

Novel approaches to store hydrogen in high capacity hydride

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Novel approaches to store hydrogen in high

capacity hydride

Wei Liu

A thesis in fulfilment of the requirements for the degree of

Doctor of Philosophy



School of Chemical Engineering

Faculty of Engineering

February 2015

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Currently, there is no practical method that satisfies the requirement of high capacity hydrogen storage under ambient conditions for on-board application. In this thesis, size effects of metal hydrides and gas-phase electrochemical charging/discharging methods were investigated to achieve a near-room-temperature hydrogen storage in high capacity metal hydride with LaNi₅ as a model and Mg as the targeted material.

Firstly, size effects were studied on LaNi₅. LaNi₅ nanoparticles by combustion-reduction method showed greatly improved kinetics but no significant changes in thermodynamics compared with bulk LaNi₅. The study was then extended to Mg nanoparticles from solution reduction method and results indicated that the decrease in particle sizes made hydrogen absorption near 100 °C possible because of the improved absorption kinetics. However, the desorption kinetics were slowed down compared to ball-milled MgH₂ due to the inactive surface, although Mg nanoparticles showed a trend of smaller particles possessing faster kinetics. Ni coating on Mg surface could activate the surface and lead to fast desorption kinetics. Furthermore, size reduction of Mg particles decreased the reaction entropy but enthalpy-entropy compensation phenomena caused the desorption temperature not to be decreased as low as expected. To finely tune the thermodynamics, elemental coating is a potential method, but further work is required to lower the desorption temperature.

Since size effects were proved not as effective as expected to reduce the desorption temperature of Mg, research was transited to the development of gas-phase electrochemical charging/discharging method, which uses proton conductive membrane as solid electrolyte and gaseous hydrogen as H source. This novel method was proved successful with reversibly charging 1.56 wt% hydrogen in LaNi₅ with humidified Nafion as solid electrolyte. The extension of its use to Mg showed that hydrogen can be reversibly charged into Mg but moisture caused oxidation of Mg/MgH₂, which prevented further charging/discharging. The use of anhydrous membrane, fluorite-treated Mg/MgH₂ plus improved proton conductivity with LaNi₅ addition avoided the oxidation and 2.53 wt% was charged into Mg. This novel method avoids the use of corrosive alkaline electrolyte and shows great potential to charge/discharge high capacity hydride near room temperature for practical on-board hydrogen storage.

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PUBLICATIONS DURING CANDIDATURE

Journal papers

- Liu W., Setijadi E. J., Aguey-Zinsou K-F. Tuning the thermodynamic properties of MgH₂ at the nanoscale via a catalyst or destabilizing element coating strategy. The Journal of Physical Chemistry C. 2014;118:27781-27792. (Published)
- Liu W., Aguey-Zinsou K-F. Size effects and hydrogen storage properties of Mg nanoparticles synthesised by an electroless reduction method. Journal of Materials Chemistry A. 2014;2:9718-9726. (Published)
- Liu W., Aguey-Zinsou K-F. Hydrogen storage properties of in-situ stabilised magnesium nanoparticles generated by electroless reduction with alkali metals. International Journal of Hydrogen Energy. 2015. (Submitted)
- Liu W., Abdul-Latif A., Aguey-Zinsou K-F. Hydrogen storage properties of LaNi₅ nanoparticle synthesised by combustion-reduction method. International Journal of Hydrogen Energy. 2015. (In progress)

Patents

- Aguey-Zinsou K-F., Liu W. (2013) Magnesium for reversible hydrogen storage, Australian Patent, Application number 2013902608.
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LIST OF ABBREVIATIONS

Abbreviation	Full name		
CV	Cyclic Voltammetry		
DOE	U.S. Department of Energy		
DSC	Differential Scanning Calorimetry		
EDS	Energy Dispersive X-Ray Spectroscopy		
HER	Hydrogen Evolution Reaction		
HOR	Hydrogen Oxidation Reaction		
ICE	Internal Combustion Engine		
ICP/OES	Inductively Coupled Plasma/Optical Emission Spectrophotometry		
Mg(Bu) ₂	Di- <i>n</i> -butylmagnesium		
MOFs	Metal-Organic Frameworks		
MS	Mass Spectrometry		
MH	Metal hydride		
NHE	Normal Hydrogen Electrode		
PBI	Polybenzimidazole		
PCI	Pressure-Composition Isotherm		
PEM	Proton Conductive Membrane		
PMMA	Poly(methyl methacrylate)		
SEM	Scanning Electron Microscopy		
STEM	Scanning Transmission Electron Microscopy		
TEM	Transmission Electron Microscopy		
THF	Tetrahydrofuran		
XPS	X-Ray Photoelectron Spectroscopy		

CHAPTER 1 INTRODUCTION

1.1 Background

The growing concern about climate change coupled with the sharply rising oil prices stimulates the great interest in using clean renewable energy. Hydrogen is widely regarded as a promising energy vector due to its clean combustion and high energy density. However, for hydrogen penetration to the global energy systems, hydrogen storage is considered to be the greatest technological barrier. Although conventional storage methods, gas cylinder and liquefaction, are mature techniques, and have found some application in hydrogen-powdered fuel cells, their wide applications are limited by problems like low storage capacity, high energy consumption, and specific requirements for container material. A more safe and efficient way to store hydrogen is using high capacity metal hydride, e.g. Mg. There have already been plenty of investigations studying Mg for hydrogen storage due to its high storage capacity, but it showed slow kinetics and high sorption temperature. The addition of catalysts and alloying has proved effective in improving its storage properties. However, it is still far from a wide use in on-board application for hydrogen storage.

1.2 Research objective

The main aim of this thesis is to store hydrogen in high capacity metal hydride at or near room temperature and ambient pressure, which can be divided into two aspects: magnesium nanoparticles for hydrogen storage and the development of a novel charging/discharging technique. The main objectives include:

- To synthesis LaNi₅ nanoparticles as a model to study the size effects on hydrogen storage
- To synthesis Mg nanoparticles to study the size effects on hydrogen storage

- To add catalyst to Mg nanoparticles to improve their hydrogen storage properties
- To develop the gas-phase electrochemical charging/discharging method using LaNi₅ as a model
- To extend the use of gas-phase electrochemical charging/discharging method to Mg

1.3 Thesis structure

Following this introduction, a thorough literature review is presented in Chapter 2, which is focused on the current state of hydrogen research, introduction of various metal hydrides, methods to improve their storage properties and current hydrogenation/dehydrogenation methods.

Chapter 3 introduces the synthesis of $LaNi_5$ nanoparticles using combustion – reduction method, and their size effects on hydrogen storage properties are evaluated as a model.

In Chapter 4, the synthesis method of Mg nanoparticles is developed. The reactants' ratio is varied to obtain different particle sizes and size effects are discussed. The effects of different reducing agents are also discussed in this chapter.

In Chapter 5, elemental coating is performed on the surface of magnesium nanoparticles to form a core-shell structure. The coating effects on kinetics and thermodynamics of magnesium nanoparticles for hydrogen storage are investigated.

Chapter 6 and Chapter 7 state the development of the gas-phase electrochemical method for charging/discharging of LaNi₅ and Mg, respectively. The concept of this novel method, cell design, electrode preparation, cell connection and electrochemical tests are introduced and proofs for electrochemically charging/discharging are provided and discussed. In Chapter 8, the main conclusions based on the research results are summarised, and Appendices are included at the end of this thesis which introduces the related characterisation techniques and experimental methods.

CHAPTER 2 LITERATURE REVIEW

2.1 Introduction

This literature survey focuses on the material aspect and charging technique aspect to review the recent progress in hydrogen storage. This provides a basic understanding for developing a practical method for a near room temperature and ambient pressure hydrogen storage technique, especially for on-board applications.

