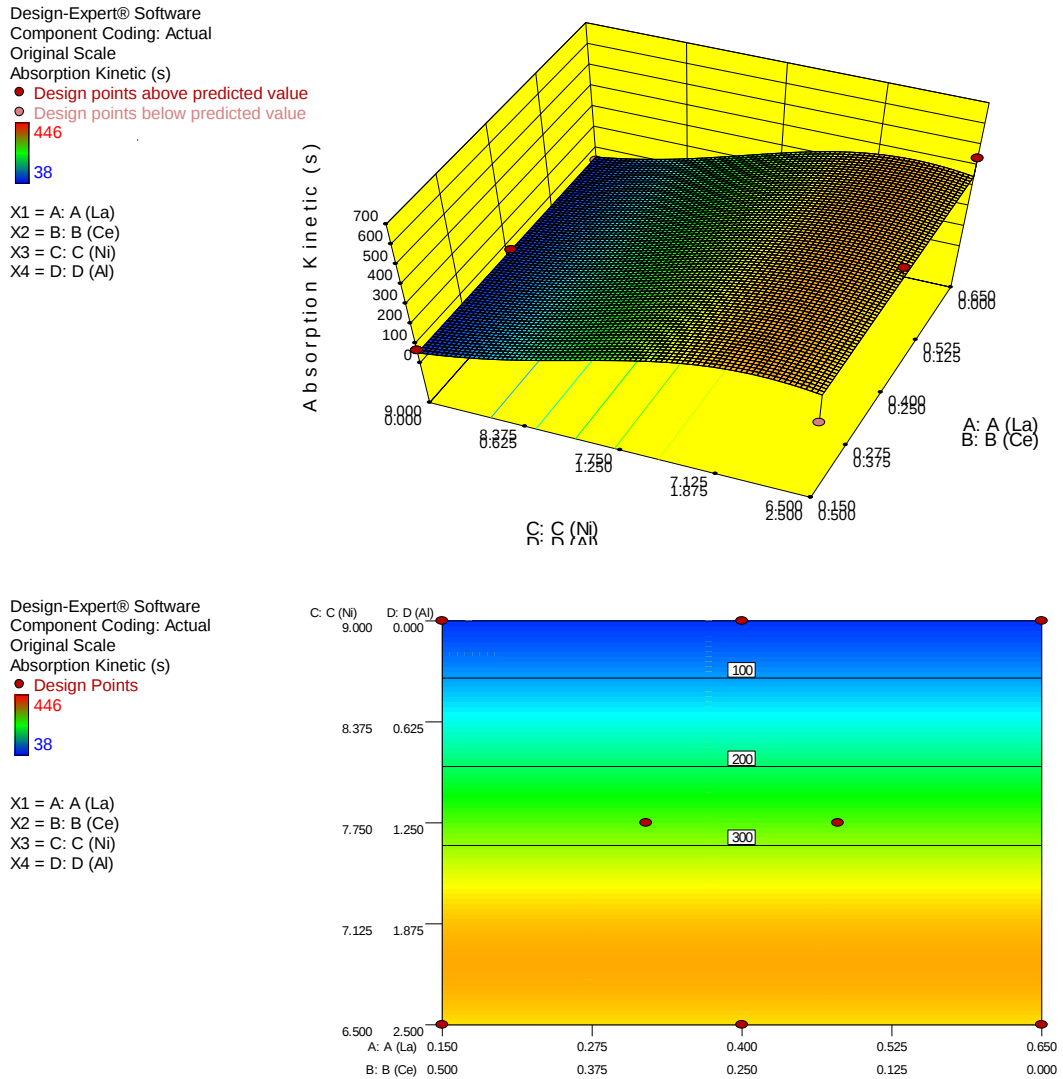


Figure 5.9 Response surface and the corresponding contour plot of absorption kinetic.

5.4 Properties Optimization

The optimization requirements have been discussed in Chapter 1, where the properties of these alloys are optimized according to the requirements of a RAPS system that coupled with an electrolyzer and a PEM fuel cell. The goals of this optimization process are to maximize the hydrogen storage capacity at a moderate operating pressure and temperature, while minimizing the residue and absorption time. Therefore, the optimization criteria were set as below:

Composition of La (<i>labeled as A</i>)	: in the range of 0.15 to 0.65
Composition of Ce (<i>labeled as B</i>)	: in the range of 0.00 to 0.50
Composition of Ni (<i>labeled as C</i>)	: in the range of 6.50 to 8.90
Composition of Al (<i>labeled as D</i>)	: in the range of 0.10 to 2.50
Absorption capacity at 1.00 MPa	: maximize
Residue capacity at 0.01 MPa	: minimize
Absorption kinetic (time to reach 80%)	: minimize
Absorption pressure plateau	: in the range of 0.50 to 1.00 MPa
Desorption pressure plateau	: in the range of 0.10 to 0.50 MPa

The numerical calculated optimum compositions and predicted properties were tabulated in Table 5.4:

Table 5.4 Possible optimal compositions and the predicted properties

	A	B	C	D	Abs.	Residue	Abs.	Des.	Abs.
#	La	Ce	Ni	Al	Capacity	Capacity	Plateau	Plateau	Kinetic
1	0.15	0.50	8.90	0.10	1.20	0.40	0.89	0.40	66.6
2	0.30	0.35	8.90	0.10	1.23	0.51	0.52	0.31	66.5
3	0.53	0.13	8.46	0.54	0.86	0.53	0.49	0.23	133.2
4	0.58	0.07	8.39	0.61	0.82	0.52	0.50	0.23	141.7

*Abbreviations: Abs., Absorption; Des., Desorption

5.4.1 Verification of optimized samples properties

Among the four optimized solutions in Table 5.4, solutions 1 and 2 had the highest hydrogen storage capacity. Hence, they were selected and relabeled as Sample OP1 (Ce=0.35, Al=0.10) and Sample OP2 (Ce=0.50, Al=0.10). Their thermodynamics and kinetics properties were characterized with the same methods and the results are presented in Figure 5.10 and Figure 5.11, respectively.

In Figure 5.10, Sample OP1 shows an absorption capacity of 1.20 wt% at 1 MPa, a residue of 0.45 wt% at 0.01 MPa, an absorption plateau of 0.50 MPa at 0.70wt%

and a desorption plateau of 0.30 MPa at 0.70 wt%. All values are consistent with the predicted optimized values from RSM. On the other hand, Sample OP2 had an absorption capacity of 0.70 wt% at 1MPa, a residue of 0.38 wt% at 0.01 MPa, an absorption plateau of 1.00 MPa at 0.70 wt% and a desorption plateau of 0.40 MPa at 0.70 wt%. All measured properties agreed well with the predicted values, except the absorption plateau was slightly higher, which therefore affected the measurement of absorption capacity. The discrepancy between the observed and predicted values was because of the logarithm scale used in the Y-axis of Figure 5.10; hence a marginal error in the prediction of absorption plateau will result in a significant variation of absorption capacity. Despite the inconsistency with a single prediction property, the overall thermodynamics properties were still in the desired and acceptable range.

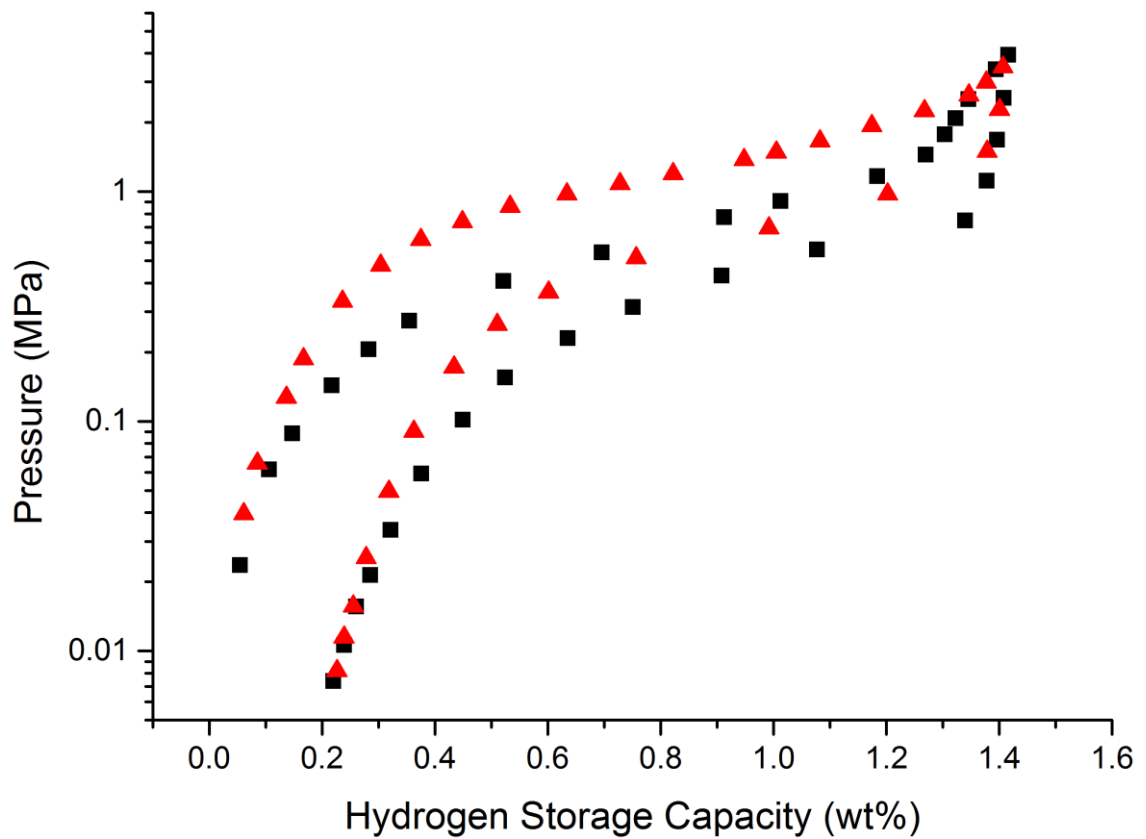


Figure 5.10 Pressure-compositions-isotherm curves of Sample OP1 (Ce=0.35, Al=0.10, ■) and Sample OP2 (Ce=0.50, Al=0.10, ▲), measured at room temperature.

The kinetics measurement of the optimum samples are presented in Figure 5.11, which confirmed that the samples took less than 50 s to achieve 80% of the maximum absorption capacity. Sample OP1 achieved saturation slightly sooner than Sample OP2, nevertheless both samples had a promising kinetic property. The effect of substitutions and hydrogen absorption kinetics will be discussed in Chapter 6. In an actual canister, the hydrogen absorption kinetics will be slower than the measured absorption time because the absorption kinetics of an actual system will be affected by other extrinsic factors. These factors, include but are not limited to the operating conditions, packing density and size of the canister, shape and arrangement of fins that act as a heat dispenser or collector, distribution of gas channels and purity of hydrogen gas. Nevertheless, all these extrinsic factors could not further improve the absorption kinetics of the overall system if the intrinsic absorption kinetic of the material is inheritably slow.

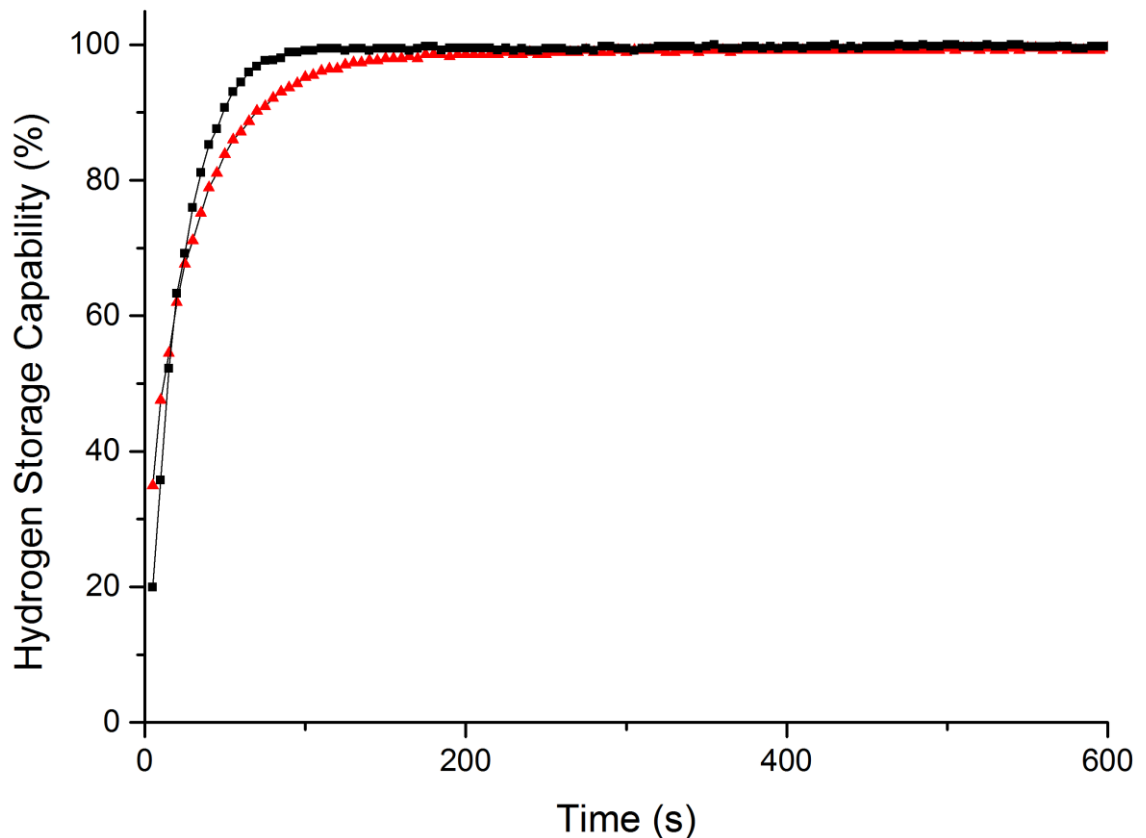


Figure 5.11 Hydrogen absorption kinetic of Sample OP1 (Ce=0.35, Al=0.10, ■) and Sample OP2 (Ce=0.50, Al=0.10, ▲), measured at room temperature with an approximate initial charging pressure of 4.00 MPa.

Pan et al. [173] has mentioned that the hydrogen storage capacity was influenced by the unit cell volume. They have demonstrated that the unit cell volumes of AB₃ and AB₅ phases decreased with the increased addition of Ce content, but did not correlate the relationship between the hydrogen storage capacities with cell volumes. It is possible that the changes in the mass of the unit cell due to the different atomic masses of the elements substituted will affect the resulting hydrogen storage capacity (in wt%). However, the influence by the mass changes is unable to confirm nor predict because of the uncertainty in the distribution of substituted elements in the respective phases in the alloys. Nevertheless, in general we can still assume that the substitution of Ce (heavier than La) increases the mass of the unit cell while the substitution of Al (lighter than Ni) decreases the mass of unit cell. Yet, the influence of mass of unit cell on the hydrogen storage capacity (in wt%) is insignificant compare to the abundance of hydrogen absorbing phase. For instance, the substitution of Al reduces the mass of unit cell, which should theoretically result in the increased of hydrogen storage capacity (in wt%), does not absorb higher amount of hydrogen. The reason is because of the excessive formation of non-hydrogen absorbing phases. The series of hydrogen storage alloys that were investigated in this work consisted of multiple phases, which were a challenge to relate them with the hydrogen storage capacity. Hence to address this challenge, the effective cell volumes were used instead. The effective cell volume is defined as the weight percent of hydrogen absorbing phase (w_i) multiplied by its corresponding unit cell volume (v_i), as shown with the following equation:

$$\text{Effective Cell Volume} = \sum_{i=1}^n w_i v_i \quad (5.7)$$

It can be seen from Figure 5.12, the hydrogen storage capacities responded linearly to the effective cell volumes, with a strong regression value of 0.90. The discrepancy of the data was due to the fact that the effective cell volume did not consider the hydrogen that was trapped in the grain boundaries and lattice defects. It was also found that the optimized samples (red dots) were located approximate to the predicted trend line, proving that the cell volume was one of the factors that contributed to the changes of hydrogen storage capacity.

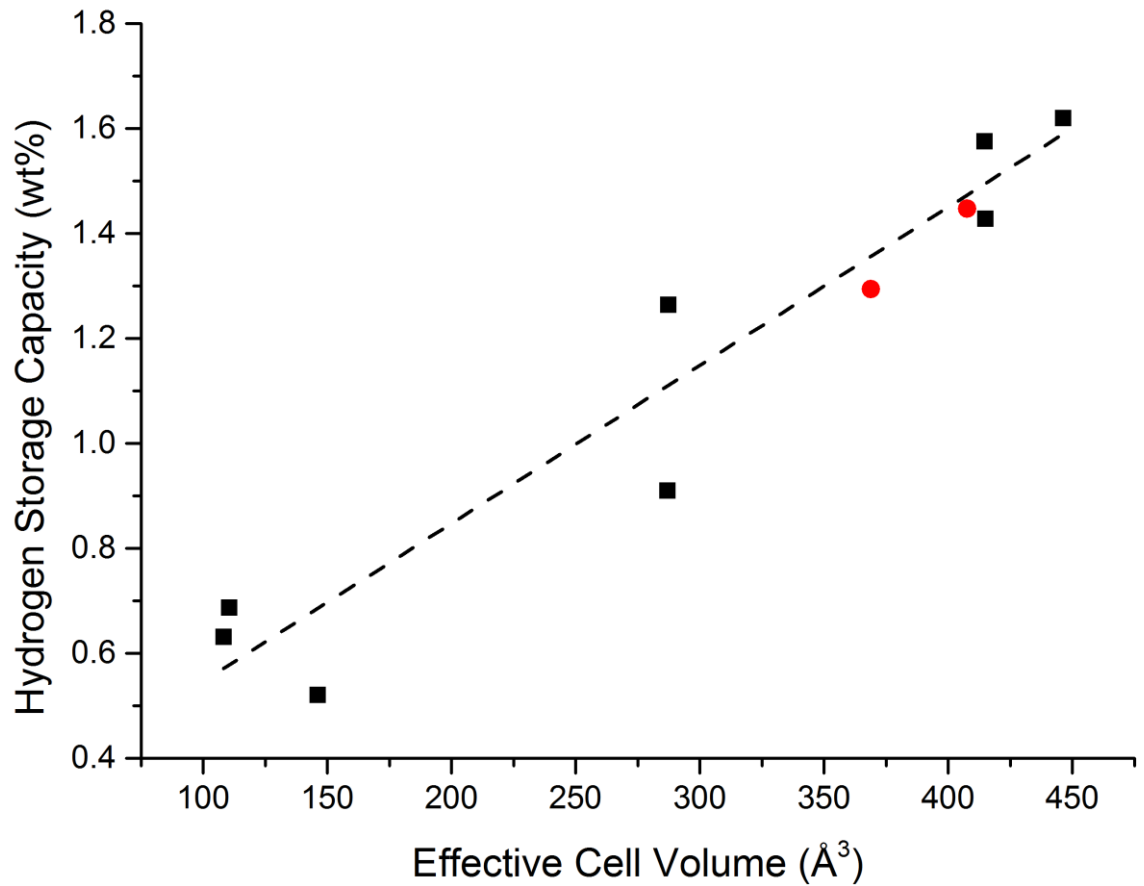


Figure 5.12 A linear relationship between hydrogen storage capacities and effective cell volumes, with both optimized samples (in red dots) located closely on the predicted trend line.

5.5 Conclusion

This work has adopted RSM as a tool to predict and optimize the compositions of alloys towards the enhancement of their hydrogen storage properties. With the empirical models proposed from the RSM analysis, four optimized compositions were suggested. Among them, two samples that had a higher hydrogen storage capacity were selected and were used to verify the properties. The samples with the compositions of $\text{La}_{0.30}\text{Ce}_{0.35}\text{Ca}_{1.03}\text{Mg}_{1.32}\text{Ni}_{8.90}\text{Al}_{0.10}$ (Sample OP1) and $\text{La}_{0.15}\text{Ce}_{0.50}\text{Ca}_{1.03}\text{Mg}_{1.32}\text{Ni}_{8.90}\text{Al}_{0.10}$ (Sample OP2) confirmed that they had the properties approximate to the predicted properties. It also revealed that there was a strong linear relationship between the effective cell volume and hydrogen storage capacity. All these conclude that the statistical method could offer a robust, feasible and efficient solution to optimize the

performance of hydrogen storage alloys. It should be emphasized that the design of experiment is not a replacement to the process and fundamental knowledge of the alloys system, instead this tool itself required the understanding of the alloys system to design a feasible experiment that could answer the research questions. It is proven in this chapter, that the empirical models developed using this statistical tool provides a fast solution and offers a possible solution to tailor design the properties of hydrogen storage alloys.

Chapter 6 Absorption Mechanism of La-Mg-Ni based Hydrogen Storage Alloys

6.1 Introduction

Partial elemental substitutions are one of the many techniques used in tuning the hydrogen storage alloys properties in terms of hydrogen storage capacity, absorption and desorption plateaus, hysteresis and kinetics. Although some elements may improve a few properties in general, they may also worsen the performance of other properties. In this study, we are particularly interested in understanding the effects of Ce and Al partial substitutions that could change the hydrogen absorption mechanism that eventually influenced the absorption kinetics of La-Mg-Ni based alloys.