Following a general introduction of the hydrogen economy, emphasis was put on hydrogen storage and its research targets. This led to the primary objective of this thesis: to store hydrogen in high capacity materials at room temperature and ambient pressure. To accomplish this primary objective, research can be carried out on the aspect of storage materials as well as the aspect of hydrogenation/dehydrogenation methods. To find the target high capacity storage material, a detailed review on various solid storage materials was carried out by comparing their storage properties and summarising the possible approaches to improve their properties. To construct a new concept for hydrogenation/dehydrogenation method, the currently used hydrogenation/dehydrogenation techniques were evaluated and the possibility of developing a novel technique independent of temperature and pressure or alkaline electrolyte was discussed. Finally, methods to achieve the primary objective were proposed and possible challenges were discussed.

2.2 Renewable energy to replace fossil fuels

2.2.1 Problems with present energy system

Fossil fuels, in the forms of petroleum, coal and natural gas, are non-renewable and limited in reserves. Based on their reserves and consumption rates, the depletion time for oil, gas and coal is approximately 35, 37 and 107 years, respectively. [1] The

combustion of fossil fuels produces tons of greenhouse gases every year, which can cause rising temperature of the earth's surface, and subsequently lead to dryness, sea level rise and loss of biodiversity. [2] Besides greenhouse gases, the emissions also contain pollutants such as sulphur dioxide and nitrogen oxide, which are the main cause of smog and acid rain that are deteriorating the air quality, destroying the ecosystem and causing serious health problems to mankind. [3]

2.2.2 Renewable energy as a solution and its storage

It is necessary and urgent to replace fossil fuels with clean and renewable energy, such as solar energy and wind energy. Many countries and companies are working to promote the application of renewable energies. This is demonstrated in Figure 2-1 with the global new investment in renewable energy in 2010 being almost ten times that of 2004. [4] As a result, renewable energy was estimated to occupy 19% of global final energy consumption in 2011 according to Renewables 2013 Global Status Report. [5]



Figure 2-1: Global new investment in renewable energy from 2004 to 2010. [4]

However, the productions of renewable energies are generally intermittent. To solve this problem, efficient storage of renewable energy is required. The stored renewable energy can then be released for use when required. There are various types of energy storage technologies developed, which includes mechanical storage systems, battery storage systems and chemical systems. For mechanical and battery systems, their application is limited to special conditions due to their low energy density, life time limitation, special geological requirement, and most of the time they are not suitable for mobile application. [6]

2.2.3 Hydrogen for renewable energy storage

For chemical energy storage, hydrogen has been proposed as the most suitable energy carrier. As indicated in Table 2-1, hydrogen has the highest energy density by mass compared with any common fuels. Its lower heating value is 140 MJ.kg⁻¹, which is nearly three times that of gasoline. [7] In addition to high energy density, hydrogen is also a clean energy vector with no CO_2 emission. In the aspect of sustainability, hydrogen is one of the most abundant elements. It constitutes 75% of the universe's elemental mass and its combustion products H₂O can be cycled to produce hydrogen. [8]

Fuel	Gravimetric energy density (MJ.kg ⁻¹)	Liquid volumetric energy density (MJ.L ⁻¹)	Volumetric energy density at 1 atm., 15 °C (MJ.L ⁻¹)
Hydrogen	140.4	8.5	0.01
Methane	43.6	20.9	0.03
Propane	28.3	23.5	0.09
Gasoline	48.6	31.2	-
Diesel	33.8	31.4	-

Table 2-1: Comparison of the energy density of hydrogen and other fuels. [7]

However, public concern with hydrogen safety needs to be overcome. In fact, to some extent, the leaking of hydrogen would lead to fewer hazards compared with conventional fuels since hydrogen, as the lightest gas, will move and diffuse quickly upward.

With its unique properties, hydrogen fuel is considered the most promising alternative to fossil fuels. It will be produced and used as the main fuel in the hydrogen economy.

2.3 Hydrogen economy

The hydrogen economy is defined as the industrial system in which one of the universal energy carriers is hydrogen (the other is electricity), and hydrogen is oxidized to water that may be reused by applying an external energy source for dissociation of water into its component elements hydrogen and oxygen. [9]

The use of hydrogen as fuel for transportation is not a new concept. As early as 1874, in 'The Mysterious Island', Jules Verne wrote, "I believe that water will one day be employed as fuel, that hydrogen and oxygen which constitute it, used singly or together, will furnish an inexhaustible source of heat and light, of an intensity of which coal is not capable. ... I believe, then, that when the deposits of coal are exhausted we shall heat and warm ourselves with water. Water will be the coal of the future ". [10, 11] Nearly one hundred years later, the term "hydrogen economy" was firstly published by John O'.M. Bockris in his paper 'The Hydrogen Economy: An Ultimate Economy'. [12, 13] The main components of the hydrogen economy as indicated in Figure 2-2 are: production, storage and transportation, and conversion of hydrogen. [14] Recently, significant progress has been made to each component with the fast developments in materials and technology in related fields. Some advancement will be discussed in detail below.


Figure 2-2: Major components of the hydrogen economy.

2.3.1 Hydrogen production

Nowadays, about 96% of hydrogen is produced with fossil fuels as the feedstock. [15, 16] When one tonne of hydrogen is produced from hydrocarbon, there is about 2.5 tonnes of carbon emitted in the form of carbon dioxide. [17] The sustainable alternative is to produce H_2 through water splitting using energy from renewables.

Water splitting can be carried out in three different processes: thermolysis, electrolysis and photo-electrolysis. Water thermolysis requires a temperature higher than 2200 °C to generate H_2 and O_2 and the required energy can be from solar or nuclear energy. [18] Suitable chemical additives, e.g. H_2SO_4 and HI, were used to form thermochemical cycles to lower the temperature below 1000 °C. [19-21] Water electrolysis is one of the most utilized industrial processes for hydrogen production today. It can be performed in three forms: alkaline-based unit, proton exchange membrane electrolysis or solid oxide electrolysis cell. [22] The process for water electrolysis requires a large amount of electricity, which is one of the main obstacles for large-scale hydrogen production. [23] Photo-electrolysis integrates solar energy absorption and water electrolysis into a single unit, which is considered the most efficient renewable method of hydrogen production. [24] The photo-catalyst at one electrode is exposed to solar radiation, leading to the required electrical energy being reduced. This technique is in development and about 18% efficiency was achieved so far. [25] At present, only about 5% of the commercial hydrogen production is primarily from water due to the high energy intensity process involved.

Biomass conversion is another sustainable way to produce hydrogen. Biomass is a renewable resource from plants' photosynthesis with carbon dioxide fixed in it from the atmosphere. This process will lead to a neutral or even negative net carbon emission if carbon capture techniques are applied. Biomass-to-hydrogen can be achieved by thermochemical process [26-28] or biological process [29-31]. However, the yield of hydrogen from biomass is low due to the low hydrogen content in biomass.

Now most of the techniques for hydrogen production based on renewable energy and green power still cannot compete with the method using fossil fuels. However, they have the potential to replace fossil fuels-based techniques to fulfil the requirements of the hydrogen economy.

2.3.2 Hydrogen use

Once hydrogen is produced, it can be used by burning it in an Internal Combustion Engine (ICE) to produce mechanical power, similar to a gasoline engine. The maximum theoretical efficiency of a hydrogen ICE is considered to be dependent on the oxygen to hydrogen ratio and the method of fuel injection. The efficiency of a hydrogen ICE can reach about 45%, much better than that of a gasoline ICE (about 25%) due to its favourable lean combustion condition. [32, 33]

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A more effective way to use hydrogen is by means of fuel cells. The fuel cell, which was invented by Sir William Robert Grove in 1838, is a device that can convert chemical energy directly to electrical and thermal energy. [34] Figure 2-3 shows the components of a proton conductive membrane (PEM) fuel cell for automobile application, which can operate at a temperature lower than 80 °C. At the anode, the supplied hydrogen is split into protons and electrons by the catalysts, typically Pt. The PEM membrane permits only protons to pass through to reach the cathode, which forces the electrons to flow to the cathode via an external electric circuit generating electric power. At the cathode, electrons, protons and oxygen react to produce water. This process has energy efficiency as high as 60% and the only by-product is water. The efficiency loss is usual due to fuel to heat or mechanical energy conversion. [35]



Figure 2-3: Components of PEM fuel cell. [36]

At present, the major challenges for fuel cells are cost and durability. The high cost of fuel cells falls on the Pt catalyst, membrane and bipolar plate. Researchers are searching for methods to lower their cost, for example, by reducing the Pt percentage in the catalyst. [37] The degradations of the fuel cell are generally caused by the impurities in hydrogen gas, which reduces the proton conductivities of both the membrane and the catalyst layer. [38] Methods, for example modifying the membrane structure, are under study to minimise the contamination effects of various impurities. [39]

2.3.3 Hydrogen storage and problems

The linkage between hydrogen production and its use is hydrogen storage and transportation, which remains the scientific and technical barrier that hinders the transition from a fossil fuel economy to a hydrogen economy. Hydrogen, even in liquid state, has much lower volumetric energy density compared with conventional fuels (Table 2-1). The low volumetric energy density means that a given volume of hydrogen contains much less energy than other fuels. For example, with the same energy content, the gas tank volume required to store hydrogen at ambient pressure is more than 3,000-fold larger than that for one tank of gasoline. [40] The storage problem becomes more complex when considering on-board storage for automobile application with restrictions on space and weight, and more importantly the safety consideration.

To guide the research and development of hydrogen storage technique, the U.S. DOE has set a series of targets for on-board hydrogen storage and that for portable equipment, and the targets are summarised in Table 2-2. [41] These targets showed that the ideal storage materials or techniques must reach the storage capacity requirement as well as the delivery temperature and fill time requirements. In the following section, conventional hydrogen storage methods will be reviewed and the primary objective of this thesis will be set based on the review.

Storage parameter	Units	On-board		Portable equipment			
		2017	Ultimate	2015	2015		2020
				Single use	Rechar -geable	Single use	Rechar -geable
System gravimetric capacity	kg H ₂ .kg ⁻¹ system	0.055	0.075	0.02	0.015	0.04	0.03
System volumetric capacity	kg H ₂ .L ⁻¹ system	0.040	0.070	0.03	0.02	0.05	0.04
Delivery temperature	°C	-40/85	-40/85	10/85	10/85	10/85	10/85
System fill time (for 5 kg)	min	3.3	2.5	-	-	-	-

Table 2-2: U.S. DOE technical performance targets for hydrogen storage systems. [41]

The simplest way to store hydrogen is with compressed hydrogen in a high-pressure cylinder (700 bar). [42] This method has been used for more than 100 years with a steel cylinder (maximum pressure of 200 bar). [43] To satisfy the requirements for automobile use, lighter storage tanks built from carbon composite materials have been developed. [44, 45] This kind of cylinder can stand hydrogen pressure up to 700 bar and store about 5 kg of hydrogen. However, potential risk due to the extreme high-pressure involved and the high cost of the cylinder brings practical problems that limit its widespread commercialisation. [46]

Another commercialised technique is to store hydrogen in liquid form in a tank. In theory, liquid hydrogen possesses much higher volumetric capacity of 0.070 kg.L⁻¹ than that of compressed hydrogen with 0.039 kg.L⁻¹ at 700 bar. This method avoids the high-pressure risk of compressed hydrogen, but two serious drawbacks prevent widespread use. Firstly, hydrogen liquefaction requires a lot of energy. The energy to liquefy one

kilogram of hydrogen from room temperature is 15.2 kWh, which almost equals to half of the energy of stored hydrogen. [47] Secondly, the stored hydrogen will gradually evaporate through boil-off. Boil-off of hydrogen can be reduced by storing at -250 °C with excellent insulation, but it cannot be prevented due to hot spots from thermal conduction and thermal radiation. Boil-off rate is reported to be 1 to 3% per day. [48] Hydrogen boil-off also brings safety problems since hydrogen can accumulate and possibly ignite in confined spaces.

High pressure and the relatively low volumetric density for compressed hydrogen gas along with the large energy loss and low temperature condition of liquid storage demand a better storage system. Solid state hydrogen storage provides a good alternative due to the possibility of high volumetric and gravimetric capacity and long term stability, and it does not suffer drawbacks such as those experienced by compressed and liquid hydrogen. Therefore, the primary objective of this thesis is to store hydrogen in solid material with high storage capacity at room temperature and ambient pressure. To find possible materials and methods to reach this objective, the following section will review the storage properties of hydrogen storage materials and methods to improve their performance as well as the techniques to load and release hydrogen.

2.4 Solid state hydrogen storage

2.4.1 Targeted bond strength range for room-temperature storage

In solid materials, hydrogen is stored by physisorption (carbon structures, metal organic frameworks) or chemisorption (complex and metal hydrides). The different storage properties for physisorption and chemisorption are mainly derived from the varied interactions between hydrogen and solid material, which can be characterised by the bond strength between hydrogen and the solid storage material. The enthalpy is used to

qualify the bond strength, and the enthalpy (ΔH^{θ}) and entropy (ΔS^{θ}) of metal hydrides can be calculated by measuring the pressure-composition isotherm (PCI) of hydrogen absorption/desorption.

A typical PCI curve is shown in Figure 2-4. When the hydrogen diffuses into metal or alloy forming solid solution (α phase), the hydrogen concentration increases with hydrogen pressure until the formation of metal hydride (β phase). Hydrogen pressure at the region where α and β phase coexist, is called the plateau pressure, P_{eq}. The plateau pressure is temperature dependent and the logarithm value at different temperatures can be plotted against the reciprocal of the absolute temperature to calculate reaction enthalpy and entropy according to the van't Hoff equation: [49]

$$\ln(\frac{P_{eq}}{P^{\theta}}) = \frac{\Delta H^{\theta}}{RT} - \frac{\Delta S^{\theta}}{R}$$
(2.1)

Where P_{eq} is the plateau pressure; ΔH^{θ} is the reaction enthalpy; ΔS^{θ} is the reaction entropy; R is the gas constant and T is the absolute temperature. The slope and the intercept of the plot give ΔH^{θ} and ΔS^{θ} , respectively.



Figure 2-4: Typical pressure-composition isotherm and van't Hoff Plot. [50]

The desirable range of bond strength that allows hydrogen release around room

temperature is $10 - 60 \text{ kJ.mol}^{-1}$ (Figure 2-5). [51] The bond strength is therefore too low for physisorption and too high for most chemisorption. The properties of various materials will be discussed in detail below.



Figure 2-5: Targeted range of bond strengths that allows hydrogen release around room temperature. [51]

2.4.2 Hydrogen storage in porous system

Porous materials, usually with high surface area, are good candidates to store hydrogen via physical adsorption. In this process, van der Vaal's interactions are used to absorb H_2 at the surface of materials. Hence, the enthalpy involved is ~ 4 to 10 kJ.mol⁻¹. [52] Therefore, to adsorb hydrogen gas on the solid surface, a low temperature will be required.