In a gas-solid absorption reaction, Johnson-Mehl-Avrami-Kolmogorov (JMAK) nucleation and growth model can be used to describe the absorption mechanism. This semi-empirical JMAK model is defined by the following equation:

$$\ln(1 - f) = \ln k + n \ln t \quad (6.1)$$

where f is the fraction of hydrides formation, k is the reaction rate constant, n is the Avrami exponent and t is the absorption time. The k constant determines both the nucleation and growth rate of hydrides phase; the n constant reflects the nuclei growth dimension, nucleation mechanism and absorption rate controlling mechanism (interface or diffusion). Hence, the Avrami exponent can be interpreted by the following equation:

$$n = a + bc \quad (6.2)$$

where, a controls the nucleation mechanism ($a = 0$ for instant nucleation, $0 < a < 1$ for depleting nucleation rate, $a = 1$ for constant nucleation rate and $a > 1$ for increasing nucleation rate), b determines the growth dimensionality ($b = 1, 2, 3$) and c indicates the

rate controlling growth ($c = 0.5$ diffusion-controlled and $c = 1$ interface-controlled) [185, 186].

The JMAK equation assumes that the nuclei are homogeneously and randomly distributed, the nucleation and growth rate of hydride phase is constant and the growth dimension can be either one-, two- or three-dimensional as illustrated in Figure 6.1. With these assumptions, the constant parameters from the Equation 6.2 are able to provide information on the nucleation and growth rate, rate-limiting step and growth dimension [187-189]. Matsumoto et al. [190] had summarized the nucleation mechanism corresponding to the values of Avrami exponent, n , in Table 6.1. The derivation of the JMAK model involves a number of ideal assumptions and does not take into consideration many other factors. Therefore, even though JMAK model is a powerful tool to understand the underlying absorption mechanism, the results must be carefully interpreted with the support of SEM and XRD results, especially when different growth mechanisms may have the same n values as shown in Table 6.1.

Table 6.1 Avrami exponents and the corresponding growth dimension and rate-controlled mechanism summarized by Matsumoto et al. [190]

Nucleation rate	Growth dimension		
	3-dimensional	2-dimensional	1-dimensional
<i>Interface-controlled growth</i>			
Constant	4	3	2
Decreasing	3-4	2-3	1-2
Zero*	3	2	1
<i>Diffusion- controlled growth</i>			
Constant	2.5	2	1.5
Decreasing	1.5-2.5	1-2	0.5-1.5
Zero*	1.5	1	0.5

**All potential nucleation sites are saturated at the beginning of the reaction therefore no more nucleation occurs.*

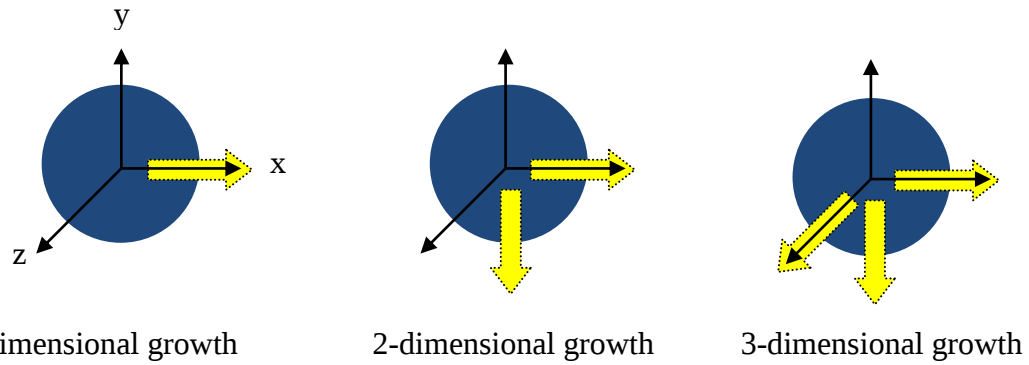


Figure 6.1 Illustration of growth dimension of hydride phase (blue) where the yellow arrows are the indication of the phase growing directions in x-, y-, z-axis.

6.2 Materials and Experimental Procedures

6.2.1 Sample Preparation and Characterizations

The same method as Chapter 4 was used to prepare La-Mg-Ni based alloys. The surface morphology of the alloys was characterized with a Hitachi 3400X scanning electron microscope (SEM) that coupled with an energy dispersive X-ray spectrometer (EDS) and a backscattered electron (BSE) detector. The crystal structure and phase compositions of the alloys were measured with a PANalytical Xpert Pro MPD X-ray diffractometer with Cu K α that operated at 45 kV and 40 mA. Full pattern Reitveld refinement was calculated with X'pert HighScore Plus software.

The kinetics of the La-Mg-Ni samples were measured with the Sieverts instrument at room temperature with 99.999% ultra-high purity hydrogen. The sample chamber was vacuumed firstly at room temperature. Subsequently, the activation process was performed under 0.50 MPa of hydrogen at 300 °C for an hour, degassed at 450 °C for an hour and cooled to the room temperature. The process was repeated for three times to ensure full activation, with the last degassing step was extended to 2 h. The absorption time was recorded immediately after the 9 ml sample chamber was charged with approximately 4.00 MPa of hydrogen from the 45 ml reservoir. A water bath was used to keep the temperature constant approximate to room temperature. The recorded data was fitted and analyzed with the semi-empirical JMAK model.

6.3 Results and Discussion

6.3.1 Phase Structure and Morphology of Alloys

The diffraction patterns of all samples in Figure 5.2 in Chapter 5, show that all samples consisted of at least two phases. Among all the phases, two main phases were responsible for hydrogen absorption. These two main phases were in the form of AB_3 and AB_5 with a $PuNi_3$ -type rhombohedral structure and a $CaCu_5$ -type hexagonal structure respectively. A small amount of A_2B_7 hydrogen absorbing phase appeared as the contaminant in all samples. In addition to these phases, an additional AB_2 in the form of $(La,Ce,Ca,Mg)Ni_2$ hydrogen absorbing phase was also observed in all samples except Sample 3 and 4. All hydrogen absorbing phase are presented in Figure 6.26. Non-hydrogen absorbing phases such as $AlNi$ and $CaMg_2$ were observed in samples that were partially substituted with Al. The effect of partial substitution with Ce and Al on the lattice parameters were summarized in

Table 6.2. Partial substitution with Ce, which has a smaller atomic size than La, reduces the cell volume. Therefore, it is expected that the Ce would affect the diffusion kinetics. Meanwhile, partial substitution with Al, which has a larger atomic size than Ni, expands the cell volume. Hence it is expected to ease the hydrogen diffusion and atom hopping between the interstitial sites. However, the observations from the kinetic curves contradicted these expectations, as will be discussed in Section 6.3.3.

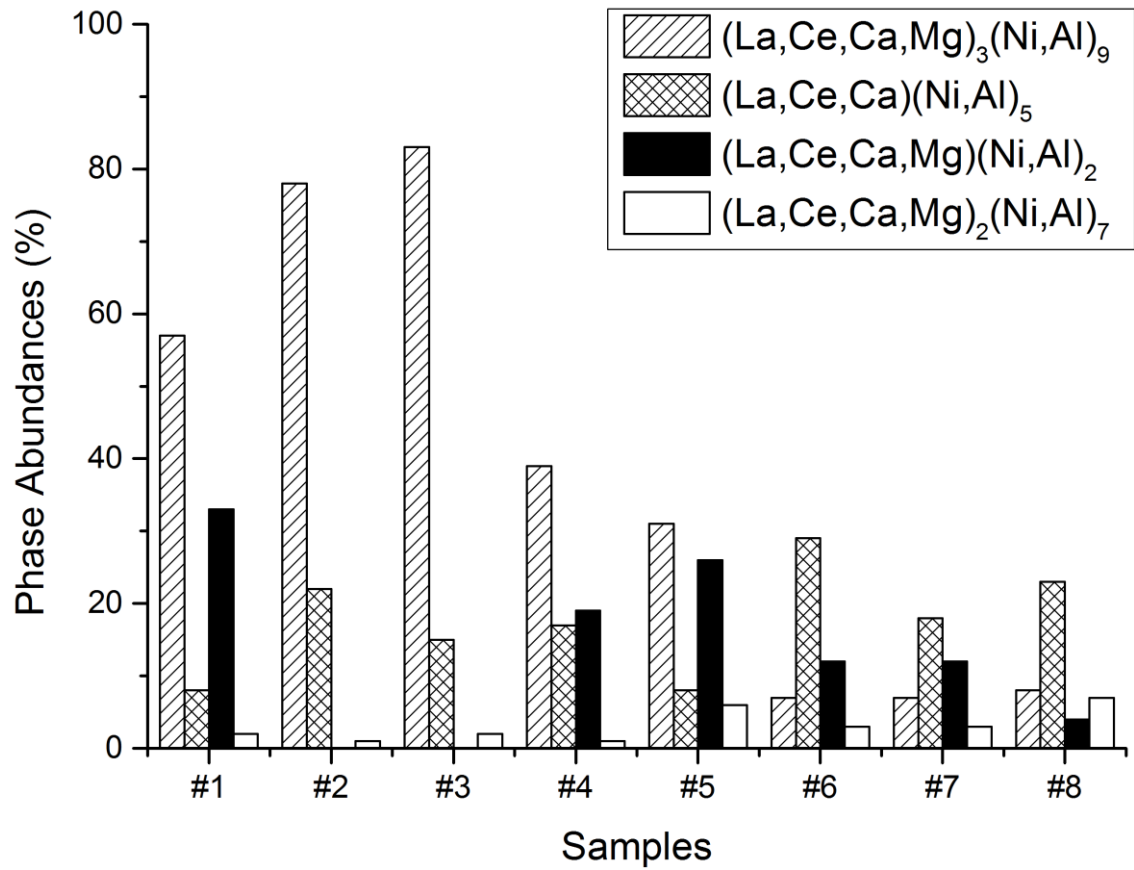


Figure 6.2 Main hydrogen absorption phases of $\text{La}_{(0.65-x)}\text{Ce}_x\text{Ca}_{1.03}\text{Mg}_{1.32}\text{Ni}_{(9-y)}\text{Al}_y$ consists of AB_3 (diagonal), AB_5 (crisscross) and AB_2 (black) phases and A_2B_7 (empty). Non-hydrogen absorbing phases (CaMg_2 and AlNi) are not included here.

Table 6.2 Lattice parameters and cell volumes of hydrogen absorbing phases of $\text{La}_{0.65}\text{Ce}_{(0.65-x)}\text{Mg}_{1.32}\text{Ca}_{1.03}\text{Ni}_9\text{Al}_{(9-y)}$

ID	Compositions	Phases	Lattice Parameters			Cell Volume
			a/Å	c/Å	c/a	V/ Å ³
#1	x=0.50, y=0.00	(La,Ce,Ca,Mg) ₃ (Ni,Al) ₉	4.928(7)	23.966(3)	4.8625	504.1828
		(La,Ca,Ce)(Al,Ni) ₅	4.921(2)	3.996(2)	0.8121	83.7956
		(La,Ce,Ca,Mg)(Ni,Al) ₂	7.021(1)	7.021(1)	1.0000	346.1250
		(La,Ca,Ce) ₂ (Ni,Al) ₇	4.925(5)	23.956(2)	4.8636	503.3287
#2	x=0.25, y=0.00	(La,Ce,Ca,Mg) ₃ (Ni,Al) ₉	4.941(5)	23.948(3)	4.8483	506.4208
		(La,Ca,Ce)(Al,Ni) ₅	4.953(9)	3.989(0)	0.8052	84.7799
		(La,Ca,Ce) ₂ (Ni,Al) ₇	4.835(3)	24.066(4)	4.9770	487.2783
#3	x=0.00, y=0.00	(La,Ce,Ca,Mg) ₃ (Ni,Al) ₉	4.957(7)	23.932(2)	4.8273	509.3615
		(La,Ca,Ce)(Al,Ni) ₅	4.991(7)	3.978(7)	0.7971	85.6466
		(La,Ca,Ce) ₂ (Ni,Al) ₇	4.972(8)	24.768(8)	4.8721	530.4502
#4	x=0.33, y=1.25	(La,Ce,Ca,Mg) ₃ (Ni,Al) ₉	4.954(9)	24.140(9)	4.8721	513.2963
		(La,Ca,Ce)(Al,Ni) ₅	4.966(1)	4.037(6)	0.8130	86.2376
		(La,Ce,Ca,Mg)(Ni,Al) ₂	6.988(1)	6.988(1)	1	341.2396
		(La,Ca,Ce) ₂ (Ni,Al) ₇	4.974(8)	24.361(1)	4.8968	522.1362
#5	x=0.17, y=1.25	(La,Ce,Ca,Mg) ₃ (Ni,Al) ₉	4.950(6)	24.096(1)	4.8678	511.3264
		(La,Ca,Ce)(Al,Ni) ₅	4.956(8)	4.029(7)	0.8130	85.7453
		(La,Ce,Ca,Mg)(Ni,Al) ₂	6.996(5)	6.996(5)	1	342.4917
		(La,Ca,Ce) ₂ (Ni,Al) ₇	4.945(8)	24.128(9)	4.8787	511.1385
#6	x=0.50, y=2.50	(La,Ce,Ca,Mg) ₃ (Ni,Al) ₉	5.006(4)	23.867(3)	4.7677	517.9839
		(La,Ca,Ce)(Al,Ni) ₅	4.952(9)	4.075(0)	0.8227	86.5786
		(La,Ce,Ca,Mg)(Ni,Al) ₂	7.030(1)	7.030(1)	1	347.4568
		(La,Ca,Ce) ₂ (Ni,Al) ₇	4.851(4)	25.798(3)	5.3176	525.8497
#7	x=0.25, y=2.50	(La,Ce,Ca,Mg) ₃ (Ni,Al) ₉	4.965(6)	24.204(5)	4.8771	516.8315
		(La,Ca,Ce)(Al,Ni) ₅	4.993(0)	4.062(9)	0.8137	87.7228
		(La,Ce,Ca,Mg)(Ni,Al) ₂	7.057(6)	7.067(6)	1	351.5483
		(La,Ca,Ce) ₂ (Ni,Al) ₇	4.938(9)	24.291(7)	4.9183	513.1738
#8	x=0.00, y=2.50	(La,Ce,Ca,Mg) ₃ (Ni,Al) ₉	4.985(2)	24.189(4)	4.8521	520.6161
		(La,Ca,Ce)(Al,Ni) ₅	5.047(0)	4.046(5)	0.8018	89.26504
		(La,Ce,Ca,Mg)(Ni,Al) ₂	7.020(3)	7.020(3)	1.0000	345.9846
		(La,Ca,Ce) ₂ (Ni,Al) ₇	4.896(2)	22.86(2)	4.6689	474.6739

Figure 6.36 shows the surface morphology of samples 3 and 6 after hydrogen activation. Backscattered imaging confirmed that both samples as identified from the XRD results consisted of multi phases. Hydrogen absorbing phases in both samples cracked upon activation. The sample with partial substitution of Al (Figure 6.36 (b)) showed that the hydrogen absorbing phases were embedded in the non-hydrogen absorbing phases, which appeared to be darker.

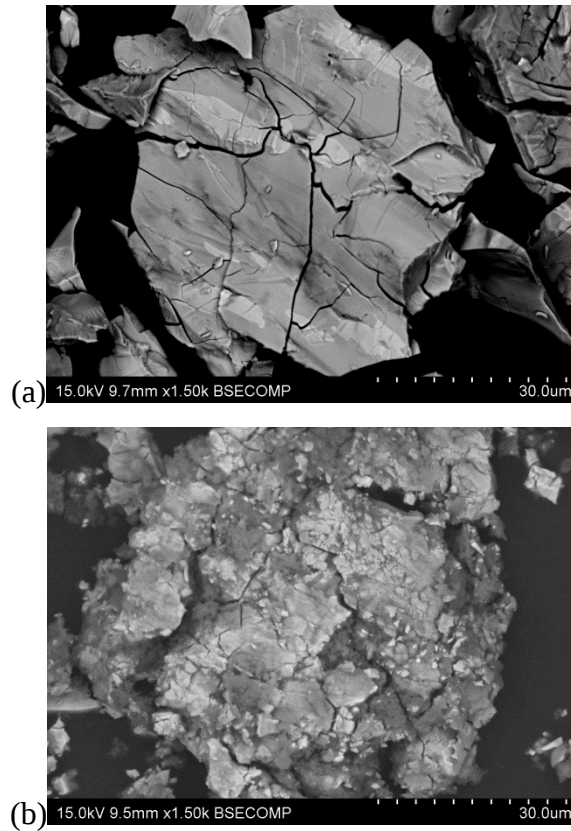


Figure 6.3 Backscattered scanning electron microscopy images of (a) Sample 1 ($\text{La}_{0.65}\text{Mg}_{1.32}\text{Ca}_{1.03}\text{Ni}_9$) and (b) Sample 6 ($\text{La}_{0.15}\text{Ce}_{0.50}\text{Mg}_{1.32}\text{Ca}_{1.03}\text{Ni}_{6.50}\text{Al}_{2.50}$)

6.3.2 Hydrogenation Kinetics

The hydrogen absorption kinetic curves of $\text{La}_{0.65}\text{Ce}_{(0.65-x)}\text{Mg}_{1.32}\text{Ca}_{1.03}\text{Ni}_9\text{Al}_{(9-y)}$ at various amount of Ce and Al partial substitution are presented in Figure 5.4. Generally, the curves could be categorized into three groups according to the amount of Al substituted (i.e. Al=0.00, 1.25 and 2.50). The samples with no Al substitution showed instant hydrides formation, where the absorption curves increased instantly and plateaued out in less than 200 second. Other samples with Al addition showed slower kinetics than those without Al addition, and the kinetics became slower with the increment of Al content. It could be observed that sample 4 and 6 had a sluggish start, which is likely due to the high content of Ce and Al.

6.3.3 Hydrogenation Mechanism

To understand the absorption behavior, the data were fitted on the $\ln(1-f)$ versus $\ln t$ graph, as presented in Figure 6.46. However, in this study, the plot of $\ln(1-f)$ versus $\ln t$ of all samples except sample 6 did not show a straight line with a single slope, i.e. two obvious slopes were observed. The changes of slopes are expected because of the existence of multiple phases and saturation of nucleation site [191-193]. Generally, all plots started with a steeper upward slope (n) and the slope steepness gradually reduced over time. Hence, in this study we fitted the data by segmenting the region according to the slopes. However, the JMAK model assumes that the measured time is when the first nucleus form [194]. Both sample 4 and 6 showed a significant incubation period at the beginning of the reaction, therefore the data in this period were trenched off from the model. Similar method has been used by Mooij and Dam [192] to describe the absorption behaviors of magnesium.

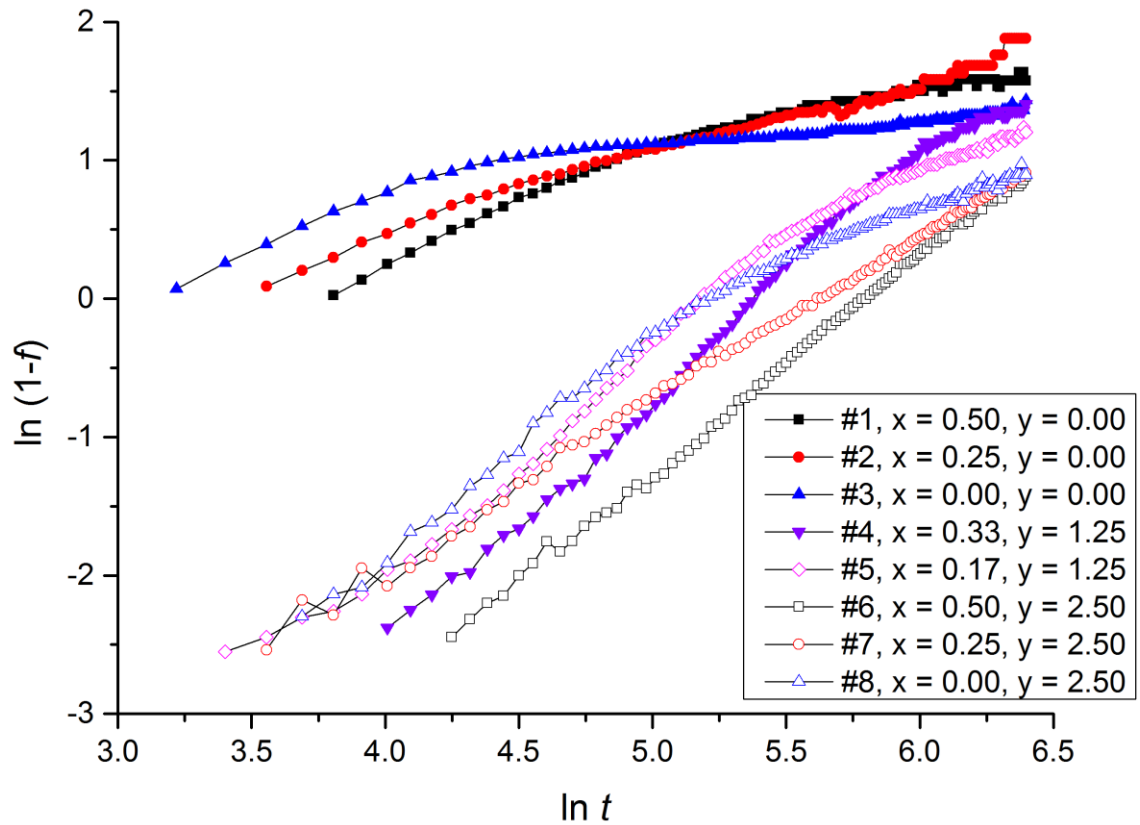


Figure 6.4 Johnson-Mehl-Avrami-Kolmogorov (JMAK) plot of $\text{La}_{0.65}\text{Ce}_{(0.65-x)}\text{Mg}_{1.32}\text{Ca}_{1.03}\text{Ni}_9\text{Al}_{(9-y)}$ (f is the reaction fraction and t is the recorded time in second) to estimate the Avrami exponent, n , from the slope and reaction constant, k , from the intercept.