Many porous materials with high surface area have been investigated for hydrogen storage. Materials that have been considered include carbon materials since they are environmentally friendly and abundant. These materials include carbon nanotube [53], carbon fibres [54], carbon nanohorn [55] and high surface area carbon [56]. Recent research showed that the storage capacity depends not merely on the surface area of carbon material but also on its pore geometry and volume. [57]

More recently, metal-organic frameworks (MOFs) have also been considered due to the possibility of developing high surface areas up to 5900 m².g⁻¹. [58] MOFs are a crystallized porous network consisting of organic linkers connecting metal ions. The first report for hydrogen storage was carried out with MOF-5 and the storage capacity reached 4.5 wt% at 78 K and 1.0 wt% at room temperature and 20 bar. [59] The maximum hydrogen uptake in MOFs is approximately proportional to the surface area and pore volume (Figure 2-6). [60-62] However, the reported heats of adsorption on many MOFs are mostly in the range of 3.5 to 7 kJ.mol⁻¹, which is low for room - temperature hydrogen storage. [63] Using more polarizing cations and increasing the degree of coordination unsaturation, the interaction energy could be improved. By this method, Dinca et al. [62] have increased the heat of adsorption of a MOF containing Mn^{2+} to 10.1 kJ.mol⁻¹, which has fallen in the desirable range of bond strength to store hydrogen at room temperature.



Figure 2-6: Maximum hydrogen storage capacity versus BET surface area or pore volume of selected MOFs. [60-62]

2.4.3 Hydrogen storage with complex hydrides

Complex hydrides include metal cations (e.g. Li, Na, Mg and Ca) bonded to hydrogencontaining anions such as BH₄⁻, AlH₄⁻ and NH₂⁻. In complex hydrides, hydrogen atoms are covalently bonded to boron, aluminium or nitrogen. Some of the complex hydrides are promising material for solid hydrogen storage due to their high gravimetric hydrogen capacity. For example, in the case of LiBH₄, the gravimetric storage capacity is 18 wt%. [64]

Complex hydrides were initially considered to be irreversible for hydrogen storage. In 2001, the research by Bogdanovich [65] showed that Na(AlH₄) can reversibly desorb and absorb hydrogen at moderate temperature and pressure with the presence of a Ti compound catalyst. Since then, complex hydrides have been extensively studied as promising material for hydrogen storage. One of the challenges for complex hydrides is slow kinetic for hydride formation. Another challenge is the stability of these hydrides and many of the high capacity hydrides requiring a high temperature to release hydrogen. Over the last decades, several methods have developed to solve these problems, such as destabilisation with MgH₂ [66], the use of catalyst [67], or through H^{δ_+} and H^{δ_-} mechanism [68, 69]. For example, using H^{δ_+} and H^{δ_-} mechanism, the mixture of LiNH₂ and LiH can release about 5.5 wt% hydrogen at 150 - 200 °C. [70] This method has been extended to other materials, e.g. LiNH₂ + LiBH₄ [71], LiNH₂ + Ca(BH₄)₂ [72], NaNH₂ + NaBH₄ [73]. Furthermore, complex hydrides still suffer a reversibility problem since after decomposition the products are too stable to be rehydrogenated. Recent reports showed that nanoconfinement of complex hydrides is a good way to improve reversibility and alter kinetics. [74-76] The concept has also been extended to core-shell hydrides, which allow higher storage capacity in addition to reversibility. [77]

However, for an on-board application purpose, more work is required to further improve kinetics and decrease the cycling temperature of complex hydrides.

2.4.4 Hydrogen storage in metal hydride

Metals or alloys can react with hydrogen to form metal hydrides, which also provides an exciting way to store hydrogen. Unlike complex hydrides, hydrogen adsorption and desorption proceed in one single step:

$$M + \frac{x}{2}H_2 \leftrightarrow MH_x + \Delta H \tag{2.2}$$

Where M is a metal or alloy; ΔH is the reaction enthalpy.

If the crystal structure of the metal does not topologically change upon insertion of H atoms, these hydrides are referred to as interstitial hydrides, such as PdH and LaNi₅H₆. If a new structural type is formed upon hydrogen incorporation, they are called structural hydrides, such as MgH₂ and AlH₃. [78] In metal hydrides, hydrogen atoms are densely packed in the metal lattice by chemical bonding. The distance between hydrogen atoms is significantly reduced so that metal hydrides usually have high volumetric capacity compared to storage in gas- or liquid form. Properties of main metal hydrides are summarised in Table 2-3.

Type of hydride	Metal/alloy	Hydride	Structure	wt% hydrogen
Interstitial	LaNi ₅	LaNi ₅ H ₆	P6/mm	1.37
Interstitial	ZrV_2	$ZrV_2H_{5.5}$	Fd3m	3.01
Interstitial	Mg ₂ Ni	Mg ₂ NiH ₄	P6mm	3.59
Interstitial	FeTi	FeTiH ₂	Pm3m	1.89
Interstitial	TiV ₂	TiV_2H_4	BCC	2.6
Structural	Mg	MgH_2	P42/mnm	7.6
Structural	Li	LiH	Fm3m	12.6
Structural	Al	AlH ₃	R3-C	10
Structural	Pd	PdH _{0.6}	Fm3m	0.55

Table 2-3: Metal hydrides and their hydrogen storage properties. [79]

Interstitial hydrides can be expressed as AB_xHn in a simple way. 'A' element is typically from rare earth or alkaline earth metals, which easily form a stable hydride. 'B' element can be a transition metal, such as Ni, Co, Cr, et al, which only forms unstable hydrides. Among interstitial alloys, LaNi₅-based alloys have been widely investigated. LaNi₅ can store and release hydrogen rapidly and reversibly at room temperature and under moderate hydrogen pressure. This has led to wide investigations to reduce its cost and improve its cycle life. As a result, LaNi₅-derived mischmetal-nickel alloy has been used as electrode material in commercial rechargeable Ni-MH batteries. [80]

In structural hydrides, magnesium is a promising material for high-capacity hydrogen storage. The theoretical capacity of magnesium reaches 7.6 wt%, which exceeds the 2017 target (5.5 wt%) and even the ultimate target (7.5 wt%) of DOE for on-board application. The process of hydrogen uptake and release can proceed at a temperature higher than 300 °C. [81] For LiH and AlH₃, their storage capacities (12.6 wt% and 10 wt%, respectively) are higher than that of MgH₂, but LiH suffers a high temperature up to 720 °C to release hydrogen [82] and AlH₃ has a reversibility problem since Al is too stable to hydride it back to AlH₃ at moderate pressure and temperature [83]. For PdH_{0.6}, it can be cycled at room temperature but its application is hindered by the low capacity of 0.55 wt%. [84]

The comparison of different hydrogen storage materials showed that magnesium is an excellent material which has potential to be used for on-board purpose. Therefore, we will target magnesium as the high capacity material for investigation. LaNi₅, as a good material for stationary application, will also be studied as a model. In the next sections, the properties of LaNi₅ and MgH₂ at the basis of this thesis are going to be discussed in more detail, and the approaches applied to improve their storage properties will be summarised.

2.5 LaNi₅ for hydrogen storage

As shown in Figure 2-7, LaNi₅ has a CaCu₅-type hexagonal structure, which has several interstitial sites for hydrogen occupation. [85] Theoretical calculation predicted that a maximum of a nine-atom hydrogen adsorption can be reached. However, the composition with the highest hydrogen content obtained is LaNi₅H_{8.35} hydrided at a pressure of 1,650 atm. [78] At low pressure, the hydride formed is usually LaNi₅H₆ with fast kinetics for adsorption and desorption. The reaction enthalpy is 30.8 kJ.mol⁻¹ H₂ with the plateau pressure for absorption and desorption at 25 °C of 1.6 bar and 2.2 bar (Figure 2-8), respectively, which makes it a good material for stationary hydrogen storage at room temperature. [86] Partial substitution and size reduction will be discussed below, which was reported to alter the properties of LaNi₅.



Figure 2-7: (a) Crystal structure of $LaNi_5$ alloy, (b) the tetrahedral sites and (c) octahedral sites for hydrogen occupancy. [85]



Figure 2-8: The PCI curve of LaNi₅ measured at 25 °C. [86]

2.5.1 Partial substitution of LaNi₅

Pure LaNi₅ can be subject to significant degradation that causes the loss of reversible capacity during cycling. After 3150 gas-phase hydrogenation/dehydrogenation cycles, the storage capacity of the activated samples were reduced by 87% and the plateau region disappeared. [87] Partial substitution of Ni with Co can significantly prolong LaNi₅ cycling life. [88] Nowadays, the typical composition of an AB₅ type electrode alloy in the commercial battery is MmNi_{3.55}Co_{0.75}Mn_{0.4}Al_{0.3}. [89] However, cobalt is much more expensive and it takes nearly half of the total raw material cost. [90] In order to reduce cost but keep cycling stability high, cobalt-free materials have been investigated as electrode material by substituting Ni with Si [91], Fe [92, 93] or Sn [94].

2.5.2 Size effects on LaNi₅

Another possible way to alter the properties of LaNi₅ is through size effects, but controversial conclusions were obtained. Joseph et al [95] studied the effect of ballmilling on the hydrogen sorption properties of LaNi₅. Their results indicated that ballmilling reduced LaNi₅ particle size and created defects on the surface. At the same time, long-time ball-milling converted a part of the LaNi₅ to a non-absorbing state. The nonabsorbing fraction in the milled sample was found to grow with increase in the ballmilling time. As a result, the non-absorbing fraction decreased the storage capacity and slowed down the absorption kinetics of LaNi₅. Further study by Joseph et al suggested that the reduced unit-cell volume and the enhanced atomic disorder in the nanostructured LaNi₅ caused a larger energy barrier for the hydrogen sorption reactions on the long-time ball-milled LaNi₅. [96]

However, Liang and Schulz reported that nano-sized LaNi₅ showed a faster desorption kinetics than that of the unmilled alloy. [97] The improvement in kinetics was also reported on mechanical grinded LaNi₅ under Ar and H₂ atmospheres. [98]

Above discussions on size effects of $LaNi_5$ showed that more studies are required to clarify the size effect of $LaNi_5$ on kinetics and to investigate size effect on thermodynamics.

2.5.3 LaNi₅ synthesis

The conventional method to prepare the LaNi₅ alloy is through arc melting of metallic lanthanum and nickel. [99] It is a multi-step process consuming large amounts of energy and the obtained particles are in the range of 20-200 μ m. [100] Ball-milling is a widely used method to reduce particle size of LaNi₅, but the particle sizes are limited to several microns even after 5 h ball milling. [101]

Recently, alternative synthesis routes have developed. Zhu et al developed an electroreduction approach to synthesize LaNi₅ in molten CaCl₂. A pellet of La₂O₃ and NiO combined with molybdenum wire was used as a cathode to undergo constant voltage electrolysis to get LaNi₅ particles in several micrometres.[102] Another recently reported method is to use La₂O₃ and Ni as starting materials for direct LaNi₅ synthesis without additional reduction procedure if the heat source for self-ignition combustion is from the hydrogenation heat of metallic calcium. The particle size of the obtained LaNi₅ is in the range of 5-500 μ m depending on the hydrogen pressure applied. [103, 104] One interesting method is through reduction-diffusion process, which uses nitrates as starting material to get oxides followed by chemical reduction with CaH₂ to obtain LaNi₅. The products are rod-like LaNi₅ with a length of about 6-10 μ m and diameter in the range of 300-500 nm. [105]

All the methods mentioned above avoided the refinery metal and high temperature for melting, they are more affordable and energy saving. However, the obtained LaNi₅ are in micrometre range and further study is needed for LaNi₅ nanoparticle synthesis. The combustion-reduction method has the potential for nanoparticle synthesis if combustion and reduction temperature could be reduced to avoid the rod growth since the reported diameter (300-500 nm) of LaNi₅ rod is in nanosize range.

2.6 Magnesium for hydrogen storage

The reaction of elemental Mg with hydrogen is one of the most widely researched reactions in the field of solid state hydrogen storage. During the reaction, the crystalline structure changes from hexagonal Mg to tetragonal MgH₂ structure as shown in Figure 2-9 of their corresponding unit cell. [42] The bonding nature of hydrogen in MgH₂ is quite complex, consisting of the intermediate of ionic and covalent bonding. [106]



Figure 2-9: Crystal structure of magnesium and low pressure magnesium hydride. [107]

Figure 2-10 shows the PCI curves of commercial MgH₂ at 350 °C. [108] The measured enthalpy value based on PCI curves is too high for room temperature hydrogen storage. The commonly accepted reference value for its enthalpy and entropy is 74.7 kJ.mol⁻¹ H₂ and -130 J.K⁻¹mol⁻¹ H₂, respectively. [109] The high enthalpy value illustrated that the Mg-H bond is too strong leading to a stable hydride during reaction (2.3). For commercial MgH₂, a temperature higher than 350 °C is required to release hydrogen. [110]



$$Mg+H_2 \leftrightarrow MgH_2 + 75 \text{ kJ/mol}$$
 (2.3)

Figure 2-10: PCI curves of commercial MgH₂ at 350 °C. [108]

In terms of on-board automobile application, magnesium also suffers from low hydrogenation and dehydrogenation rate and several hours are required for a full desorption from bulk material. [111] The kinetics depend on several parameters, such as the shape of the material, the size of the particle, the state of the surface, the thickness of the oxide layer, the presence of impurities, the presence of additives, etc. [112] Numerous attempts were made to alter the thermodynamics and improve the kinetics of magnesium for hydrogen storage. Some of the approaches will be discussed below.

2.6.1 Alloying to alter thermodynamics

Theoretical calculation of the influence of several alloying elements, such as Al, Ti, Fe, Ni, Cu or Nb, on the stability of MgH₂ showed that the selected alloying elements destabilize the hydride by decreasing the heat of formation due to a weakened bonding between magnesium and hydrogen atoms. Hence, the dehydrogenation properties of MgH₂ were expected to be improved to a different extent by the addition of alloying elements. [113]

The alloying effect of Ni was investigated as early as 1968 [114] and the reaction enthalpy for the hydride (Mg₂NiH₄) formation from Mg₂Ni is 67 kJ.mol⁻¹ H₂, [115] which is thus 9 kJ.mol⁻¹ H₂ lower than that of MgH₂. However, the hydrogen storage capacity decreases at the same time to 3.6 wt%, which is too low for most applications. Furthermore, hydrogen uptake and release temperature are near 300 °C, which is still too high. To overcome these drawbacks, research into multiphase alloys was carried out. Hence, with a partial substitution of Mg with La, the La-Mg-Ni alloy reversibly stored more than 2.5 wt% hydrogen at 200 °C. [116]

Many Mg-containing alloys were investigated, such as Mg-Al,[117] Mg-Co,[118] Mg-Fe[119-121] and Mg-Si[122]. Among these alloys, Mg₂Si has the potential to store hydrogen at or near room temperature. This alloy was prepared by dehydriding the mechanically milled MgH₂ + Si. The equilibrium pressure for hydrogen desorption at 300 °C is above 7.5 bar, which is more than 4 times the plateau pressure for pure MgH₂. The formation of Mg₂Si reduced the standard enthalpy of dehydrogenation of MgH₂

from 76 kJ.mol⁻¹ H₂ for pure MgH₂ to 36 kJ.mol⁻¹ H₂ for MgH₂ +1/2Si. Hence, from these thermodynamic parameters, an equilibrium pressure of 1 bar at about 20 °C can be predicted. However, reversibility has proven to be challenging since even under high pressure the Mg₂Si phase cannot be rehydrogenated due to the slow kinetics. Attempts were made to modify the crystal structure by partly substituting Si by ternary alloying additions like Li, C, Al, Ca, Co, Ni, Cu and Y. However, new phases were only observed in the systems Mg–Si–Ni–H and Mg–Si–Cu–H, which still did not show any reversible hydrogen reactions under moderate conditions. [66]

2.6.2 Catalysts to improve kinetics

The use of a catalyst is an effective pathway to improve kinetics for MgH_2 desorption by lowering the activation energy for hydrogen dissociation. Up to now, the investigated catalysts can be divided into several categories: metals, alloys and metal oxides.