The Avrami exponents, n , determined from the slope, and, the reaction rates, k , determined from the intercept, were tabulated in Table 6.3. The subscript 1 indicates the first region with a steeper slope; while the subscript 2 indicates the second region with a gradual slope. The n values in the first and second regions could be categorized into two ranges: n less than 1 ($n < 1$), and n in the range of 1 and 2 ($1 < n < 2$), which both corresponding to the different nucleation growth dimensions and mechanisms. The k values for the first and second regions could also be divided into two ranges: k more than 10^{-2} ($k > 10^{-2}$) and k less than 10^{-2} ($k < 10^{-2}$) in the first region, and k more than 10^{-1} and k less than 10^{-1} ($k < 10^{-1}$) in the second region. To ensure the Avrami parameters obtained from JMAK model agreed with the observation, all kinetic curves were reconstructed with the corresponding Avrami parameters and plotted in Figure 6.56. All

models fitted majority parts of the experimental data seamlessly except with some expected deviations at the beginning of a few samples.

Table 6.3 Avrami parameters obtained from the slopes (n) and intercepts ($\ln k$) of JMAK model in Figure 6.46.

ID	Avrami Parameters			
	k_1/s^{-1}	n_1	k_2/s^{-1}	n_2
#1	3.62×10^{-2}	0.89	5.66×10^{-1}	0.34
#2	7.03×10^{-2}	0.78	2.86×10^{-1}	0.46
#3	7.70×10^{-2}	0.83	1.34	0.16
#4	5.16×10^{-5}	1.83	3.08×10^{-2}	0.76
#5	2.44×10^{-4}	1.59	3.01×10^{-2}	0.74
#6	1.16×10^{-4}	1.56		
#7	1.08×10^{-3}	1.21	1.49×10^{-3}	1.16
#8	1.33×10^{-3}	1.27	3.27×10^{-2}	0.68

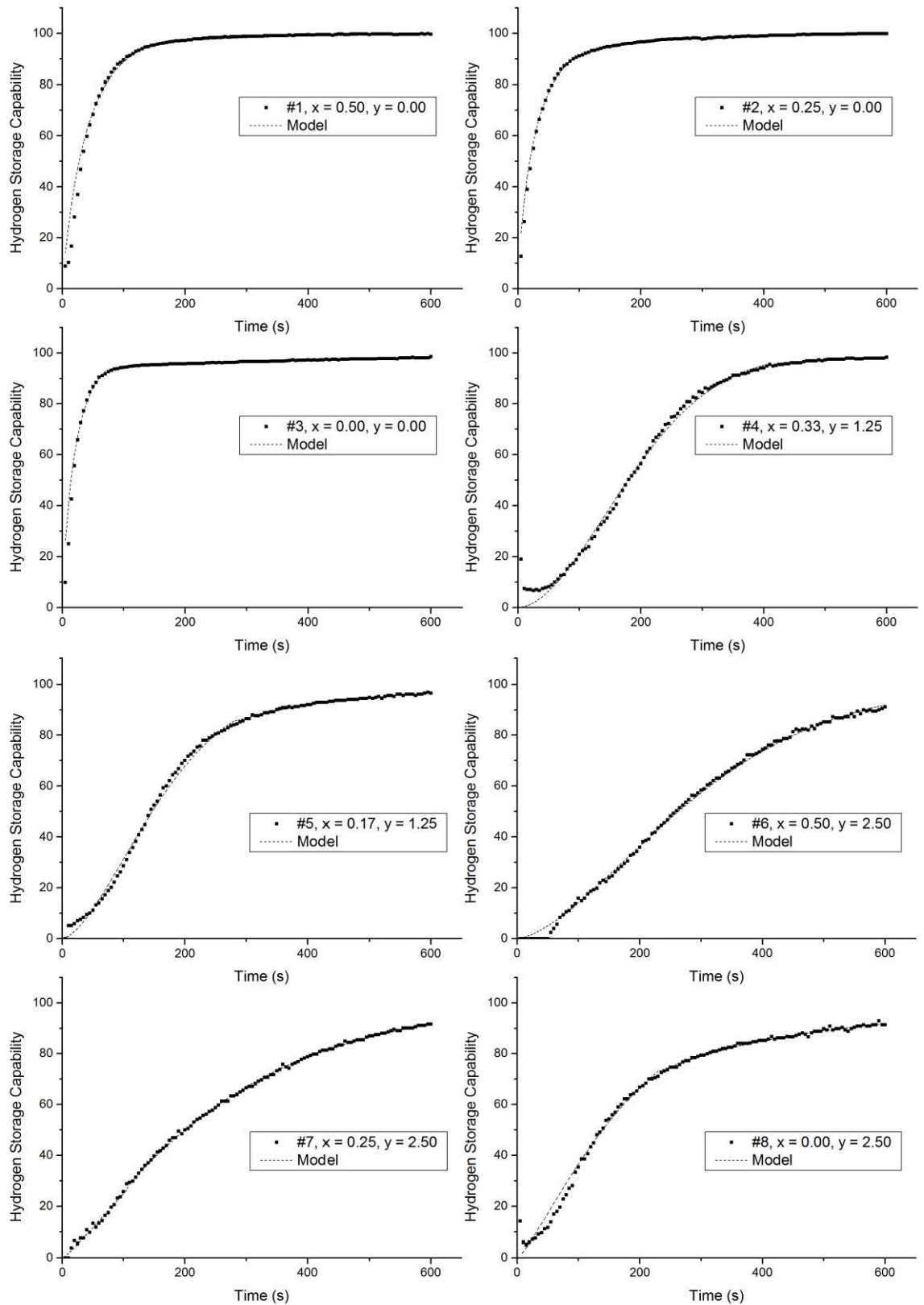


Figure 6.5 Fitting experimental data (■) to JMAK model (dotted line) constructed with the respective Avrami parameters listed in Table 6.3.

The n values of sample 1, 2 and 3 in the first region, which was the initial reaction between the hydrogen and activated metal hydrides sample, were less than 1 suggesting that the nucleation growth was one-dimensional and the rate-limiting step of hydrogen absorption of these samples was likely to be diffusion. Referring to Eq. 2, the non-integer n values also suggested that the nucleation rate was not constant and depleting over time. This mechanism was in agreement with the kinetic graph in Figure 6.56 where instantaneous and fast absorption were observed at the initial stage.

The n values of other samples in the first region were more than 1 indicating that the rate-limiting step of hydrogen absorption could be either interface-controlled or diffusion-controlled growth depending on the nucleation growth dimension. Samples 4, 5 and 6, with n values more than 1.5, fell into one of the following rate-limiting hydrogenation mechanisms: one-dimensional interface-controlled growth, two- or three-dimensional diffusion-controlled growth, with decreasing nucleation rate; while the rate-limiting step of sample 7 and 8, with n values in the range of 1 to 1.5, could be possibly a one-dimensional interface-controlled or a one-dimensional diffusion-controlled growth. It is believed that the rate-limiting hydrogenation mechanism of these samples is a one-dimensional interface-controlled reaction because of the formation of additional non-hydrogen absorbing phases i.e. AlNi and CaMg₂, which are the byproduct of Ni substitution by Al. The SEM micrographs in Figure 6.36 show that a significant portion of the hydrogen absorbing phases were embedded in these non-hydrogen absorbing phases. These non-hydrogen absorbing phases reduced the active surface area of hydrogen absorbing phases which caused the hydrogen nucleation to be highly site preferential. Therefore, high dimensional nucleation growth is unlikely. Among the possibilities listed above, we expected that the one-dimensional interface-controlled is the rate determination step. However, this does not imply that the two- and three- dimensional diffusion growth do not exist in the absorption.

The boundaries of the second region varied with the samples and were determined by the changes of slopes in the $\ln(1-f)$ versus $\ln t$ graph of which the absorption reaction has occurred over a certain period of time. All n values in the second region were smaller than their respective n values in the first region. A smaller n

value at the second region was expected because the continuing formation of hydride phases reduced the available nucleation sites and disrupted the hopping path of hydrogen atoms. The hydride phases possessed a similar obstructive effect of the aforementioned non-hydrogen absorbing phases. Apart from the limitation by nucleation and growth mechanism, the existence of multi hydrogen absorbing phases also contributed to the reduction of n value because of the differences in hydrogenation rate of different phases, which probably initiated a secondary nucleation and growth mechanism.

In the second region, the n values of sample 1, 2 and 3 are contradicting to the JMAK equation of which the n values were less than the theoretical minimum Avrami value of 0.5 that implied no nucleation and one-dimensional diffusion-controlled nucleation growth. Nonetheless, these values were expected because of the simplicity of JMAK equation, which supposed that the nucleation happens randomly and homogeneously with no preferential nucleation sites, the nucleation and growth rate were time independent, and the growth dimension was either one-, two- or three-dimensional [187-189]. In polymer chemistry, n values that are less than 0.5 are commonly observed. The exceptionally low value of Avrami exponent is related to a highly restricted low dimensional growth, which is due to the decreased in nucleation growth rate in addition to the limiting size of nuclei [195-197]. Pradell et al. [198] also observed a similar low n values at the end of the phase transformation in FINEMET alloys. In nucleation and growth mechanism, growth rate is always the dominant factor in determining the behavior of Avrami exponent [198], only when the growth rate is negligible, the nucleation rate becomes dominant. In this case, we could therefore deduce that the hydrogenation kinetics at the second part of the phase transformation is dominated by the reduced nucleation rate. It is also logical to assume that the fast hydrides formation rates of these three samples at the initial stage suppressed the growth of nucleus at the later stage. The n values of other samples in the second region fitted into the one-dimensional diffusion-controlled growth model. This also indicates that the hydrides formation of remaining samples will eventually shift to diffusion-controlled growth regardless of the initial absorption mechanism.

The k values of sample 1, 2 and 3 in the first region were more than 10^{-2} s^{-1} , which were at least one order of magnitude higher than the k values of other samples. This also indicates that the overall reaction rates of sample 1, 2 and 3 were faster than other samples. As the k value was the indication of the overall absorption rate (consisting of nucleation and growth rate) at the beginning, we could suggest that the rate limiting step with a higher k value could be related to diffusion. The activated and faceted surfaces of hydrogen absorbing phases shown in Figure 6.36 allow rapid interface reaction to occur instantly. This argument agrees well with the observation from the corresponding n values. The k values in the second region displayed the similar behavior where the k values of sample 1, 2 and 3 were more than 10^{-1} s^{-1} and at least an order of magnitude higher than the k values of other samples. In addition, all k values in the second region were higher than that of in the first region which corresponded to the abovementioned observation that the absorption eventually dominated by diffusion-controlled growth.

The Avrami parameters (n and k values) are independent from the reaction fraction and reaction time. Given that all measurements were conducted at room temperature, the k values should also remain constant. It is interesting to discover that there is a strong correlation relationship between these two parameters presented in Figure 6.66, where $\ln k$ decreased linearly with n , signifying that the absorption rate depends on the nucleation and growth mechanism.

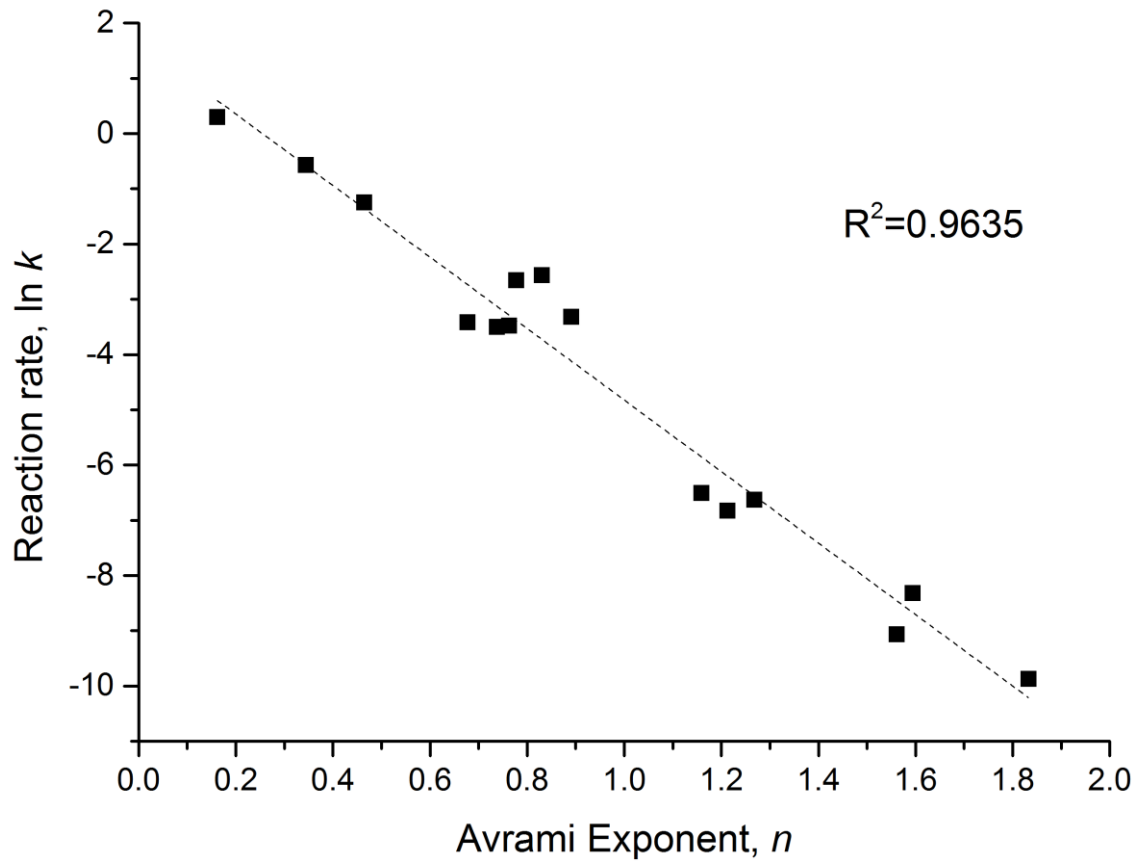


Figure 6.6 A linear relationships between the reaction rate and Avrami exponent.

6.4 Conclusion

Both element substitutions prolong the absorption kinetics. However, Al substitution have a greater effect than Ce substitution. Ce with a smaller atomic radius than La contributes to a smaller crystal volume hence creating a higher resistivity for hydrogen to diffuse into the interstitial site. Even though Al has a larger atomic radius than Ni, the addition of Al forms additional non-hydrogen absorbing phases that inhibit the hydrogen gas from reacting with the alloy surface. The rate limiting step, either dominated by the diffusion or interface reactions, determines the hydrogenation rates. It is also found that the interface-controlled reaction is usually slower than diffusion-controlled reaction.

Chapter 7 Cycle Stability of La-Mg-Ni based Hydrogen Storage Alloys

7.1 Introduction

In recent years, La-Mg-Ni based alloys have received a lot of attention because of their high hydrogen storage capacity. For example, the $\text{La}_{0.7}\text{Mg}_{0.3}\text{Ni}_{2.8}\text{Co}_{0.5}$ alloy made by Kohno et al. [199] achieved a maximum discharge capacity of 410 mAh/g, which was equivalent to approximately 1.54 wt% hydrogen storage capacity. This value was almost 1.2 times higher than the storage capacity of LaNi_5 alloy. Additionally, Kadir et al. [8] have successfully synthesized $\text{La}_{0.65}\text{Ca}_{1.03}\text{Mg}_{1.32}\text{Ni}_9$ that has a capacity of 1.87 wt% with low cost elements (Ca and Mg), but the cycle stability was unclear. Despite their high storage capacity, La-Mg-Ni based alloys are still not ready for commercial production due to their susceptibility to degradation upon cycling [86, 89, 93, 97]. In any case, in most of the literature studies [37, 83-98], the cycle stability tests were conducted in an electrochemical environment.

From the previous chapters, the La-Mg-Ni based alloys that were partially substituted with Ce and Al have shown promising properties to be used as energy storage for a remote area power supply system. In the electrochemical cycle tests, both Ce and Al substitutions [127, 173, 174, 200] have yielded a remarkable improvement in the cycle stability of La-Mg-Ni systems. Although the electrochemical cycle test does not have a direct correlation to a gas-solid reaction, it is believed that these elements may still contribute to a better cycle stability. The previous chapters have shown that Al reduced the hydrogen storage capacity, but it is still important to be included in the system for their superior properties in improving the cycle life. Hence, in Chapter 5, a small amount of Al ($y = 0.10$) was set as part of the desired compositions.

In this chapter, the effects of Ce and Al on the cycle life of La-Mg-Ni based alloys were investigated. The cycle life performances of these alloys were compared with a CaNi_5 system (a more affordable type of AB_5 alloys) [71], which has an approximately 1.20 wt% of hydrogen storage capacity. This work also studied the cycle life of the alloy after it has been regenerated.

7.2 Materials and Experimental Procedures

7.2.1 Sample activation and characterizations

The samples activation was conducted with a Sieverts apparatus under 0.50 MPa of 99.999% ultra-high purity hydrogen at 300 °C for 1 h, degassed at 450 °C for an hour and cooled to the room temperature. The activation process was repeated for three times with the duration of the last degassing step was extended to 2 h. The isothermal hydrogen pressure cycle test began by charging approximately 2.00 MPa of hydrogen into the sample chamber; allowing 10 min of resting time to ensure full absorption; and, desorbing the hydrogen with the assistance of a rotary vacuum pump for 10 min. All reversible hydrogen was assumed to have desorbed at this point, except of those that form very stable hydrides that could not be easily removed without thermally treated. The absorption capacity was calculated at the end of the each 10 min resting time. A complete absorption-desorption process is defined as a cycle, which is illustrated in Figure 7.1. Each sample was run for 500 cycles and a PCI measurement was recorded for comparison.

The surface morphology of the samples was observed using a Hitachi 3400X scanning electron microscope (SEM) coupled with an energy dispersive X-ray spectrometer (EDS). The crystal structure and phase compositions of the alloys were measured with a PANalytical Xpert Pro MPD X-ray diffractometer with Cu K α radiation that operated at 45 kV and 40 mA. The powder diffraction patterns were then analyzed with X'pert HighScore Plus software.

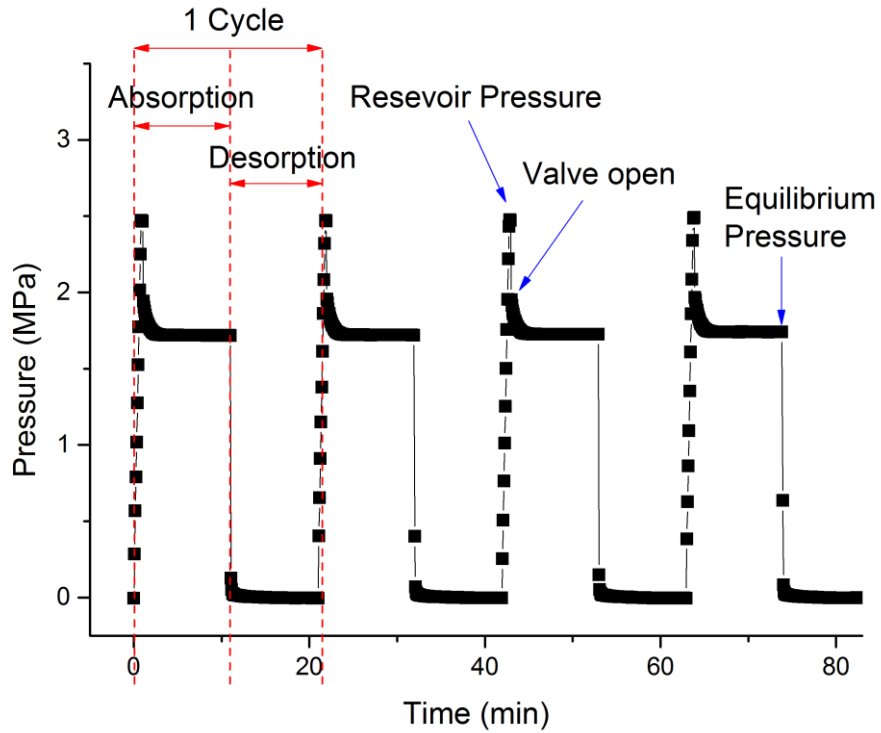


Figure 7.1 An example of the pressure profile over time during hydrogen charge-discharge cycle in a Sieverts instrument, where the absorption and desorption time were set at 10 min.