Investigations on MgH₂ ball-milled with transition metals (Ti, V, Mn, Fe and Ni) showed that MgH₂-V possessed the fastest desorption kinetics followed by MgH₂-Ti, MgH₂-Fe, MgH₂-Ni, MgH₂-Mn. The absorption kinetics was in the order of Mg-Ti, Mg-V, Mg-Fe, Mg-Mn and Mg-Ni. For all samples, formation enthalpy and entropy of MgH₂ did not change but activation energy of desorption was reduced drastically. However, nano-sized catalysts (Fe, Co, Ni, and Cu) seemed to act differently according to research on the nanoparticle transition metals as catalysts for MgH₂. Accordingly, Ni nanoparticles catalysed MgH₂ showed the most superior hydrogen storage properties with good reversible hydriding/dehydriding cycles even at 150 °C, which was attributed to the good dispersion of Ni nanoparticles. [123] Theoretical studies proposed that the activity of 3d transition metals is related to their 3d orbital occupancy. When the Mg–H bond of MgH₂ is activated by the transition metal, the electrons of the bonding orbitals

of the MgH₂ are donated to the unoccupied orbitals of the M (donation), and subsequently, the electrons of the occupied orbitals of the M are back donated to the antibonding orbitals of the MgH₂ (back-donation). Therefore, the catalytic activities of Sc and Ni are predicted to be comparatively high due to electron donation and back-donation, respectively. The catalytic activities of the other elements (Ti, V, Cr, Mn, Fe, Co, Cu and Zn) tend to be lower due to the difference of the 3d orbital occupancies from the extremes (Sc and Ni). [124]

Metal oxides, such as Nb₂O₅ [125-128], TiO₂ [129, 130], SiO₂ [129] and NiO [125], were also used as catalysts to improve the kinetics of MgH₂ desorption. Among these oxides, Nb₂O₅ catalysed MgH₂ showed some of the best improvements with the store and release of 6.0 wt% of hydrogen in less than 200 s instead of 1000 s for pure MgH₂ at 300 °C. [131] A synergetic effect of Nb₂O₅ and Ni on MgH₂ was observed with Nb₂O₅ which decreased the grain size while Ni on MgH₂ surface decreased the unit volume of MgH₂, leading to fast desorption kinetics. [132]

2.6.3 Nano-sizing to improve storage properties

Alloying with other metals or adding catalyst in magnesium in general leads to a significant decrease in storage capacity. For example, alloying Mg with Ni decreases the storage capacity from 7.6 wt% to 3.6 wt% with high temperature still required to absorb and desorb hydrogen. An alternative that has emerged is through nanosizing. Indeed, theoretical calculations predicted a possible reduction of enthalpy upon particle size reduction in the nanosize region. [133-136] This may be due to additional terms, which had to be taken into account in van't Hoff equation when the particle size is in the nanoscale.

$$\ln \frac{P_{\text{eq,nano}}}{P^{\theta}} = \frac{1}{RT} (\Delta H^{\theta} + \Delta W_{\text{surf}}) - \frac{\Delta S^{\theta}}{R}$$
(2.4)

In this equation, ΔW_{surf} relates to energy involved in additional surface energy [109]. Hence upon the generation of the right surface places, a decrease in enthalpy may be observed as shown in Figure 2-11.[109]

Furthermore, upon nanosizing, the increased surface area of nanosized particles should lead to a high number of surface active sites and thus faster kinetics. More importantly, the shortened diffusion distance of hydrogen atoms in nanoparticles could accelerate greatly the kinetics since their diffusion rate in both Mg and MgH₂ is significantly slow, $4 \times 10^{-13} \text{ m}^2.\text{s}^{-1}$ for Mg and $1.5 \times 10^{-16} \text{ m}^2.\text{s}^{-1}$ for MgH₂.

These theoretical predictions have promoted extensive research on the synthesis of Mg nanoparticles and investigations of their hydrogen storage properties. To date, magnesium nanoparticles have been prepared by different methods including ball-milling, electrochemical reduction, vapour transfer, chemical reduction.



Figure 2-11: Size effect on hydrogen desorption enthalpy of Mg according to surface energy of Mg surface plane. [109]

Obviously, for reaching sub-nano and nanometre nanoparticles, ball-milling is not an appropriate method. The particles size reduction is usually limited due to the continuous

fracturing, agglomeration and cold-welding process involved. By ball-milling, magnesium powders with particle size varying from several micrometres to less than 30 nm were obtained. The obtained magnesium particles with size of 30 nm and 50 nm adsorbed hydrogen up to about 6 wt% in 2 hours at 300 °C while at the same condition unmilled magnesium about 1 µm showed almost no hydrogen absorption. [137] If NaCl was added during milling of Mg, the average size further reduced to 17 nm and the material adsorbed 3.8 wt% hydrogen at 300 °C. [138]

To overcome size limitation of ball-milling, various bottom-up methods have developed. Sonoelectrochemical method was reported to be effective to synthesize 4 nm sized magnesium particles with Grignard reagents, ethyl magnesium chloride and butyl magnesium chloride as electrolyte in ethers. [139] Nanoparticles in 5 nm were prepared using magnesium acetate in THF as electrolyte without ultrasonic treatment but with surfactant as a stabiliser. This 5 nm magnesium showed remarkable hydrogen storage properties with hydrogen uptake at 60 °C and release at 85 °C. [140] Chemical reduction is another effective way for the synthesis of magnesium nanoparticles. Magnesium in hexagonal platelet geometries with size ranging from 100 to 500 nm was obtained by chemical reducing methyl magnesium chloride precursor in THF with lithium naphthalenide [141] and a particle size at 300 nm was obtained using MgCl₂ as precursor [142]. A detailed study of the particle size effect on hydrogen storage properties was reported on magnesium nanoparticles prepared using a magnesocene precursor. The prepared sample had crystallite sizes of 25 nm, 32 nm and 38 nm, respectively. The hydrogen sorption kinetics was shown to be dramatically faster for nanocrystals with smaller diameters although there was no big change in activation energy. The authors explained that the large rate of enhancement was likely due to coeffect of the reduction of particle size and the increase of defect density present in

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smaller nanocrystals. [143] Jeon et al [144] reported the use of gas-selective polymer poly(methyl methacrylate) (PMMA) to stabilise Mg nanoparticles prepared by electroless chemical reduction method. Magnesium nanoparticles embodied in polymer matrix had a particle size of 4 nm and showed rapid kinetics for hydrogen loading up to 4 wt% in less than 30 min at 200 °C. Recently, a new method has developed to prepare polymer-stable magnesium nanocomposites using laser ablation and similarly low temperature (250 °C) hydrogen uptake with fast rate was observed. [145]

From the above summarized results, one can conclude that nanosizing of magnesium could speed its kinetics for hydrogen uptake and release, and possibly lower the absorption temperature. However, in the above reported results, no alteration on thermodynamic parameters was characterised on nanosized magnesium. Only recently, a reduction in enthalpy of about 10 kJ.mol⁻¹ H₂ was reported on Mg with particle size smaller than 10 nm, which was confined in carbon aerogels. [146] Another report showed a reduction in enthalpy of 11 kJ.mol⁻¹ H₂ compared with bulk magnesium with magnesium particles ~ 40 nm prepared by acetylene plasma metal reaction. [147]

Therefore, nanosizing has the potential to effectively alter both kinetics and thermodynamics. However, full control of the particle size and further understanding of size effects needs to be achieved.