7.3 Results and Discussion

7.3.1 Phase structure and Morphology of Alloys after Cycle Test

Figure 7.2 compares the normalized X-Ray diffraction patterns of the La-Mg-Ni based alloy before and after 500 cycles of hydrogenation and dehydrogenation. All broadening peak shapes indicates pulverization and the decreased of crystallite size. Sample 3 experienced a significant peak shift to a lower angle, suggesting that the cell volume expanded after the cycle test. The apparent expansion of cell volume signified that the dissolved hydrogen atoms were trapped in the host lattice and were unable to desorb at room temperature. This result is consistent with the PCI curve in Figure 5.3, whereby the hydrogen desorption was incomplete even below 0.01 MPa. The AB_2 phase detected in Sample 3 also confirmed that the possibility of AB_3 phase decomposed into its subunit phases.

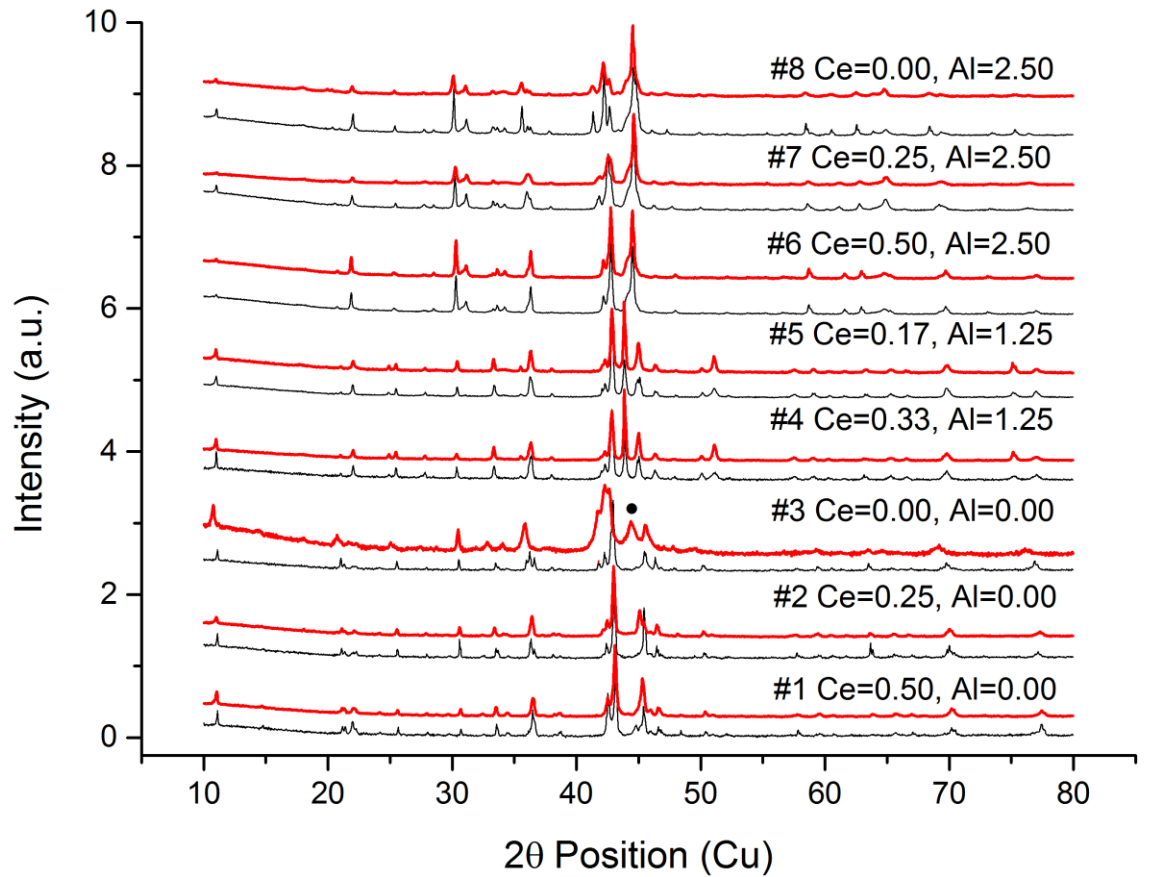


Figure 7.2 Comparison between the normalized XRD patterns of $\text{La}_{(0.65-x)}\text{Ce}_x\text{Ca}_{1.03}\text{Mg}_{1.32}\text{Ni}_{(9-y)}\text{Al}_y$ with x ranging from 0.00 to 0.50 and y ranging from 0.00 to 2.50 before (in black) and after (in red) 500 cycles test, with the formation of AB_2 (●) phase. Refer Figure 5.2 for the labels of original phases.

The particle sizes of Sample 1 and Sample 3 were approximately 70 μm before the cycling test. After 500 cycles, the particle size distributions of Sample 1 and Sample 3 in Figure 7.3 (a) and (b) were reduced to approximately 30 μm . These observations agreed well with the work of Yuan et al. [201]. They claimed that the particles did not further pulverize when the particle size was smaller than 325 mesh (approximately 44 μm). The unchanged particle size was attributed to the micro plasticity behavior in intermetallic alloys [112]. It is implausible that the particle sizes of Sample 6 and Sample 8 will be equal to Sample 1 and Sample 3 because of the excessive formation of non-hydrogen absorbing phases. However, the particle sizes remained almost constant after long number of cycling. This can be seen from Figure 7.3 (c) and (d), where both particle sizes and morphologies of Sample 6 and Sample 8 were reasonably similar. Even though, the severity of pulverization of those samples treated with Al should be

lesser because of a larger cell volume, the excessive formation of non-hydrogen absorbing phases around the hydrogen absorbing phase (as mentioned in Chapter 4) limited the volume expansion during absorption and propagated the micro cracks. Nevertheless, a large majority of the particles was still intact and had a bigger size particle (approximately 80 μm) than those samples with no substitution of Al.

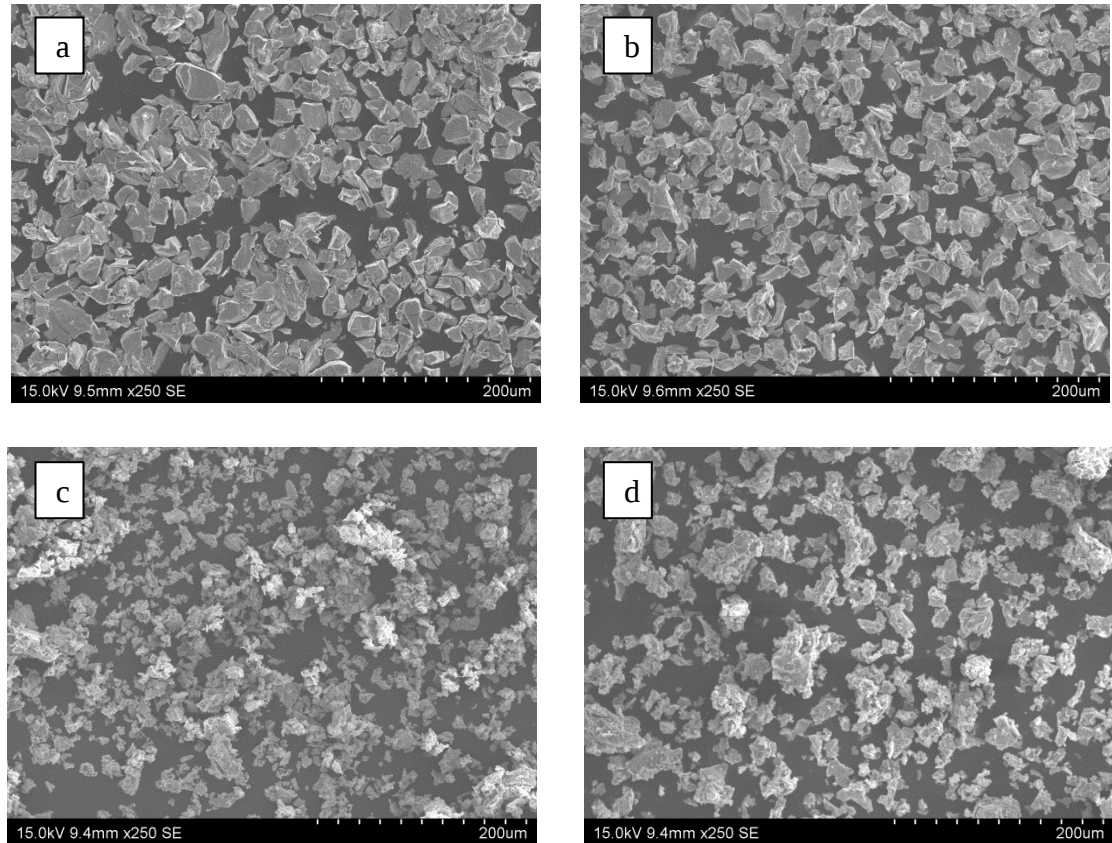


Figure 7.3 Scanning electron microscopy images of (a) Sample 1, (b) Sample 3, (c) Sample 6 and (d) Sample 8 after 500 cycles.

As abovementioned, the pulverization resistivity of the samples is related to the addition of Al. Both Sample 1 and Sample 3, which have no addition of Al, show a very identical morphology after cycle test. Similarly to those Sample 6 and Sample 8 which have the same Al concentration ($\text{Al}=2.50$), the morphologies of both samples are identical. Hence, both Sample 3 and Sample 8 were chosen as the representation of Al and none Al treated groups, respectively. The morphologies of randomly selected particles of Sample 3 and Sample 8 after activation and after cycle test at a higher magnification, are presented in Figure 7.4. It could be seen that Sample 3 decrepitated and cracked upon activation (Figure 7.4 (a)). After 500 cycles, the alloy experienced

severe pulverization where more cracks and fractures were formed on the surface (Figure 7.4 (b)). The faceted surfaces of Sample 8 in Figure 7.4 (c) and (d) were the hydrogen absorption phase. It is noticeably that the morphology variation before and after cycling was not obvious, whereby the cracks on hydrogen absorption phase were identical. The post-cycled Sample 3 also suffered from a serious disproportionation, which can be seen from the EDS mapping in Figure 7.5. The mapping showed that the agglomeration of Ca and Ni precipitates formed on the particle.

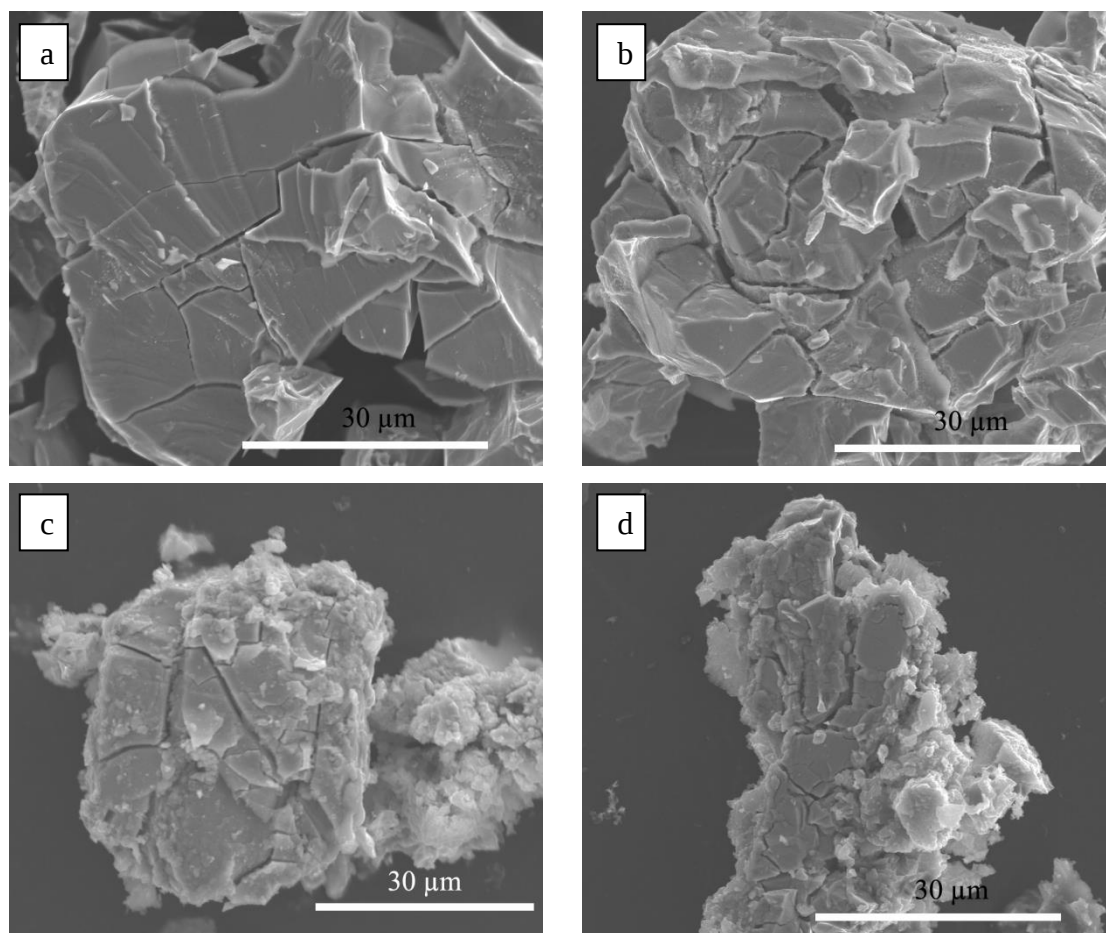


Figure 7.4 Pulverization of Sample 3 after (a) initial activation and (b) 500 cycles; Sample 8 after (c) initial activation and (d) 500 cycles.

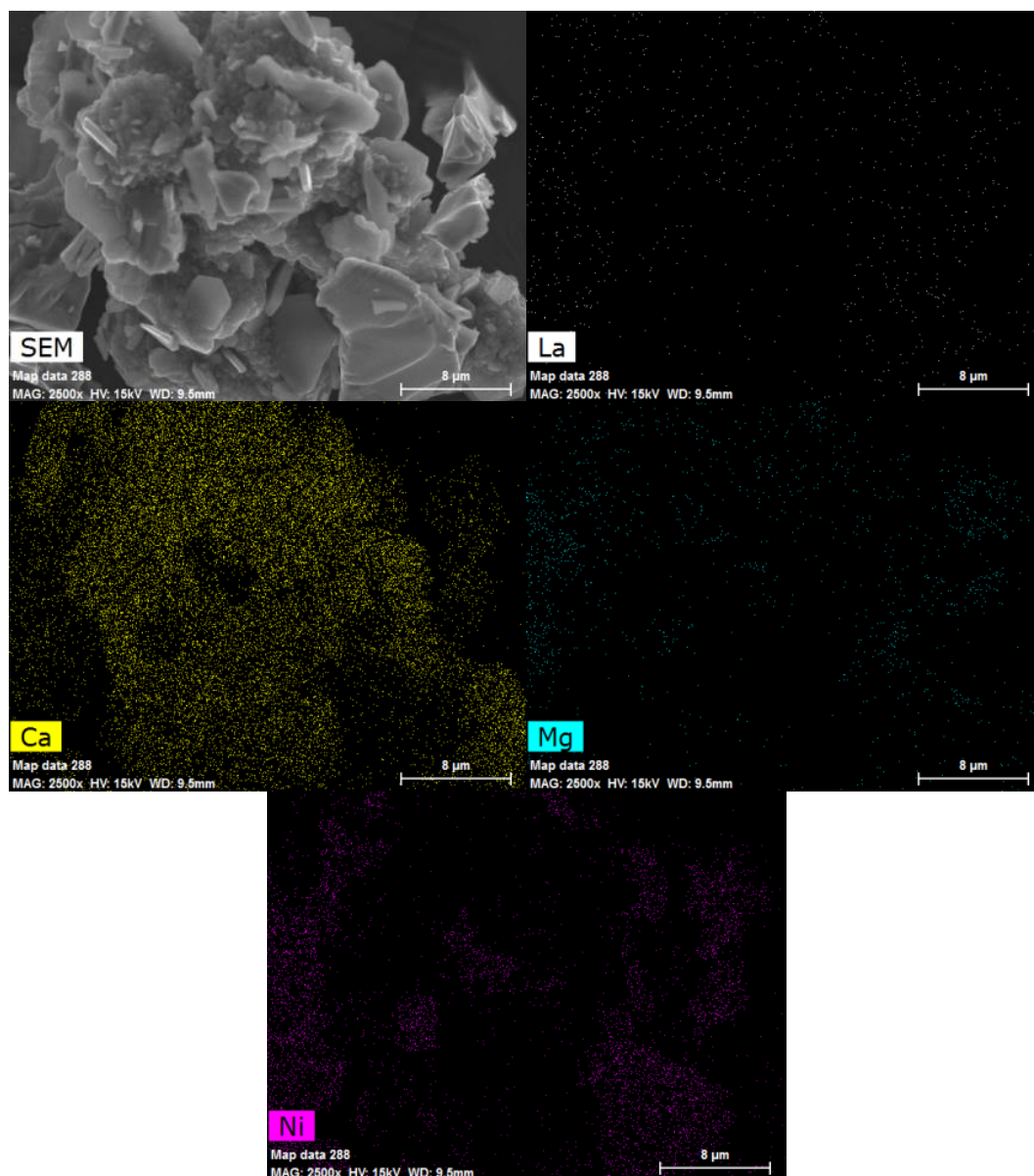


Figure 7.5 Energy dispersion spectrometer (EDS) mapping of Sample 3 after 500 cycles: La (white), Ca (yellow), Mg (aqua) and Ni (pink).

7.3.2 Pressure-Compositions-Isotherm Properties after Cycle Test

The pressure-composition-isotherm (PCI) curves in Figure 7.6 were measured at room temperature after the cycle test without heat treatment at a higher temperature. In other words, the curves presented the reversible hydrogen storage capacity at the end of 500 cycles only, but they could not be used to distinguish the amount of hydrogen entrapped in the alloys or of those that formed stable hydrides during disproportionation. These experimental conditions were slightly different from Tanaka et al. [202], which

desorbed the hydrogen at a higher temperature (353 K). According to their method, more hydrogen could be desorbed from the system. Hence, their PCI curves did not reflect the hydrogen storage capacity that corresponded to the respective cycle profiles. Contrary to their approach, this study omitted the non-reversible hydrogen storage capacity part and compared the PCI curves before (Figure 5.3) and after (Figure 7.6) cycle test. It is obvious that the plateau regions became shorter, the plateau pressure slope became steeper and the hysteresis became smaller. The sloppy plateaus were contributed by the rise of lattice strain contributed by the trapped hydrogen atom and lattice defects [142]. The figure also shows that Samples 1, 2 and 3 suffered from apparent reduction in hydrogen storage capacity because they had the highest phase abundance of AB_3 .

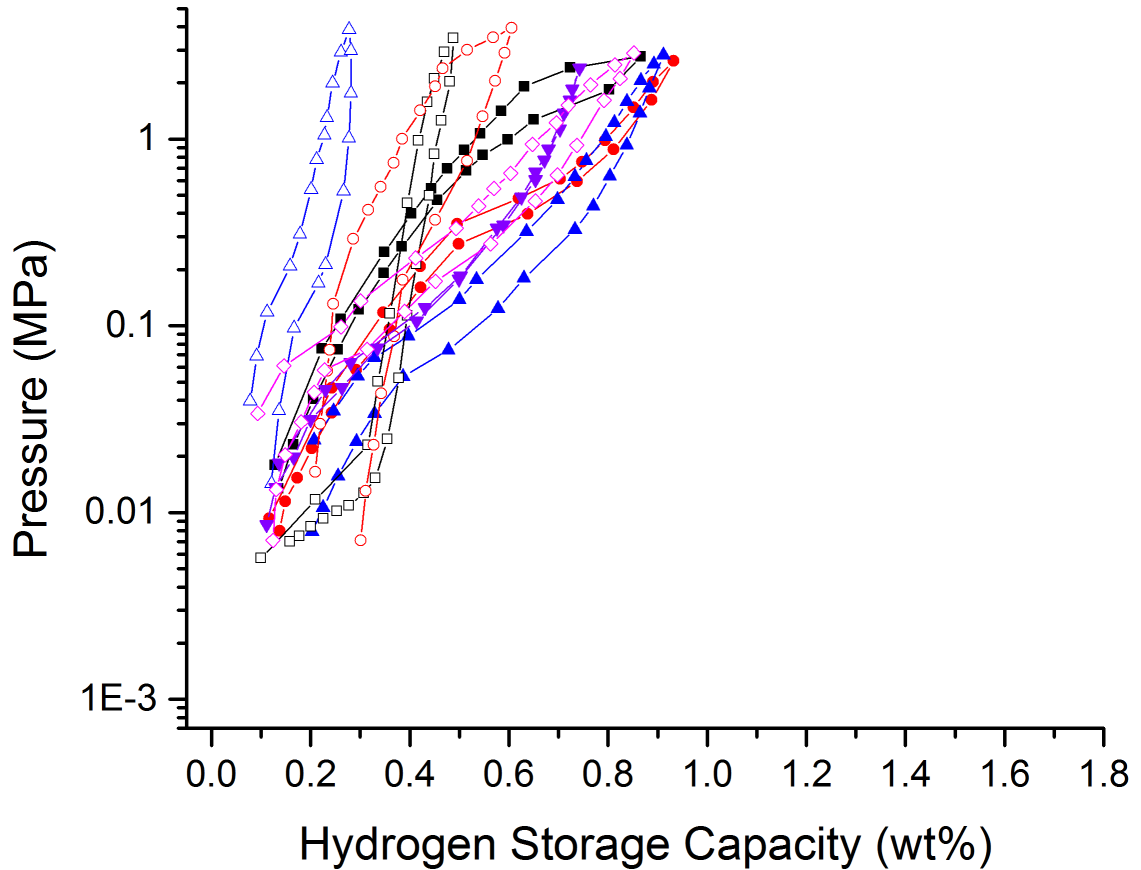


Figure 7.6 Pressure-compositions-isotherm curves of $La_{(0.65-x)}Ce_xCa_{1.03}Mg_{1.32}Ni_{(9-y)}Al_y$ after 500 cycles measured at room temperature: Sample 1 (■), Sample 2 (●), Sample 3 (▲), Sample 4 (▼), Sample 5 (◆), Sample 6 (□), Sample 7 (○), and Sample 8 (△).