2.7 Methods for hydrogenation/dehydrogenation of Metal Hydride

Material based research is one possible way to obtain room-temperature hydrogen storage and another pathway is the exploring of a novel hydrogenation/dehydrogenation technique that can charge and discharge hydrogen at room-temperature. In following sections, review of existing techniques for hydrogenation/dehydrogenation will provide a basic background for a novel method.

2.7.1 Direct gas phase method

Direct gas phase method is the simplest and most used method for hydrogen storage in solid materials. Thermodynamics and kinetics are two main aspects of characterizing hydrogen storage materials during this process. The method to measure thermodynamics (enthalpy and entropy) using van't Hoff equation has been discussed in section 2.4.1. For hydrogenation at a certain temperature, a hydrogen pressure above the absorption plateau will drive the formation of hydride. For dehydrogenation at a certain temperature, a hydrogen pressure lower than the desorption plateau will lead the hydrogen release from the hydride.

For kinetics of hydrogenation/dehydrogenation, it is often hard to determine the ratelimiting step since the formation of metal hydrides is a complex process. Figure 2-12 is a one-dimensional Lennard Jones potential curve describing the reaction of hydrogen gas with a metal or alloy. [148] Approaching the surface of metal or alloy surface, hydrogen is physically adsorbed on the surface with E_{phys} of 6 kJ.mol⁻¹ H due to the Van der Waals attractive interactions. Hydrogen physisorption is a fast process and hence generally not rate limiting. [149] The rate-limiting step is usually either the dissociation of hydrogen at the surface, or the diffusion of hydrogen through the hydride to the metal/hydride interface, or a combination of both. [149] The activation barrier (Point 1 in Figure 2-12) for dissociation and formation of the hydrogen-metal bond depends on the chemical composition of the surface and the hydrogen diffusion rate will depend on the diffusion coefficient of hydrogen in Mg and MgH₂ is 4×10^{-13} m².s⁻¹ and 1.5×10^{-16} m².s⁻¹, respectively. So the formed hydride shell has been considered as one factor slowing down the kinetics. [109]



Figure 2-12: One-dimensional Lennard Jones potential curve of the reaction of hydrogen gas with a metal or alloy. [150]

The direct gas phase method is widely used and it provides an effective way to store hydrogen in materials by varying temperature and pressure. However, one problem of this method is heat management since the hydrogenation reaction is exothermic and dehydrogenation reaction is endothermic.

2.7.2 Electrochemical storage method

Electrochemical splitting of an electrolyte is another commonly used technique to store hydrogen in metals or alloys. The experimental setup of an electrochemical system consists of two electrodes immersed in an alkaline electrolyte, e.g. KOH. In the process, the charging is through three steps (Figure 2-13). The first step is hydrogen atoms to adsorb the surface the electrode on of by charge transfer reaction ($H_2O + e^- \leftrightarrow OH^- + H_{ad}$) at the electrode and electrolyte interface. Then the adsorbed hydrogen atoms (H_{ad}) diffuse into the host material to form subsurface hydrogen. Lastly, subsurface hydrogen penetrates into the bulk of the material to form hydride (H_{ads}) . For discharge, the process is reversed. The overall reaction can be expressed as:

$$M + \frac{x}{2}H_2O + \frac{x}{2}e^- \leftrightarrow MH_x + \frac{x}{2}OH^-$$
(2.5)



Figure 2-13: Scheme for electrochemical charging/discharging of metal hydride.

An electrochemical PCI isotherm can be similarly measured as for the gas-phase reaction study of thermodynamics of hydrogen absorption and desorption process.[151] The charge and discharge curves measured on MH alloys at increasing constant current steps (galvanostatic mode) represent the electrochemical equivalent of PCI isotherms in the gas/solid-phase reaction. In fact, there is a strong thermodynamic correlation between the equilibrium pressure measured in gas phase and the electrode potential (E) measured in solution. The E value of the metal hydride electrode could be linked to the hydrogen equilibrium pressure, using Nernst equation. [152]

$$\mathbf{E} = -\frac{\mathbf{RT}}{\mathbf{nF}} \ln \mathbf{P}_{\mathrm{H2}} \tag{2.6}$$

Where E is the equivalent potential; *R* is the universal gas constant: R = 8.314 J.K⁻¹.mol⁻¹; *T* is the absolute temperature; *n* is the number of moles of electrons transferred; *F* is the Faraday constant: $F = 9.648 \times 10^4$ C.mol⁻¹; P_{H2} is the equilibrium pressure.

An advantage of this electrochemical method is that the hydrogen content can be precisely calculated from the amount of charge (Q) that is used during electrochemical (de)hydrogenation. Furthermore, it does not need gaseous hydrogen, so high pressures and high temperatures can be avoided. For example, an Mg₂Ni-based alloy was reported to be hydrogenated and dehydrogenated at 12 mAh.g⁻¹ in 6 M KOH at room temperature and atmospheric pressure instead of gas-phase cycling at 200-300 °C and 28 bar hydrogen pressure. More importantly, according to equation (2.6), a low potential in electrochemical cell is equivalent to a high hydrogen pressure, which has been applied to make AlH₃ reversible at room temperature and atmospheric pressure. [152]

However, the uses of highly alkaline electrolytes limits its application to hydrides with high corrosion resistance, such as LaNi₅ [78, 153, 154] or Mg₂Ni [91, 155, 156] and carbon materials [92, 157, 158], since most of the hydrogen materials are sensitive to corrosion.

2.7.3 Microwave irradiation dehydrogenation

Microwave irradiation can be used to replace the heat energy used in direct gas-phase method, because microwaves can enhance the diffusion of elements within materials and the heating up of materials.

Several groups have carried out research using the microwave process for dehydrogenation of various hydrides. Yuko Nakamori's group has studied a lot of metal hydrides (LiH, MgH₂, CaH₂, TiH₂, VH_{0.81}, ZrH₂, and LaH_{2.48}) and alkali borohydrides (LaBH₄, NaBH₄, and KBH₄) enhanced by microwave irradiation [109, 114, 159]. Their results showed that the microwave irradiation has almost no effect on the temperature change of LiH, MgH₂ and CaH₂, while leading to a rapid temperature rise in TiH₂, VH_{0.81}, ZrH₂ and LaH_{2.48}. However, ZrH₂ and LaH_{2.48} showed no hydrogen desorption

and TiH₂ and VH_{0.81} showed only a small amount of hydrogen with 0.3 and 0.5 wt%, respectively.