7.3.3 Cycle Stability

The reduction of hydrogen storage capacity in a gas-solid system could be attributed to the degradation of the quality of hydrogen storage alloys, which was usually related to decrepitation, disproportionation and retardation. In this study, degradation due to retardation either by poisoning or oxidation was unlikely because ultra-high purity hydrogen was used in the cycle test. Hence, the main contributions to the degradation of hydrogen storage capacity over the course of 500 cycles were decrepitation and disproportionation.

In Figure 7.7, two types of degradation pattern were observed: one with an exponential decay rate and the other with a linear decay rate. The general trend was the decay rate changed from exponential to linear degradation with the increased of Al substitutions. Overall, both elements improved the cycle life of the alloys, but also reduced the reusable hydrogen storage capacity. These observations were similar to those obtained by other researchers [127, 173, 174] who have partially substituted their alloys with either Ce or Al elements. In this study, although those samples with no Al addition managed to retain a higher initial hydrogen storage capacity, the hydrogen storage capacity degraded exceptionally fast for the first 100 cycles as compared to those with Al addition. For instance, the maximum capacity of Sample 3 degraded approximately 50% of its maximum capacity after 500 cycles. Tanaka et al. [202] who had studied the Ca-Mg-Ni systems also concluded that the degradation of this type of alloy was enormous with approximately of 50% capacity loss, same as Sample 3.

Among these three samples that had a higher capacity, only Sample 2 had a slightly higher hydrogen storage capacity than Sample 3 because Sample 2 had a better reversibility, whereby the desorption plateau was raised by the addition of Ce, as shown in Figure 5.3. In general, Ce reduced the unit cell volume and contributed to a lower hydrogen storage capacity. Nonetheless, the reduction of hydrogen storage capacity also lessened the expansion of unit cell during hydrogenation hence resulting in fewer decrepitation and improvement in cycle life [173]. Unfortunately, the sample remained at a similar but slightly higher hydrogen storage capacity than Sample 3 at the end of 500 cycles. Comparable to the work of other researchers [173, 174, 200] that partially substituted La with Ce, further increment of Ce content (Sample 1) reduced the

hydrogen storage capacity in the cycle profile. The long range stacking arrangement of superstructure AB_3 phase was subjected to decompose into AB_5 phase and AB_2 phase [142]. Zhang et al. [203] claimed that the AB_2 Laves phase could be easily disproportionated and transformed into amorphous phase. The claim also agreed with the result of Sample 1 that had a higher content of AB_2 phase, which degraded marginally faster than Sample 3. The degradation to amorphous phase was also confirmed by the observation of Ca precipitations formation in Figure 7.5 which was invisible to XRD characterization.

While partial substitution of Ni with Al was proven to enhance the cycle stability performance, it also significantly reduced the hydrogen storage capacity. As abovementioned, the degradation rate was decelerated with the addition of Al where the degradation trends became linear with cycle numbers. In fact, only Sample 4 showed a slight negative slope, while Sample 5, 6, 7 and 8 virtually showed no sign of degradation after the first cycle. The abrupt drop of capacity after the first cycle was possibly caused by the irreversible solid solution phase at room temperature as shown in the PCI curves (Figure 5.3). We believed that the capability of the alloys to retain the cycle life was due to the improvement of pulverization resistivity. The postulation agreed well with the SEM images in Figure 7.3 and Figure 7.4, where larger particle sizes were detected, as well as, the crack formation after activation was similar to those after cycle test. Therefore, it could be assumed that the minimization of pulverization did not affect the packing density significantly hence the thermal driven disproportionation process was suppressed.

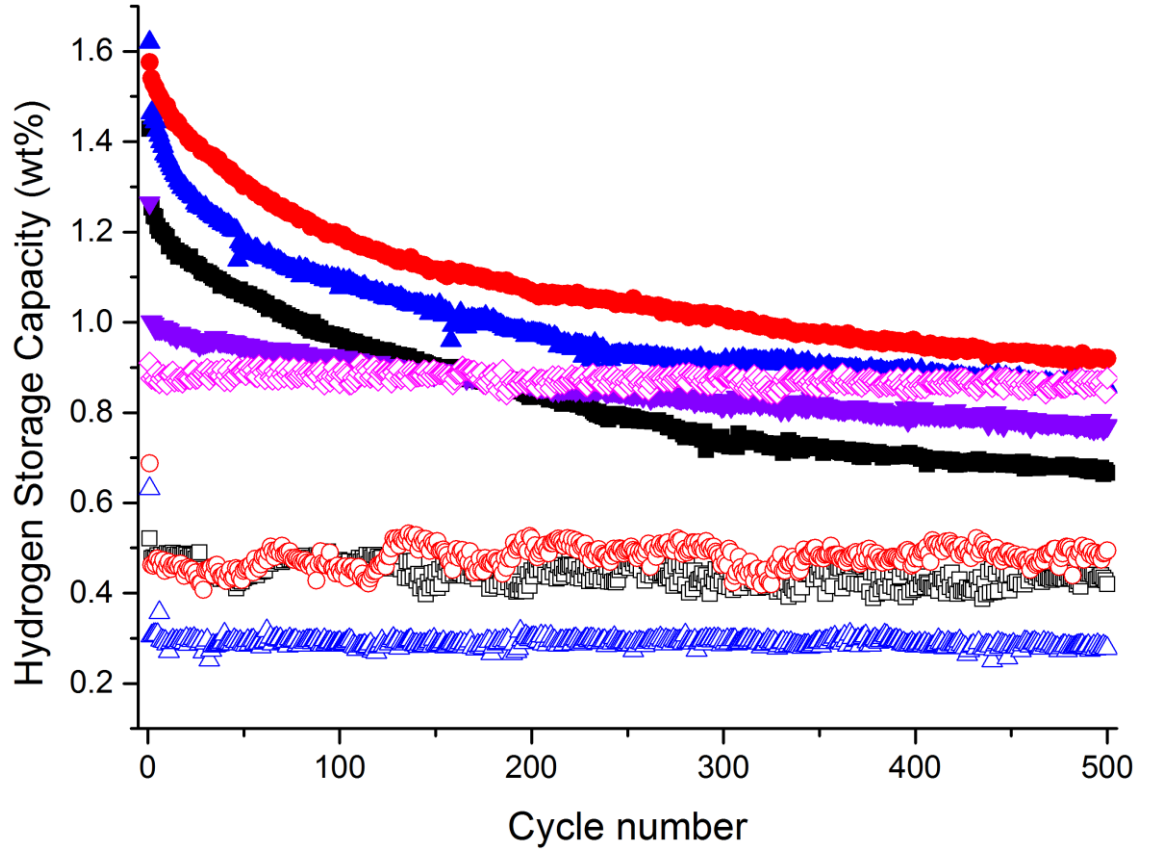


Figure 7.7 Changes of hydrogen storage capacity of $\text{La}_{0.65}\text{Ce}_{(0.65-x)}\text{Mg}_{1.32}\text{Ca}_{1.03}\text{Ni}_9\text{Al}_{(9-y)}$ over 500 hydrogen pressure cycles at room temperature. The samples labeling were: Sample 1 (■), Sample 2 (●), Sample 3 (▲), Sample 4 (▼), Sample 5 (◇), Sample 6 (□), Sample 7 (○), and Sample 8 (△).

The other indication of good pulverization resistivity is to compare the lattice parameters c/a ratios, which are illustrated in Figure 7.8. Both AB_3 and AB_5 phase of all samples, except those in Sample 6 had a higher c/a ratio than Sample 3. A higher c/a ratio of main hydrogen absorbing phases improved the movement of hydrogen atoms into the crystal lattice, therefore reduced the lattice stress during the hydrogen and dehydrogenation process [204]. Hence, samples that had a higher c/a ratio than Sample 3 should have a longer cycle life. This agrees well with the cycle profiles in Figure 7.7. Although the AB_3 phase in Sample 6 had a lower c/a ratio, it did not affect the overall cycle performance because the AB_3 phase was not the main hydrogen absorbing phase. In fact, the difference between c/a ratio of AB_5 phases of Sample 3 and Sample 6 was the largest.

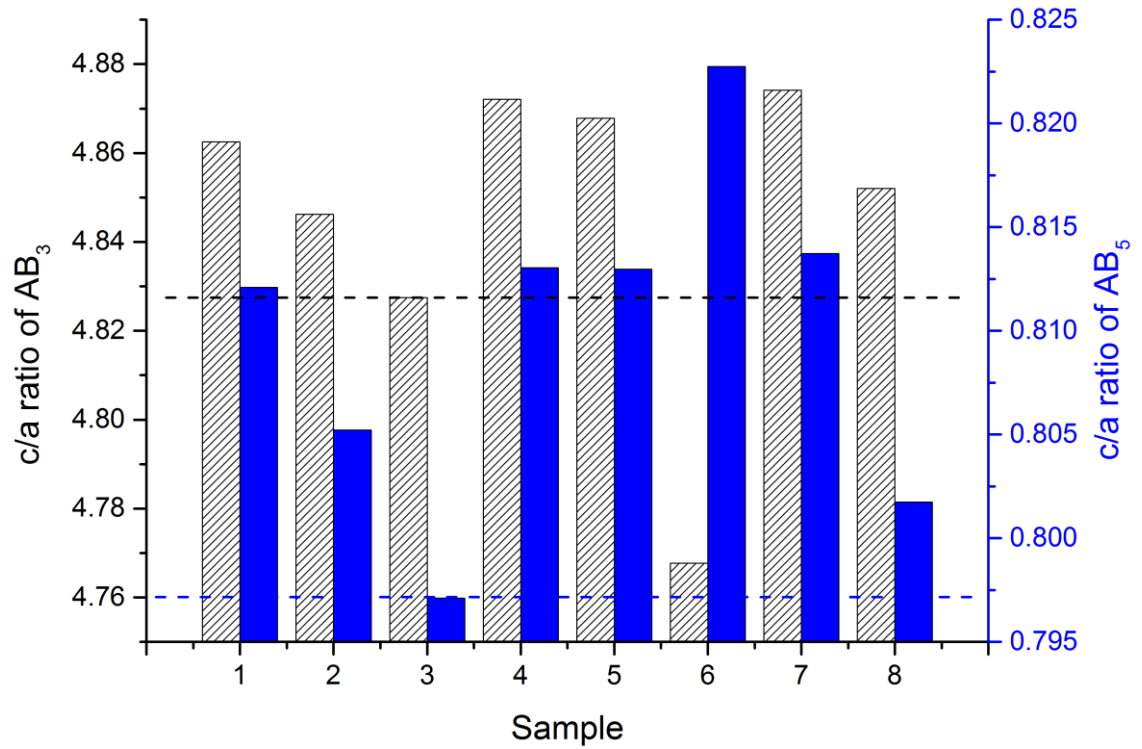


Figure 7.8 The c/a lattice parameters ratios of the main hydrogen absorbing phases of $\text{La}_{(0.65-x)}\text{Ce}_x\text{Ca}_{1.03}\text{Mg}_{1.32}\text{Ni}_{(9-y)}\text{Al}_y$: AB₃ phase (diagonal) and AB₅ phase (blue).

The cycle stability of the sample with no element substitution (Sample3) was compared with the optimized samples (Sample OP1 and Sample OP2) from Chapter 5 and CaNi_5 from Chumphongphan et al. [71], where the results are presented in Figure 7.9. Although both Sample OP1 and Sample OP2 started with a lower hydrogen storage capacity, the degradation trends were slightly improved. The cycle stability improvements of both samples could be observed from the inset graph of Figure 7.9, where the hydrogen storage capacity retentions of all samples were compared with their respective initial maximum hydrogen storage capacity. Both samples possessed similar degradation curves and had higher capacity retentions than the untreated sample (above 60%). This confirmed that the optimized designed samples from Chapter 5 were able to perform better than the untreated sample. The hydrogen storage capacity of CaNi_5 sample started from a much lower point than those La-Mg-Ni based alloys. Its hydrogen storage capacity reached the same capacity Sample OP2 in approximately 100 cycles. The trend predicted that its hydrogen storage capacity will continue to degrade even after 350 cycles; hence it is expected that its capacity retention would be surpassed by La-Mg-Ni based alloys after 500 cycles. For that reason, the optimized samples were

still a better candidates after taking into considerations on the hydrogen storage capacity and cycle performance.

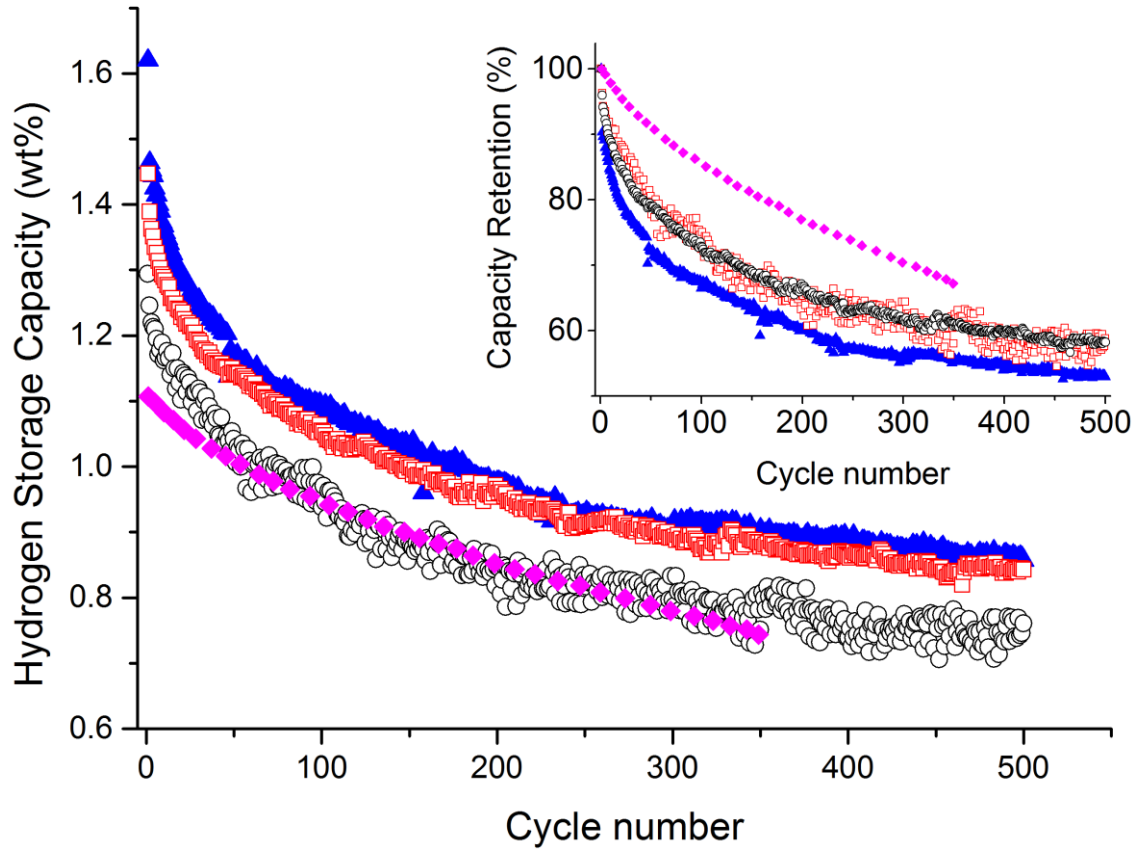


Figure 7.9 Cycle profile of Sample La_{0.65}Mg_{1.32}Ca_{1.03}Ni₉ (▲) compared with Sample OP1 (Ce = 0.35, Al=0.10, □), Sample OP2 (Ce = 0.50, Al = 0.10, ○) and CaNi₅ (◆) [71]. The inset graph was the changes of capacity retention with cycle number.

7.3.4 Regeneration by heat treatment

Sample OP1 had the closest cycle performance as the untreated sample but with a slight improved in cycle stability. Sample OP2 had a similar degradation profile as Sample OP1, hence it is expected that its regeneration profile will be similar to Sample OP1. However, the absolute hydrogen storage capacity of Sample OP2 was lower than that of Sample OP1; hence, Sample OP1 was chosen for regeneration study. After 500 pressure cycles, the sample was heated to 450 °C under continuous vacuum by a rotary pump for 2 h. In Figure 7.10, the regenerated sample showed markedly, though not fully,

recovered the hydrogen storage capacity. In this case, approximately 85% of hydrogen storage capacity was restored. Nonetheless, the degradation slope was steeper than the as-cast sample, indicating the degradation rate was higher after regeneration. After 200 cycles, the hydrogen storage capacity has achieved almost similar performance as the as-cast sample. At this point, the same method was used to regenerate the sample again, the hydrogen capacity restoration was lesser and the degradation rate was even greater than the previous treatment. These results were similar to the observations by Friedlmeier et al. [141] in a $\text{LaNi}_{4.7}\text{Al}_{0.3}$ system, although they did not provide any further explanation. We could relate this high degradation rate to the smaller particle size contributed by the pulverization process from the previous cycle test and was not able to fully recover during the heat treating process. The effect of particle sizes on the cycle stability was studied by Ise et al. [205] and Yuan et al. [201]. In their electrochemical studies, they attributed the degradation were caused by the contact resistance between the particles, hence reduced the conductivity. However in a gas-solid reaction, contact resistance issue was caused by the contact between the gas and solid phases. The smaller particle size increased the packing density leading to the formation of internal gas impedance, hence reducing the absorption capability [57]. In addition, the higher packing density and the poor heat conductivity of metal hydrides characteristic gave rise to the formation of localized hot spots during exothermic absorption. These hot spots generated excessive heat the expedited the disproportionation process, hence leading to a faster degradation.

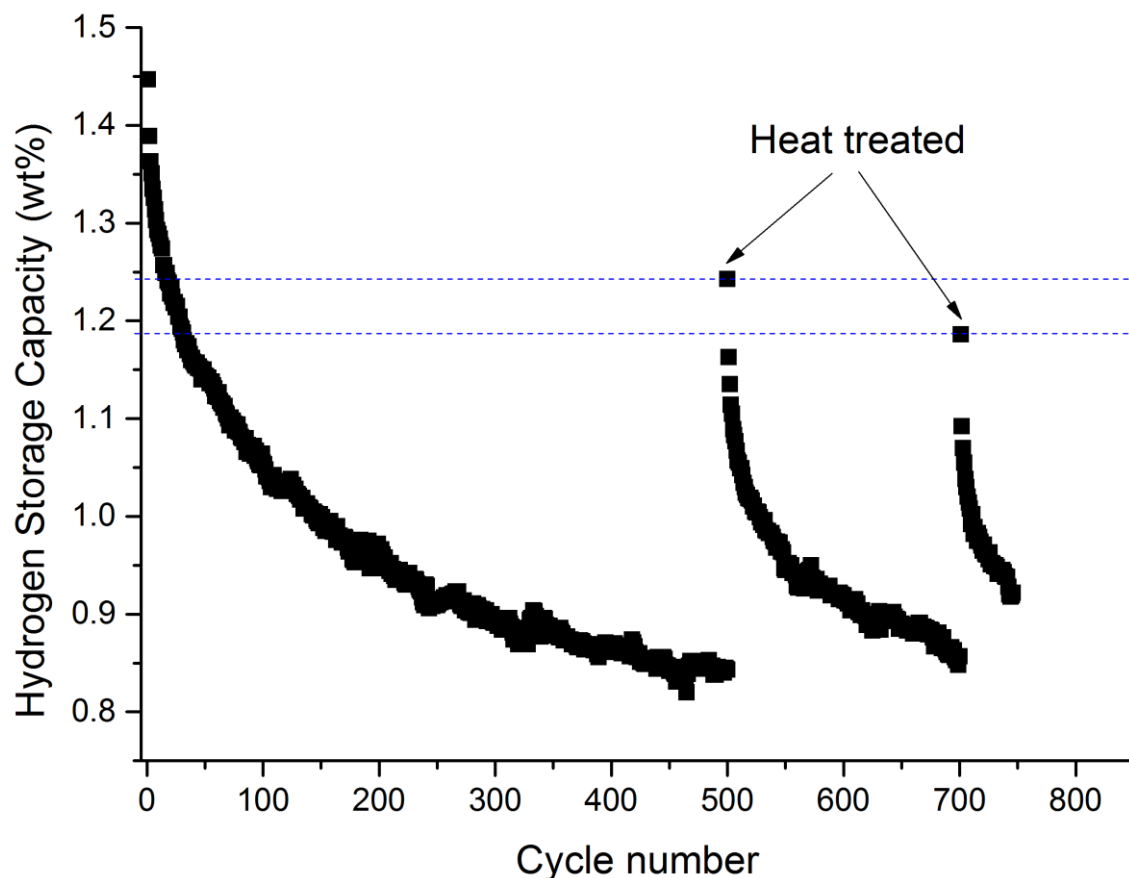


Figure 7.10 Regeneration of Sample OP1 by heat treatment at 450 °C.

7.4 Conclusion

This chapter has successfully improved the cycle stability of La-Mg-Ni based alloys with partial substitution of La and Ni by Ce and Al, respectively. Both Ce and Al were important in improving the cycle life of the La-Mg-Ni based alloys; however the partial substitution of these elements had adverse effects on the usable hydrogen storage capacity where the reduction was especially significant with the addition of Al. Even though optimized samples of Chapter 5 were able to improve the cycle life, the reduction in hydrogen storage capacity was still unavoidable. Nevertheless, considering the trade-off between the capacity and cycle life performance, the optimized samples were still the best candidates as compared to the untreated sample and CaNi_5 sample.

Chapter 8 Cycle life Improvement of La-Mg-Ni based Alloys via Composite Method

8.1 Introduction

Cycle stability is one of the key indications that govern the commercial viability of hydrogen storage alloys regardless of their applications in electrochemical cells, compressor or gas storage. The alloys that have a longer cycle life reduce the price to performance ratio; therefore improve the market competitiveness [206]. Even though La-Mg-Ni based alloys possess remarkable properties that are useful for fuel cell applications, yet practical engineering data of these alloys to use with a fuel cell system is limited. Their cycle stability properties for gas phase applications are especially inaccessible. Most cycle stability tests on La-Mg-Ni based alloys were conducted in a nickel metal hydrides batteries [37, 83-98], where the degradation factors might be different from a gas-solid reaction.

In electrochemical reactions, several groups [86, 88, 91-93, 95-97, 207] have attempted to improve the cycle stability by element substitutions but most of the outcomes were accompanied with a significant reduced hydrogen storage capacity or incremental improvement. For example, Ren et al. [91] partial substituted Ni with Cu; however the degradation rates were very similar to the non-substituted one. Zhang et al. [96] improved the cycle stability by partial substituting Ni with Fe, but the maximum hydrogen storage capacity dropped 40% compared to the non-substituted sample. The gas-solid cycle test in Chapter 7 also showed that the improvement with element substitutions technique had its limitation.

Lately, some researchers [83, 84, 89, 145] have found that the cycle stability properties could possibly be improved by hybridizing two different types of hydrogen storage alloys. Chu et al. [83, 85] have studied the cycle stability of a composite of Ti-V based alloys and La-Mg-Ni based alloys and concluded a 35% improvement of capacity retention with a 40 wt% Ti-V addition. Lu et al. [90] ball milled La-Mg-Ni based alloys with Zr based AB₂ type alloys, where the 5 min ball mill treated sample was found to be the optimum sample with 92% of capacity retained. Ball mill treatment longer than 5

min degraded the hydrogen storage capability. Both Chu et al. [83, 85] and Lu et al. [90] concluded that the improvement of cycle stability of composite was related to the enhancement of corrosion resistivity because of a better surface contact between the additives and matrix.

However, we believe that in a gas-solid reaction, anti-corrosion characteristic might not be a critical factor in prolonging the cycle life; hence it is possible that ball milling treatment is unnecessary. For these reasons, we have attempted to investigate the effects of AB₅ addition at different weight fraction on the microstructure, hydrogen storage and cycle stability properties of La_{0.65}Ca_{1.03}Mg_{1.32}Ni₉ alloys in pressure cycle tests. In addition, we have also compared the ball mill treated sample and untreated sample to confirm our hypothesis. These data were used to optimize the compositions, cost and performance of composites.

8.2 Materials and Experimental Procedures

8.2.1 Sample Preparation

The fabrication of La-Mg-Ni based alloy was similar to Chapter 4. The sample was then mechanically crushed into smaller pieces, ground into finer powder and mixed with different amount of La-rich AB₅ type alloy to form the composite samples. The commercial AB₅ type alloy was supplied by HBank Technologies, Inc., Taiwan. The composites samples were labeled as Sample C1 (no AB₅ addition), Sample C2 (20 wt% of AB₅), Sample C3 (40 wt% of AB₅), Sample C4 (50 wt% of AB₅), Sample C5 (80 wt% of AB₅) and Sample C6 (100 wt% of AB₅). An additional sample was prepared by ball milling Sample C4 (labeled as Sample C4BM) in SPEX 8000, using ball to power weight ratio of 10:1, with a total duration of 5 min. The short milling time was to minimize amorphization [208] but sufficient to form a better surface contact between these two alloys through collision.

8.2.2 Sample Activation and Characterization

The composites were activated in a Sieverts apparatus under 0.50 MPa of 99.999% ultra-high purity hydrogen at 300 °C for 1 h, degassed at 450 °C for an hour and cooled to the room temperature. To ensure full activation, this process was repeated for three

times with the length of the last degassing step was extended to 2 h. A pressure-composition-isotherm (PCI) curve was measured before the cycle test. The pressure cycle test was conducted isothermally at room temperature: charging approximately 2.00 MPa of hydrogen into the sample chamber; allowing 10 min of resting time to ensure full absorption; and desorbing the hydrogen with the assistance of a rotary vacuum pump for 10 min. It was assumed that all reversible hydrogen was desorbed at this point, except of those that form very stable hydrides that could not be easily removed without thermally treated. The absorption capacity was calculated at the end of the each 15 min resting time. A complete absorption-desorption process is defined as a cycle. Each sample was run for 500 cycles and a second PCI measurement was conducted for comparison.

The surface morphology of the composites was observed using a Hitachi 3400X scanning electron microscope (SEM) coupled with an energy dispersive X-ray spectrometer (EDS). The crystal structure and phase compositions of the alloys were measured with a PANalytical Xpert Pro MPD X-ray diffractometer with Cu K α radiation that operated at 45 kV and 40 mA. The powder diffraction patterns were then analyzed with X'pert HighScore Plus software.

8.3 Results and Discussion

8.3.1 Phase Identification and Morphology of Alloys

Figure 8.1 shows the X-Ray diffraction patterns of the La-Mg-Ni based alloy, AB₅ type alloy and composites of these two alloys at different ratios. La-Mg-Ni based alloy consisted of two main phases in the form of AB₃ (PuNi₃-type) and AB₅ (CaCu₅-type), as well as a minor phase of A₂B₇ (Ce₂Ni₇-type). The Reitveld refinement indicated that the phase abundances of AB₃, AB₅ and A₂B₇ were approximately 83 wt%, 15 wt% and 2 wt%, respectively. Meanwhile, the commercial AB₅ type alloy consisted of only a single CaCu₅-type phase with a hexagonal structure. The composite samples were synthesized by mixing the aforementioned alloys at different weight ratios, hence it is expected that no additional new peak would be detected. To confirm this hypothesis, Sample C4 composite was chosen to represent the composites' patterns. The results

agreed with the hypothesis, where all identified peaks matched with the corresponding peaks of both Sample C1 and Sample C6, indicating no additional phase was formed.

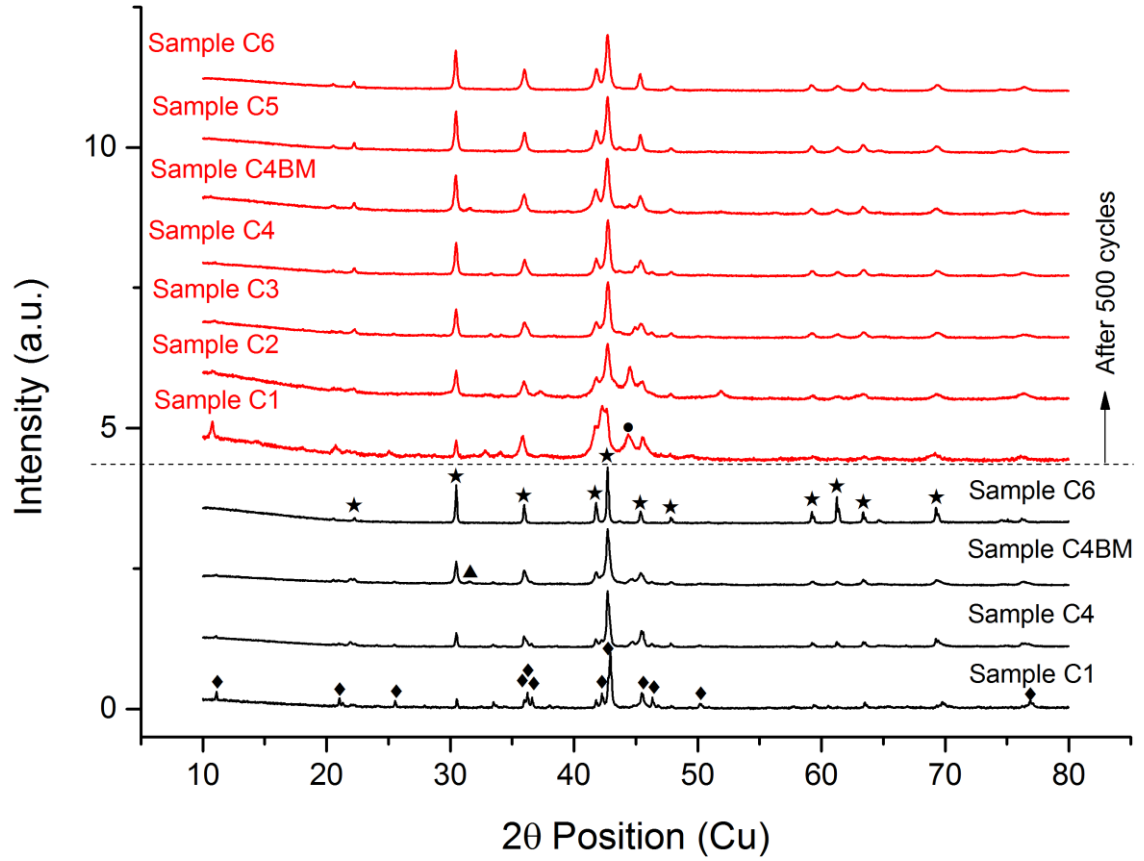


Figure 8.1 XRD patterns before (in black) and after (in red) cycle test: AB₃ phase (◆), AB₅ phase (★), AB₂ phase (●) and La₂NiO₄ (▲).

It was expected that the XRD pattern of ball mill treated composite (Sample C4BM) should have similar peaks as Sample C4 with no additional phase, because 5 min of ball milling duration was too short to achieve any alloy formation. However, it is evident from the peak at 31.4977° that the ball milling process has introduced approximately 2.50 wt% of rare-earth nickel oxide (La₂NiO₄) as a contaminant into the composite [209]. This oxide contaminant did not contribute to hydrogen absorption that led to a lower hydrogen storage capacity, which will be shown in the PCI results. Apart from the formation of oxidation product, the ball milling process also changed the peak shape of Sample C4BM. For comparison, the $\langle 011 \rangle$ peaks of both samples were normalized to the same maximum intensity as shown in Figure 8.2. Interestingly, high

energy ball milling treatment did not shift the peak position but broaden the peak width, where the full width height maximum (FWHM) increased from 0.1824 to 0.2227. This peak broadening was attributed to the reduction of crystallite size and the introduction of lattice defects that contributed to anisotropic micro strain [210].

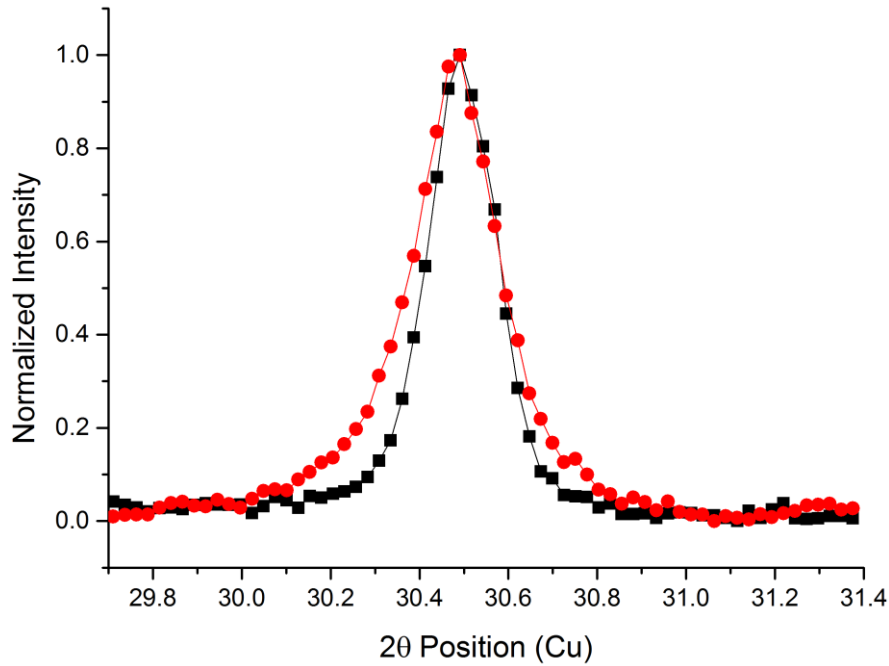


Figure 8.2 Broadening of normalized $\langle 011 \rangle$ peak of ball-milled treated of 50 wt% addition AB_5 composite (Sample C4BM (●)) compare to the untreated sample (Sample C4 (■)).

In general, all post-cycled samples showed partial amorphization and experienced peak broadening. As proposed by Nakamura et al. [211, 212], the peak broadening was contributed by anisotropic and isotropic strains. Anisotropic strain developed rapidly at the beginning of the cycle and saturated with cycling, whereas isotropic strain accumulated steadily with cycling. Sample C1 had a significant peaks shift to lower angles in addition to the peak broadening. Besides, AB_2 phase was also detected which was possibly contributed by the decomposition of AB_3 phase into its subunits (i.e. AB_2 and AB_5 phases) as suggested by Xie et al. [142]. Zhang et al. [166] also proposed that the severe amorphization was caused by the AB_2 subunits, which further disproportionated to into elemental hydrides. The peak shifting was possibly caused by the entrapped hydrogen in solid solution, which resulted in an obvious

expansion of cell volume and both lattice constants as shown in Table 8.1. After 500 cycles of hydrogenation and dehydrogenation, the cell volumes of AB₃ phase increased while that of AB₅ phase reduced. Taking these facts into consideration, it is reasonable to deduce that AB₅ phase improved the reversibility of La-Mg-Ni based hydrides.

Table 8.1 Lattice parameters of La-Mg-Ni and AB₅ composites before and after cycle test

Sample	Phase	a (Å)	c (Å)	V (Å ³)
C1	AB ₃	4.9573	23.9286	509.2518
C6	AB ₅	4.9926	3.9951	86.2419
After 500 Cycles				
C1	AB ₃	5.0054	24.4127	529.6812
C2	AB ₃	4.9005	25.0919	521.8456
	AB ₅	4.9918	3.9896	86.0929
C3	AB ₃	4.9587	24.1945	515.2184
	AB ₅	4.9898	3.9925	86.0885
C4	AB ₃	4.9549	24.1902	514.3900
	AB ₅	4.9887	3.9954	86.1123
C5	AB ₃	4.9658	23.9473	511.3996
	AB ₅	4.9905	3.9981	86.2335
C6	AB ₅	4.9860	3.9978	86.0713

Figure 8.3 presents the SEM morphologies of Sample C1 after 500 cycles test. The particle was severely pulverized and two types of surface morphologies were observed. A further characterization with EDS mapping on these surfaces at higher magnification is presented in Figure 8.4. The faceted surfaces appeared to be the La-Mg-Ni based alloys, whereas the rough surfaces were predominantly Ca. It is impossible to map hydrogen element with EDS, but we believed that the Ca was likely attributed by the amorphous elemental hydride as mentioned in the XRD results.

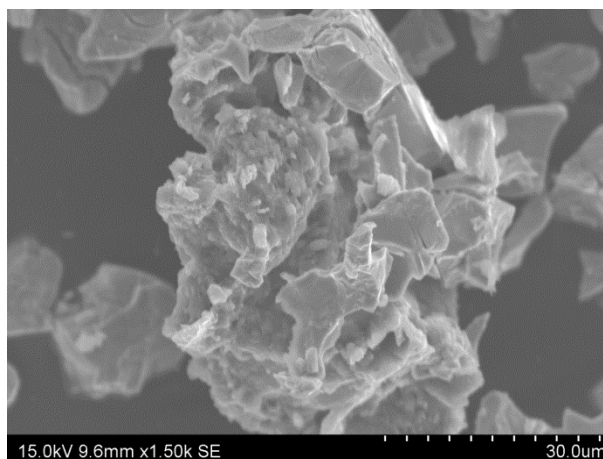


Figure 8.3 SEM image of Sample C1 ($\text{La}_{0.65}\text{Ca}_{1.03}\text{Mg}_{1.32}\text{Ni}_9$)

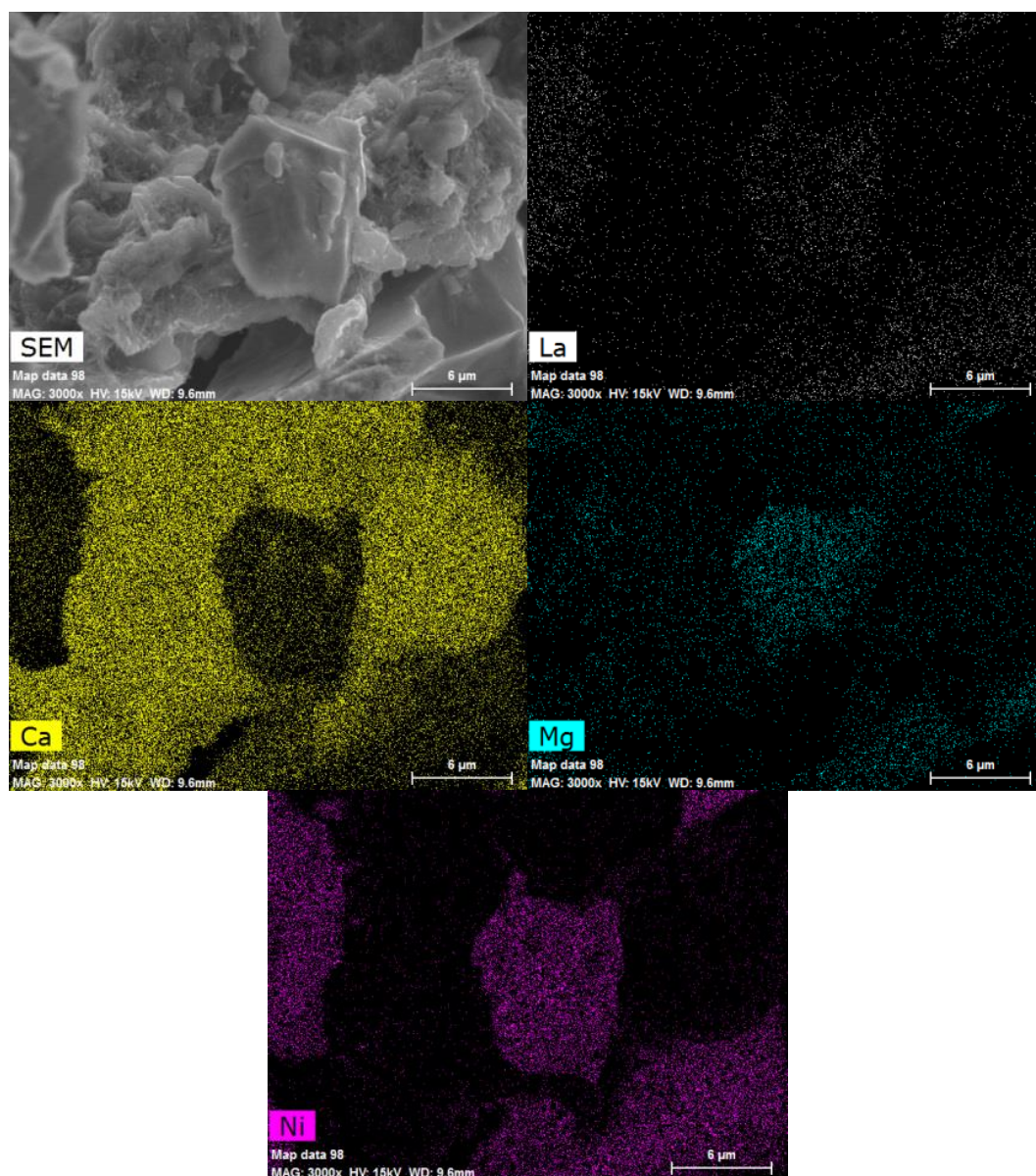


Figure 8.4 EDS mapping of Sample C1 after 500 cycles: La (white), Ca (yellow), Mg (aqua) and Ni (pink).

The SEM of post-cycle Sample C4 composite was compared with that of the ball mill treated Sample C4BM composite, in Figure 8.5. At a lower magnification, it could be seen that the overall particle size of ball mill treated sample was slightly smaller than that of the untreated sample. The particle size of La-Mg-Ni based alloys with a larger diameter was reduced from approximately 70 μm to 50 μm . Moreover, the smaller particles of AB_5 alloys were embedded on the surface of La-Mg-Ni based alloys in the ball mill treated sample, indicating a better surface contact compared to the untreated sample. However, the degree of pulverization of La-Mg-Ni based alloys of these two samples was however less severed compared to Sample C1.

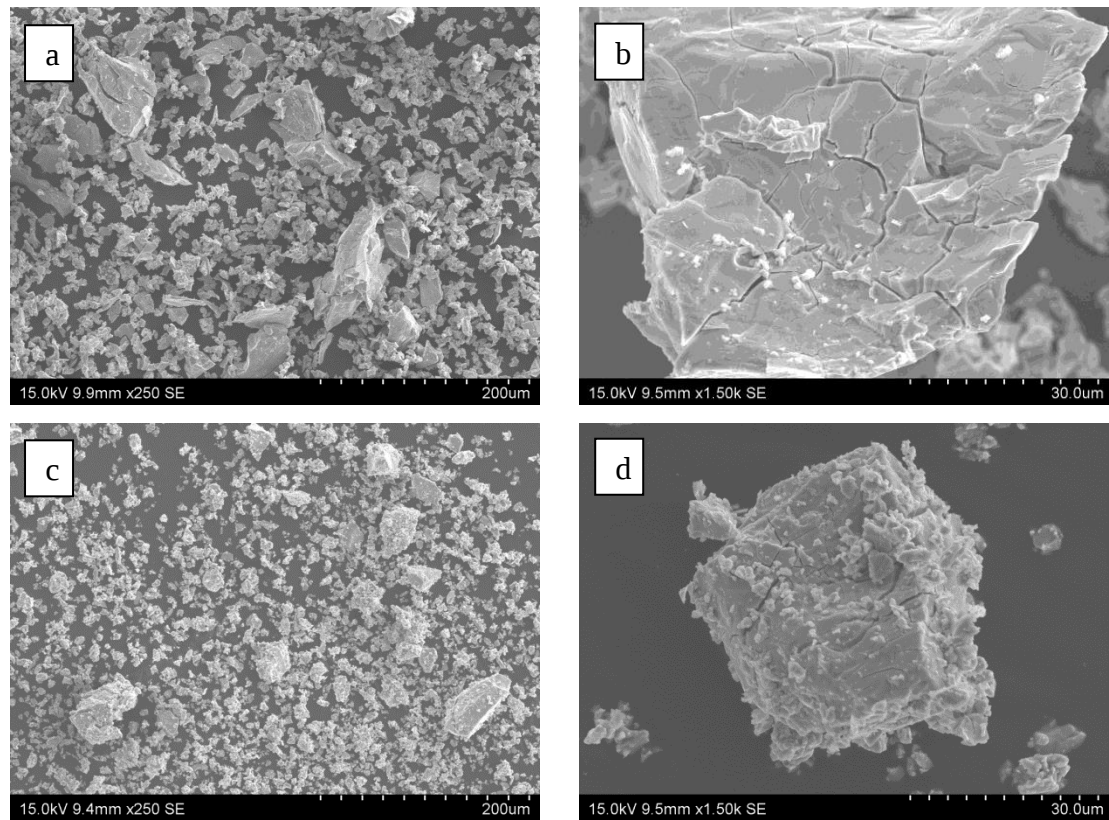


Figure 8.5 SEM image of Sample C4 (a and b) and Sample C4BM (c and d) at 250 $\times$ (a and c) and 1500 $\times$ (c and d) magnification, where in the lower magnification, the bigger particle were $\text{La}_{0.65}\text{Ca}_{1.03}\text{Mg}_{1.32}\text{Ni}_9$ alloys and the smaller particle were AB_5 alloys.

8.3.2 Pressure-Compositions-Isotherm Properties

The pressure-composition-isotherm (PCI) curves of the composites at room temperature, before and after the cycle test, are presented in Figure 8.6 and Figure 8.7, respectively. Figure 8.6 shows that Sample C1 had steep plateau slopes which were contributed by the co-existence of multi-phases as confirmed in the XRD results. The maximum hydrogen absorption capacity of Sample C1 was 1.67 wt%, which was the highest among all other samples. The inclined absorption pressure plateau slope enabled Sample C1 to absorb hydrogen even at a pressure lower than atmospheric pressure. However, a low absorption plateau pressure also resulted with a lower desorption plateau pressure, where a significant amount of hydrogen was unable to desorb at 0.10 MPa, inhibited the reversibility of hydrogen storage capability at room temperature. Meanwhile, Sample C6, with a maximum hydrogen storage capacity of 1.47 wt%, had flat plateau pressures. The absorption plateau pressure was approximately 0.50 MPa, while the desorption plateau was pressure approximately 0.20 MPa. Both plateau pressures were in the range of 0.10 MPa to 1.00 MPa, indicating that this type of alloy had a superior reversibility compare to the La-Mg-Ni based alloy. However, the higher absorption plateau pressure prevented it from storing hydrogen at a lower hydrogen pressure.

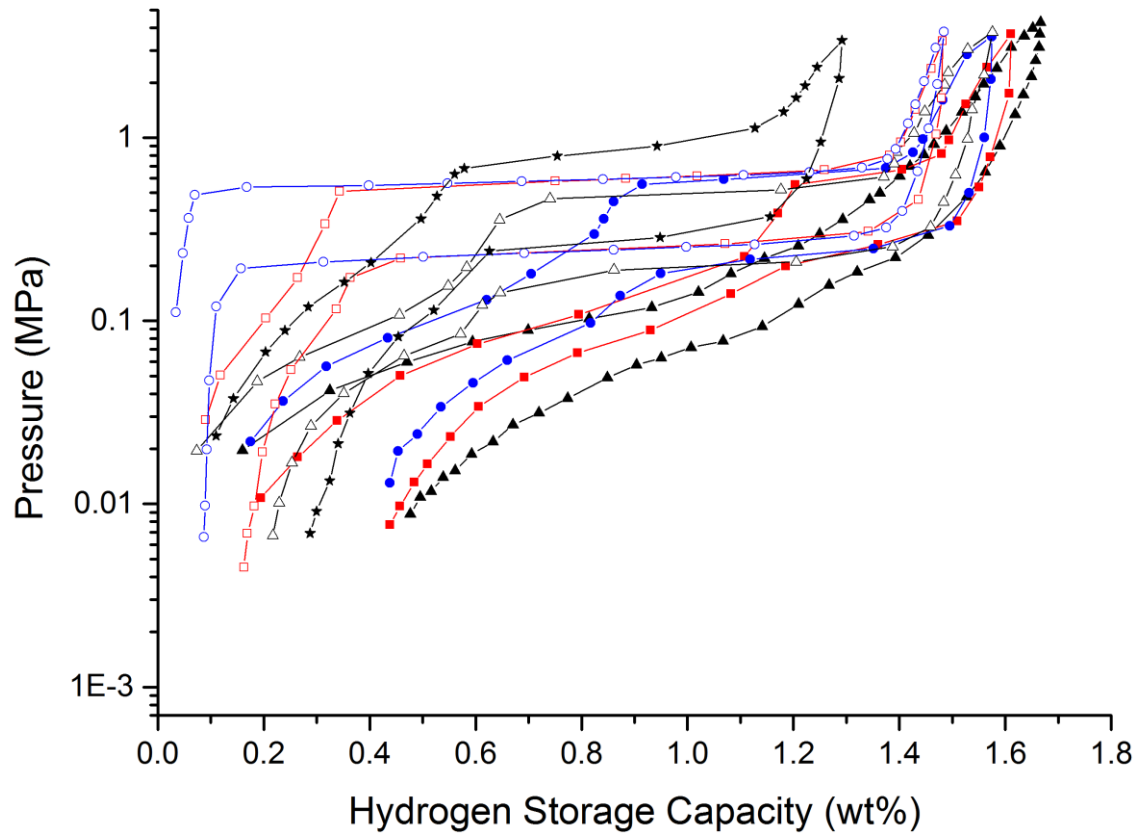


Figure 8.6 Pressure-compositions-isotherm curves of $\text{La}_{0.65}\text{Ca}_{1.03}\text{Mg}_{1.32}\text{Ni}_9$ at different addition of AB_5 alloys before cycle test, measured at room temperature: Sample C1 (0 wt% AB_5) ($\blacktriangle$), Sample C2 (20 wt% AB_5) ($\blacksquare$), Sample C3 (40 wt% AB_5) ($\bullet$), Sample C4 (50 wt% AB_5) ($\triangle$), Sample C4BM (50 wt% AB_5 ball milled treated) ($\star$), Sample C5 (80 wt% AB_5) ($\square$), and Sample C6 (100 wt% AB_5) ($\circ$).

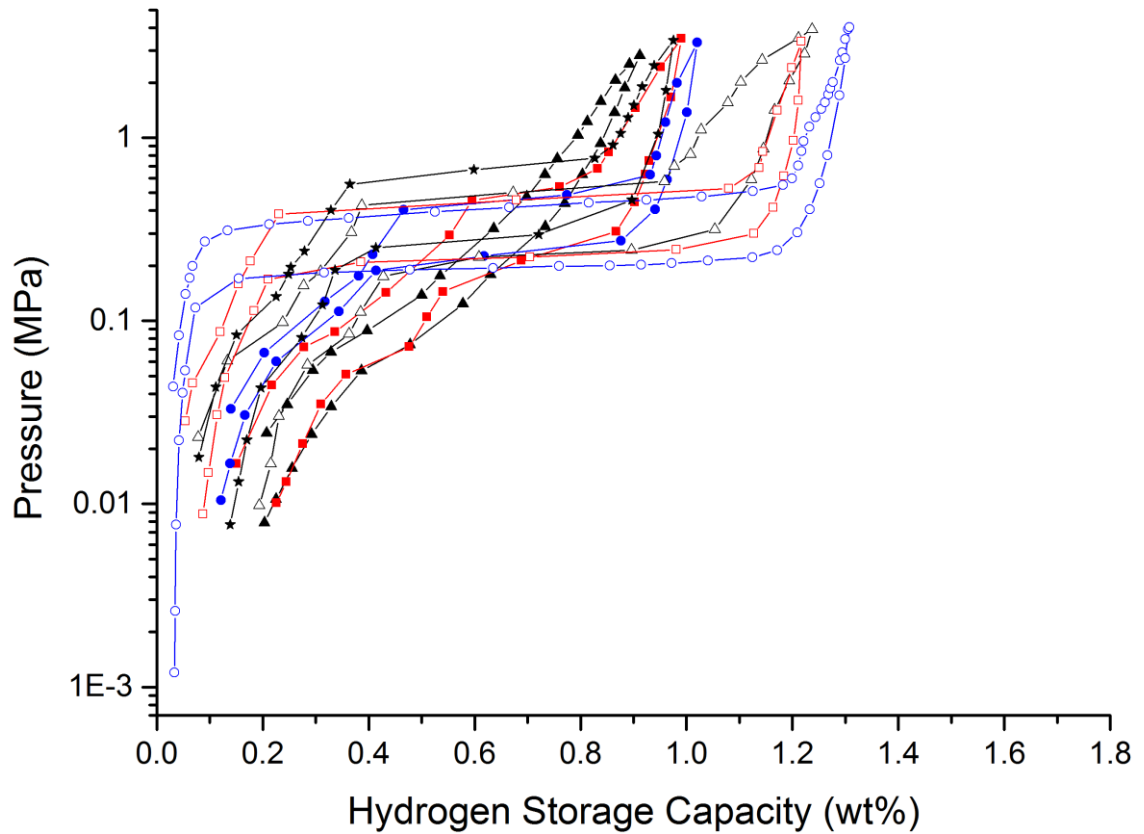


Figure 8.7 Pressure-compositions-isotherm curves of $\text{La}_{0.65}\text{Ca}_{1.03}\text{Mg}_{1.32}\text{Ni}_9$ at different addition of AB_5 alloys after 500 cycles, measured at room temperature: Sample C1 (0 wt% AB_5) ($\blacktriangle$), Sample C2 (20 wt% AB_5) ($\blacksquare$), Sample C3 (40 wt% AB_5) ($\bullet$), Sample C4 (50 wt% AB_5) ($\triangle$), Sample C4BM (50 wt% AB_5 ball milled treated) ($\star$), Sample C5 (0 wt% AB_5) ($\square$), and Sample C6 (0 wt% AB_5) ($\circ$).

In general, the composite samples (Samples C2, C3, C4 and C5) had characteristics inherited from both Sample C1 and Sample C6. Their PCI curves could be distinctively classified into two regions according to their plateau pressures. The initial steeper and lower plateau pressures at the lower storage capacity region were dominated by La-Mg-Ni based alloys, while the flatter and higher plateau pressures at the higher storage capacity were dominated by Sample C6, which is the AB_5 type alloy. The lengths of the plateaus were also proportionate to the weight ratios between Sample C1 and Sample C6; the higher the amount of Sample C6 the longer the flat plateau pressures were. In addition, the maximum hydrogen storage capacities of all these samples were between the maximum hydrogen storage capacities of Sample C1 and

Sample C6, but gradually decreased with the amount of AB₅ addition. This observation was reasonable because the higher capacity phase was replaced by a lower capacity phase systematically. From Figure 8.6, it could be observed that the increased of AB₅ type alloy addition also improved the reversibility of the composites effectively, which was attributed by its higher desorption plateau, as well as, the abundance of high Ni content that has an excellent catalytic characteristic. However, the ball milled composite (Sample C4BM) showed a lower hydrogen storage capacity with higher and inclined absorption and desorption plateaus. These observations agreed with the XRD results, as well as, the work of Liang et al. [213] on AB₅ system, Singh et al. [214] on BCC system and Zhu et al. [98] on AB₃ system, of which they proposed that the degradation was caused by the grain size reduction or partial amorphization. Another possible reason of the degradation of hydrogen storage capacity could be attributed to the unavoidable oxide product generated from ball milling which inhibited the composites to absorb hydrogen. In addition to the degradation of capacity, ball milling also contributed to the steep plateaus, where these slopes were caused by the strain introduced during the process [215].

Figure 8.7 shows the PCI curves of all samples after undergoing 500 pressure cycles. Overall, all post-cycled samples suffered from capacity loss but of varying severity. The capacity degradation of Sample C1 was obvious, with only approximately 50% capacity was retained, whereas the capacity of Sample C6 decreased approximately 10%. Due to the severity of capacity degradation of Sample C1, it could be inferred that the capacity degradation of composite samples (Samples C2, C3, C4 and C5) were mainly contributed by Sample C1. This assumption was supported by the fact that the lengths of plateau pressures contributed by Sample C6 still retained approximately 90% of their original lengths. The capacity retention improved with the increment of AB₅ additions and the degradation trends will be further discussed in cycle test section 8.3.3. Apart from the capacity loss, both absorption and desorption plateau pressures also experienced some minor changes. All absorption plateaus were slightly reduced while desorption plateaus were increased. These changes were commonly observed in all types of hydrogen storage alloys [216-218], which were caused by the repeating phase conversion of metal-hydrogen system. During phase transformations in the pressure cycle test, the alloys experienced successive cell volume expansion and

contraction, which eventually resulted in pulverization, producing smaller particle size with large surface areas. These larger surface areas reduced the energy barrier for hydrogenation and dehydrogenation processes to take place, hence yielding a smaller hysteresis, i.e. decreasing and increasing of absorption and desorption plateaus, respectively.

8.3.3 Cycle Stability

The cycle stability profiles curves were constructed by recording the reversible hydrogen storage capacity at each cycle, where the performances of the hydrogen storage systems were compared based on the absolute values. Another cycle stability indication was based on the percentage of hydrogen capacity retained with respect to its maximum hydrogen storage capacity. The hydrogen capacity retention (HCR) was calculated with equation 8.1 and the HCR at 500th cycle were presented in Figure 8.10 in Section 8.3.4. In general, HCR is used as the cycle stability indication; nonetheless, to maintain a reasonable hydrogen storage capacity is also important. Hence, these two indications will be used to justify the cycle performance of the composites.

$$HCR_n = \frac{\text{Hydrogen storage capacity at } n^{\text{th}} \text{ cycle}}{\text{Maximum Hydrogen storage capacity}} \times 100\% \quad (8.1)$$

Figure 8.8 shows the cycle stability profiles of La-Mg-Ni based alloy, AB₅ type alloy and composites with different mixing ratios. The cycle performance of La-Mg-Ni based alloy (Sample C1) itself was significantly poor, with a sharp drop of hydrogen storage capacity from 1.67 wt% to 1.08 wt% in the first 50 cycles, equivalent to a 40% capacity loss. The capacity degradation was severe where only 50% of its maximum hydrogen storage capacity was retained at 250th cycle. At the end of the 500th cycle, the hydrogen storage capacity was less than 1.00 wt%, corresponding to the aforementioned PCI curve. The unit cell of AB₃ superstructure is formed by a long-range stacking of one third of AB₅ unit and two thirds of AB₂ unit [8, 79, 143]. As discussed in the XRD results and confirmed by the SEM results, the continuous changes of volume in the cycle test resulted in cracks and pulverization to smaller particles, exposing more surface areas. In addition to the non-reversible solid solution hydrogen, this superstructure had a tendency of decomposing into AB₅ and AB₂ upon cycling [142]; while AB₅ preserved the crystalline structure, AB₂ Laves phase was easily amorphized

[166]. Considering the fact that Ca precipitations were observed in the SEM, we suggested that the amorphous phase was further disproportionated to amorphous elemental hydrides, which was not able to be detected in XRD. Meanwhile, the cycle performance of AB₅ type alloys (Sample C6) began with a hydrogen storage capacity of 1.42 wt% and gradually reduced to approximately 5% of its reversible capacity in the first 50 cycles. Its hydrogen storage capacity remained almost unchanged for the next 450 cycles with a hydrogen storage capacity of 1.28 wt% at the 500th cycle, which was approximately 10% of total capacity loss. The capacity retention of this type of alloy was 40% better than the La-Mg-Ni based alloy (Sample C1).

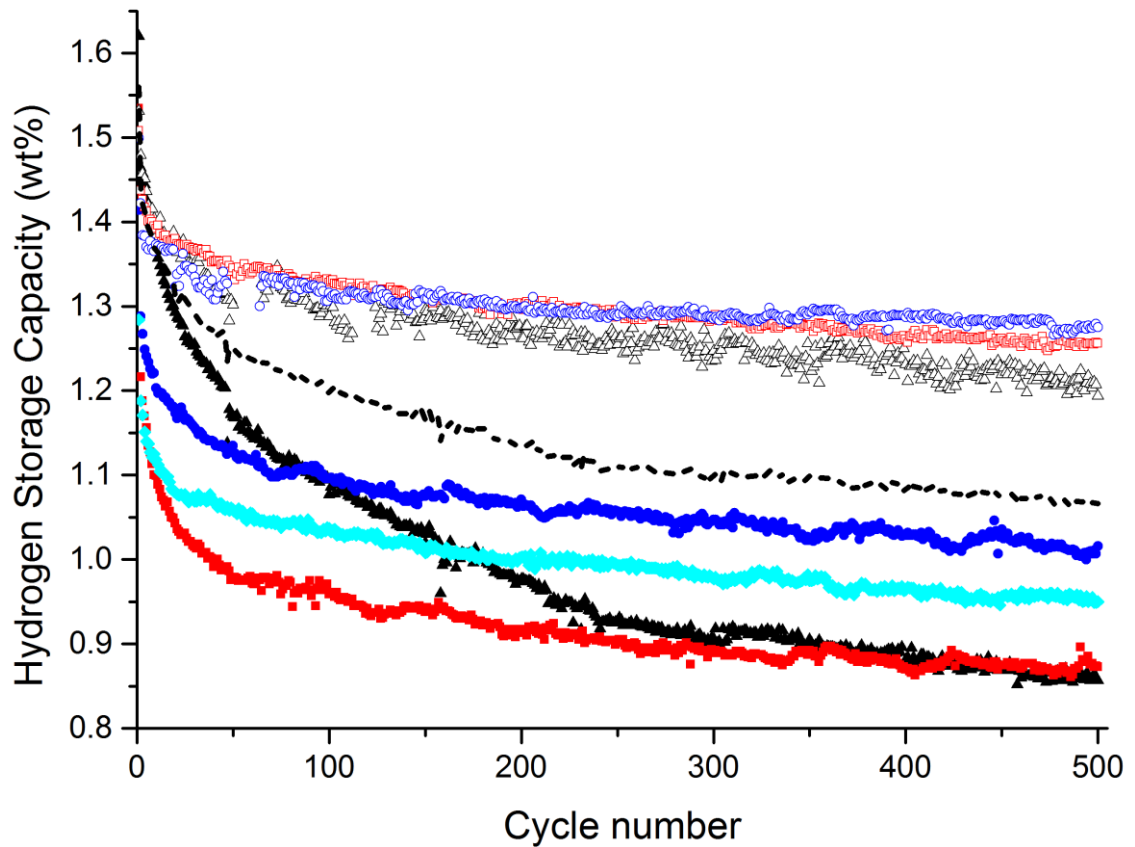


Figure 8.8 Changes of hydrogen storage capacity of composites over 500 hydrogen pressure cycles at room temperature, where the dotted line (--) was the predicted cycle life of 50 wt% AB₅ addition. The samples labelling were: Sample C1 (0 wt% AB₅) (▲), Sample C2 (20 wt% AB₅) (■), Sample C3 (40 wt% AB₅) (●), Sample C4 (50 wt% AB₅) (△), Sample C4BM (50 wt% AB₅ ball milled treated) (◆), Sample C5 (80 wt% AB₅) (□), and Sample C6 (100 wt% AB₅) (○).

Sample C2, with a 20 wt% AB₅ alloy addition, started with a hydrogen storage capacity between Samples C1 and C6 (lower than Sample C1 but higher than Sample C6). Its hydrogen storage capacity degraded exceptionally fast at the first 100 cycles compared to Sample C1, however, the cycle stability was superior for the subsequent 400 cycles. The hydrogen storage capacity at 500th cycle was similar to Sample C1. With an increase of AB₅ alloy addition to 40 wt%, the cycle stability of Sample C3 enhanced. The degradation characteristics were similar as those in Sample C2, where the capacity degradation was dramatic for the first 100 cycles. However, Sample C3 cycle plateau had a 0.20 wt% margin higher than that of Sample C2. The hydrogen storage capacity even surpassed the Sample C1 after 100 cycle with a HCR₅₀₀ close to 70%. The increment of AB₅ type alloy to 50 wt% (Sample C4) and 80 wt% (Sample C5) further enhanced the cycle stability, with both HCR₅₀₀ were above 75%. The corresponding hydrogen storage capacities of both samples at the end of 500 cycles were approximately 1.20 wt% and 1.26 wt% respectively, which were roughly on a par to Sample C6. Both degradation trends were also identical to Sample C6, hence it could be concluded that samples with AB₅ addition above 50 wt% were close to their optimum performance. Nevertheless, it appeared that the addition of 80 wt% of AB₅ (Sample C5) did not improve the cycle performance radically. The ball-milled sample appeared to have a similar degradation trend as Sample C4 except with a lower hydrogen storage capacity because of the oxide products. We used the average capacity decay rate to quantitatively compare the samples where the rate was calculated by taking the difference between the maximum and minimum hydrogen storage capacity and divided with 500 cycles. The results were plotted in Figure 8.9. It is clearly that the Sample C4 BM data point was superimposed on the Sample C4 point, indicating that both samples had the same decay rate. This implied that surface contact has no implication on the enhancement of cycle stability property. We could therefore infer that ball milling is not a necessary step; in fact, this additional step required inert processing environment to reduce the oxide formation which incurred additional manufacturing cost.

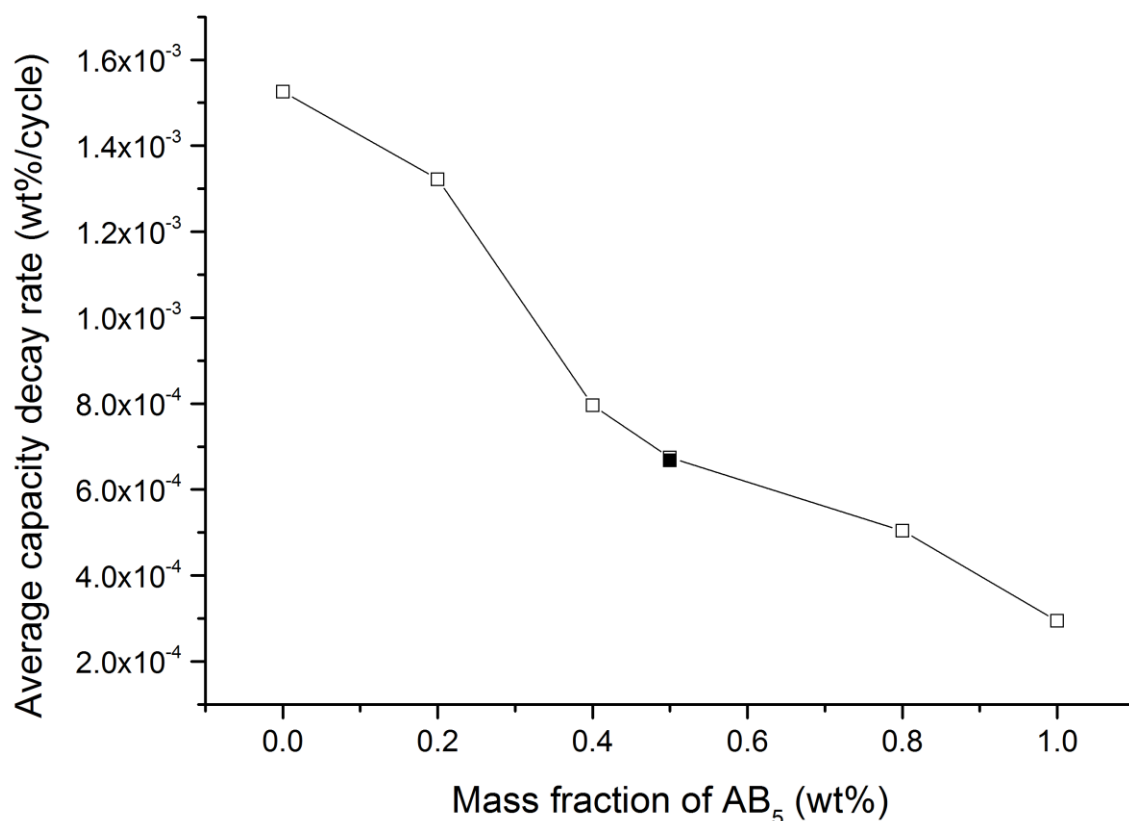


Figure 8.9 The changes of average capacity decay rates with the increased amount of AB₅ additions, where the ball mill treated sample was labeled as a filled black square (■).

It is noteworthy that the improvement of cycle stability was not proportionated to the addition of AB₅ alloy. This is particularly obvious where 50 wt% addition of AB₅ alloy improved the cycle stability tremendously. The cycle performance of Sample C4 was compared with its calculated cycle profile, of which the calculated profile was estimated by averaging between the cycle profile of Sample C1 and Sample C6. Hypothetically, the cycle profile of Sample C4 should fit the predicted profile; however, the experimental profile deviated from the predicted profile greatly, indicating that the existence of synergetic effect between these two types of alloys (Sample C1 and C6). As is discussed in the Introduction, most literatures [83-85, 89, 145] on cycle stability of composites of two hydrogen absorbing alloys were conducted in an electrochemical cell. It was believed that the enhancement of cycle stability attributed to the anti-corrosion and anti-pulverization characteristics of AB₅ alloys. Although anti-corrosion may be the reason of improvement in an electrochemical cell, this factor may not be

applicable in a gas-solid reaction. Hence, we proposed that the improvement of cycle stability was attributed to load sharing, analogous to a metal matrix composite system where AB₅ alloys acted as the reinforcement. In general, all samples underwent a similar degradation trend, where the capacities were decayed at a higher rate initially and became slower at a later stage. The high decay rate was likely dominated by the inevitable pulverization process upon hydrogen charging [71, 219]. Depending on the pulverization resistivity of the samples, after certain number of cycles the degradation was subsequently dominated by disproportionation, which was temperature dependent and a relatively slow process. Despite the fact that the temperature of the cycle test was maintained with a water bath, charging the alloys with a higher hydrogen pressure may generate substantial localized heat during the exothermic absorption that further promoted the segregation of elements [220]. The higher the overpressure was, the faster the degradation rate [71, 219]. Therefore, when AB₅ alloy was added to the composite, its preserved hydrogen absorption capability lowered the hydrogen pressure at equilibrium state hence reducing the disproportionation rate of La-Mg-Ni based alloys.

8.3.4 Feasibility Study and Optimization

To optimize the viability, cost and performance of the composites, it is important to compare the hydrogen storage capacity, hydrogen capacity retention (HCR, as aforementioned) and price to performance (PTP) after undergoing certain number of cycles of hydrogen absorption and desorption. The hydrogen storage capacity indicates the physical hydrogen storage capability of the alloys, while the HCR indicates the quality of hydrogen storage alloys with respect to its maximum storage capability. However, both hydrogen storage capacity and HCR are performance indications and do not correlate with the cost of alloys, which is one of the key indications in optimizing the composite ratios. A high performance alloy may not be economically feasible in commercialization. Hence, PTP was introduced to compare the cost of alloys at a ground of the same hydrogen storage capacity. It was defined and calculated with the following equation:

$$PTP = \frac{\text{Price of alloys per kg}}{\text{Hydrogen storage capacity at } n^{th} \text{ cycle}} \quad (8.2)$$

The price of alloys was merely estimated based on the cost of raw materials according to the price of metals listed in Table 8.2.

Table 8.2 The price of metal obtained from www.mineralprices.com as of 31 Dec 2013

Metal	Price (\$USD/tonne)
La	\$28,000
Ce	\$25,000
Mg	\$3,325
Ca	\$3,420
Ni	\$17,010
Al	\$2,045
Mo	\$25,750

Table 8.3 The price of composite estimated from metal price

Metal	Price (\$USD/tonne)
C1 (0 wt% AB ₅)	\$16,999
C2 (20 wt% AB ₅)	\$17,819
C3 (40 wt% AB ₅)	\$18,639
C4 (50 wt% AB ₅)	\$19,050
C5 (80 wt% AB ₅)	\$20,280
C6 (100 wt% AB ₅)	\$21,100

Figure 8.10 shows the changes of post-cycled hydrogen storage capacity, HCR and PTP with respect to the amount of AB₅ type alloy added, after 500 cycles. The post-cycled hydrogen storage capacity showed an increasing trend with the increase addition of AB₅ type alloy. The hydrogen storage capacity increased drastically from 0.87 wt% to 1.01 wt% with the addition of 40 wt% of AB₅; subsequent additions improved the capacity to more than 1.20 wt% but almost unchanged with further addition. The post-cycled HCR also presented a similar increasing trend with an increase amount of AB₅ type alloy additions, as well as, showed a sudden rise in HCR at 40 wt% of AB₅. Both properties indicated that AB₅ additions were favourable in improving the performances of the composites.

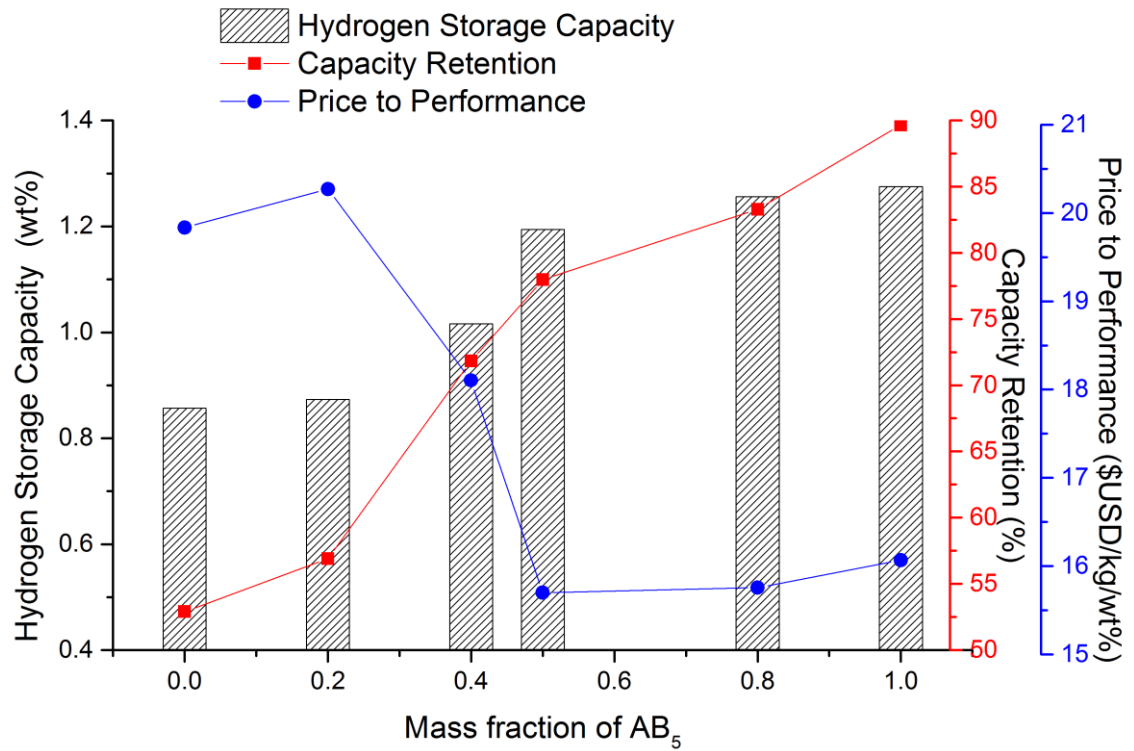


Figure 8.10 Cost-performance analysis with different amount of AB₅ addition.

On the other hand, the post-cycled PTP was highly influenced and fluctuated by hydrogen storage capacity, for instance, the PTP increased with the addition of 20 wt% of AB₅ but reduced subsequently. Interestingly, in the range of 40 wt% to 50 wt% of AB₅ additions, the PTP was significantly reduced, where 50 wt% of AB₅ addition contributed to approximately 20% of cost saving. Nonetheless, the increment of AB₅ additions of more than 50 wt% did not further improve the PTP, in fact, the PTP values are showing an increasing trend. The great reduction of PTP was mainly due to the improvement of hydrogen storage capacity and capacity retention. Therefore, from this figure, we could conclude that the optimum trade-off between performance and cost could be achieved with 50 wt% of AB₅ addition.

8.4 Conclusion

This study has investigated the effects of commercial AB₅ addition on the performance of La-Mg-Ni based alloys. The composites have successfully improved the cycle

stability and hydrogen capacity retention, superior to that of La-Mg-Ni based alloy itself. The addition of AB₅ alloy did not change the crystal structure of La-Mg-Ni based alloy; however, the AB₅ alloy reduced the overall hydrogen storage capacity of the composites. The results also indicated that the weight fraction of AB₅ addition was the main contribution towards the performance enhancement of composites, while the impact of ball milling treatment was insignificant. The cycle life improvement of the composite was likely attributed to load sharing between AB₅ and La-Mg-Ni based alloys. According to the feasibility study, the composite with 50 wt% of AB₅ addition was identified to be the cost and performance optimum compositions, which could save approximately 20% cost compared to using AB₅ only.

Chapter 9 Final Remarks and Future Work

9.1 Conclusion

In this work, the properties of La-Mg-Ni based hydrogen storage alloys had been investigated. Element substitution technique was applied in an attempt to improve the thermodynamic and kinetic properties of these alloys. It was found that both Ce and Al additions greatly improved the reversibility of hydrogen storage capacity. However, the maximum hydrogen storage capacity and absorption kinetics can be reduced by the additions. At the meantime, factorial study also discovered that both Ce and Al gave opposite effects on the absorption and desorption plateaus, which can be useful to tune the properties of the alloys to meet desired operating conditions.

Inductively coupled plasma spectroscopy has confirmed that the synthesized samples had chemical compositions approximate to the design values. From the characterization of optimized samples, it could be concluded that the response surface methodology approach could be a tool for predicting the hydrogen storage properties of the alloys, which allows the possibility to optimize the compositions for better performance of hydrogen storage alloys. To our best knowledge, this is among the first attempt that adapts statistical tools in designing the hydrogen storage alloys.

The hydrogen absorption kinetic was prolonged by the element substitutions of Ce and Al. However, Al substitution had a greater effect than that of Ce. It was found that the excessive addition of Al contributed to the formation of non-hydrogen absorbing phases that inhibit the hydrogen gas from reacting with the alloy surface. Hence, it is suggested that those with slow absorption kinetics was due to one-dimensional interface-controlled reaction. The interface-controlled reaction is slower than those with diffusion-controlled reaction.

The study on the cycle life of La-Mg-Ni based alloys under gas-solid reaction was very limited. This study offers a more representative cycle stability data of La-Mg-Ni based alloys to be used as hydrogen gas storage. The degradation of La-Mg-Ni based alloys hydrogen storage capacity upon cycle test was caused by both disproportionation

and pulverization processes. Nonetheless, partial element substitutions with Ce and Al had successfully improved the cycle stability of La-Mg-Ni based alloys in a gas-solid reaction. The addition of Al was particularly significant in prolonging the cycle life. However, both elements had an adverse effect on the usable hydrogen storage capacity. Hence, the optimized samples were designed with only $y = 0.10$ addition of Al. The cycle stability of the optimized samples was found slightly better than the untreated samples. Even though the hydrogen retention rates of the optimized sample were lower than that of CaNi_5 , the absolute hydrogen storage capacities were still higher than that of CaNi_5 .

Another attempt to improve the cycle life of the hydrogen storage system was by mixing a commercial AB_5 type alloys with the La-Mg-Ni based alloys. The composites not only successfully prolonged the cycle stability, but also maintained a hydrogen storage capacity higher than La-Mg-Ni based alloys itself. Ball milling did not improve the cycle performance, instead due to the formation of oxide layer, the hydrogen storage capacity was reduced. Nonetheless, the capacity decay rate of ball mill treated sample was similar to the sample without ball mill treatment. It was also found that 50 wt% of AB_5 alloy addition was the optimum compositions to minimize the cost and maximize the performance. The composite was estimated to be able to reduce the raw material cost by 20%.

In consideration of the trade-off between the cost and performance of all samples, Sample C4 with a composition of 50 wt% $\text{La}_{0.65}\text{Ca}_{1.03}\text{Mg}_{1.32}\text{Ni}_9$ and 50 wt% of AB_5 was identified to be the best candidate for storing hydrogen in RAPS in this work. The estimated price of the composite was USD\$19/kg. The proposed composite had the capability to store up to 1.53 wt% of hydrogen and had an approximately 78% of capacity retention after 500 cycles. The hydrogen storage capacity at the end of the cycle test was 1.20 wt%.

9.2 Future work

There are rooms to improve the cycle stability while maintaining the hydrogen storage capacity of La-Mg-Ni based alloys. As in this work, commercial AB_5 was able to

improve the cycle stability of La-Mg-Ni based alloys significantly, it is worth to explore other type of alloys that could provide a similar or better cycle stability enhancement. Element substitution method is still relevant; however neutron diffraction should be used to identify the preferred hydrogen storage sites. Computational simulation method could then be used as a complementary technique to calculate the bonding energy between atoms that could lead to the formation of disproportionation. This data will provide a better fundamental understanding in elements selection.

The present work was designed to work in ideal conditions, where the contamination and supply fluctuation factors from the hydrogen source was excluded in this study. The project should therefore extend to a construction of a prototype storage tank that couple with a PEM electrolyzer and a PEM fuel cells system, which approximate to an actual system. It is important to design the properties of metal hydrides to meet the actual operating conditions.

Firstly, one could study the design of thermal management system that could reduce localized heat generation during exothermic absorption, as well as, to provide necessary heat to expedite the desorption process. The factors that should be considered in the design including shape and arrangement of fins, type and flow of coolant, heat conductive additives, thermal diffusivity of metal hydrides, fluctuation of gas supply and distribution of gas channels. This study will provide valuable data in designing alloys that have a better disproportionation resistant.

Secondly, in an actual system, water and gas contaminations from the hydrogen source are unavoidable. This study should investigate the contamination resistivity of the metal alloys in a cycle test that is run with a mixture of gas and controlled humidity. It is expected that the cycle life will be reduced unanimously but that will supply data on the contamination limits and duration before regeneration.

List of Publications

Book Chapter

Lim, K.L., Duraman, N., and Chan, S.L.I. *Batteries for remote area power supply systems* in *Advances in Batteries for Medium and Large-scale Energy Storage: Applications in Power Systems and Electric Vehicles*, edited by Menictas, C., Skyllas-Kazacos, M. and Lim, T.M., Woodhead Publishing.

Refereed Journal Article

Lim, K.L., Liu, Y., Zhang, Q.-A., and Chan, S.L.I., *Effects of Partial Substitutions of Cerium and Aluminum on the Hydrogenation Properties of $\text{La}_{(0.65-x)}\text{Ce}_x\text{Ca}_{1.03}\text{Mg}_{1.32}\text{Ni}_{(9-y)}\text{Al}_y$* , *International Journal of Hydrogen Energy*, 2014. **39**: pp.10537-10545.

Conference Proceeding and Presentation

Chan, S.L.I, Lim, K.L. and Duraman, N., *Hydrogen Storage in Nanomaterials and Thin Films*, Energy Storage Workshop, 11 November 2010, University of New South Wales.

Lim, K.L. and Chan, S.L.I. *Hydrogen Storage Materials in Remote Area Power Supply (RAPS)*, International Symposium on Metal-Hydrogen System 2012 (MH2012), 21 - 26 October 2012, Kyoto, Japan.

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