For complex hydrides, microwave irradiation showed ineffective heating for NaBH₄ and KBH₄ and a rapid heating above 380 K for LiBH₄. During the microwave irradiation, about 13.7 wt% of hydrogen, almost equal to the theoretical value (13.8 wt%), was desorbed from LiBH₄ in about 30 min. They proposed that the difference upon microwave irradiation is due to the different microwave penetration depth and/or the temperature saturation during the microwave irradiation. [114, 159] The addition of microwave absorbers, such as B and C, increased the dehydrogenation rate of LiBH₄ under microwave irradiation and the desorption time decreased to below 5 min but the released hydrogen reduced to only 6 wt%. [109] Recent research by Zhang et al extended this method to most of the hydrides by supporting the hydrides on an Nicoated honeycomb ceramic monolith and the results showed that the hydrides, such as MgH_2 , $NaAlH_4$ and $NaBH_4$ and LiH, could fully release their hydrogen in 2-3 min. [49] It can be concluded that microwave irradiation could be an effective way to provide energy for hydrogen release from metal hydrides. However, it has no effect on most hydrides if there is no Ni-coated honeycomb ceramic monolith support, but with support the capacity will certainly decrease significantly. Furthermore, the weight of a microwave oven further reduces the storage capacity of metal hydrides.

2.7.4 Laser-assisted hydrogenation and dehydrogenation

Laser energy is another method of heating metal hydrides to store and release hydrogen. Based on this concept, a laser hydriding method was developed by Schwickert et al [160] and this method was used to store hydrogen in titanium and crystalline silicon. Their results showed that this method can effectively store hydrogen up to 47 atom% in titanium in the form of TiH_2 and 8 atom% in crystalline silicon. Recently, Plasma Kinetics Corporation [81] used continuous wave and pulsed laser energy to raise the temperature of MgH₂ or MgNiH₄ + MgH₂ compact disk (CD) to their desorption temperature. These CD disks released 5 wt% hydrogen at the 390 °C beam radius to a depth of 20 μ m. With 11,884 disks, about 4.1 kg hydrogen can be released, which can fuel hydrogen fuel cell vehicles for above 200 miles.

2.6.5 Ultrasonic irradiation dehydrogenation

With an energy carrier medium, ultrasonic irradiation can generate hot spots, which could possibly be adapted for hydrogen desorption from metal hydrides. The treatment of Mg-based hydride in an ultrasonic water bath released hydrogen from the hydride. [161] However, Ares et al. [162] did not detect hydrogen release from MgH₂ decomposition when MgH₂ in decane was ultrasonically treated. The sonication process led to smaller MgH₂ particle size, but no kinetics improvement was found due possibly to the formation of carbon compounds on the surface of MgH₂ hindering its thermal decomposition.

To conclude, the direct gas-phase method is temperature- and pressure dependent and heat management is a problem. The energy required in direct gas-phase method can alternatively be generated by microwave, laser irradiation or sonication to avoid heating the whole system, but these methods are still in research and have limitations, such as they are not applicable to most metal hydrides, the extra weight and volume for the microwave, laser irradiation or sonication generator. Electrochemical method has the ability to charge and discharge metal hydride at room temperature and atmospheric pressure, but the use of the alkaline electrolyte limits its application to corrosiveresistant materials. Therefore, if the alkaline electrolyte can be avoided, it will be possible to charge high capacity metal hydride at room temperature and atmospheric pressure.

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2.8 Summary

It is inevitable that we must turn our fossil fuel based economy to a clean energy based economy due to climate change, environmental problems and rising oil prices. Hydrogen can be an excellent candidate due to its high gravimetric energy density, infinite quantity and zero pollution emissions. Nevertheless, the remaining challenge for the transition from a fossil fuel economy to a hydrogen economy is hydrogen storage. Although many hydrogen storage materials have been studied and several hydrogenation/dehydrogenation techniques have been developed, few of them can satisfy the DOE targets for on-board application. The review on nanosized Mg for hydrogen storage indicated that it can improve kinetics and alter thermodynamics for hydrogen storage. This would be one direction to find suitable material for on-board hydrogen storage. Another approach could be the development of а hydrogenation/dehydrogenation technique that does not rely on pressure and temperature or an alkaline solution to allow room temperature storage in high capacity hydrides. In this thesis, the following routes are going to be investigated:

- 1) Nanosize effects on LaNi₅ and Mg hydrides;
- Novel charging/discharging approach to store and release hydrogen at room temperature and ambient pressure;

The reason for focusing on Mg is because this is a very promising hydrogen storage material. Magnesium has a storage capacity of 7.6 wt% with good reversibility, and it is abundant, inexpensive and nontoxic. The reason for looking at LaNi₅ is because it is widely studied and its study could assist in understanding the evolution of hydrogen storage properties with size effects.

The challenges to achieve the above are:

- 1) To explore the synthesis method for LaNi₅ nanoparticles ;
- 2) To synthesis Mg nanoparticles in a controllable way;
- To develop an electrochemical charging/discharging method which can avoid the use of alkaline electrolyte

The methods that will be implemented are

1) Combustion – reduction method for LaNi₅ nanoparticle synthesis

This method was chosen because I have learnt from the literature that the La-Ni oxide obtained after combustion can be reduced by CaH_2 to obtain LaNi₅. It is possible to obtain nano-sized LaNi₅ by adjusting the combustion temperature and the reduction temperature.

2) Solution reduction method for Mg nanoparticle synthesis

This method was selected because a similar method has been used to synthesise magnesium nanoparticles. By varying the reactants' ratio and type of reducing agent, particles with controllable sizes are expected for the study of size effects on hydrogen storage properties.

3) Gas-phase electrochemical method for room-temperature hydrogen storage

This is a new concept, which combines the advantages of the gas-phase method and the electrochemical method. In this method, a solid electrolyte will be used to replace alkaline electrolyte and gaseous hydrogen as the H source to charge and discharge LaNi₅ and Mg at room temperature and atmospheric pressure.

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CHAPTER 3 SYNTHESIS OF LANI5 NANOMATERIALS AND THEIR HYDROGEN STORAGE PROPERTIES

3.1 Introduction

The first aim of this thesis is to prepare LaNi₅ nanomaterial and study the size effects on hydrogen storage properties as a model of metal hydrides. As discussed in Chapter 2, the conventional method for LaNi₅ production is by melting and casting the individual pure metal La and Ni. The particle size of the commercially obtained LaNi₅ is therefore in the order of 20-200 μ m. [1] To obtain LaNi₅ nanoparticles, a new route that can eventually be adapted for LaNi₅ nanoparticle synthesis needs to be developed.

In this chapter, the new synthetic route of LaNi₅ using combustion-reduction method will be reported. In this process, metal nitrates were used as a starting material and glycine was used as fuel for the solution combustion. The product after combustion was reduced to obtain LaNi₅ nanoparticles. The as-synthesised sample is active for hydrogen storage and the activation procedure can be avoided. Based on their storage properties, size effects of LaNi₅ were discussed compared to commercial LaNi₅. Furthermore, efforts to support LaNi₅ on carbon support were made with the aim of generating smaller nanoparticles.

3.2 LaNi₅ synthesis

LaNi₅ nanoparticles were prepared by combustion – reduction method. Firstly, LaNi_xO_y oxide was synthesised from nitrates of La and Ni using solution combustion method and LaNi_xO_y was then reduced to LaNi₅ nanoparticles with CaH₂ as reducing agent.

3.2.1 Chemicals

Lanthanum nitrate hexahydrate and nickel nitrate hexahydrate from Aldrich and glycine from Merck were used as received for solution combustion. Calcium hydride from Merck and lithium chloride from Sigma-Aldrich were used to reduce lanthanum nickel oxide to LaNi₅. The products were washed with acetic acid from Univar or ammonia chloride from Sigma in absolute ethanol. For supported LaNi₅, graphite supplied by Carbone Lorraine was used as support, which was pre-treated by refluxing in nitric acid and washing with water until pH ~ 7. For comparison purpose, commercial LaNi₅ was purchased from Aldrich and activated by cycling at 80 °C with 40 bar hydrogen pressure for absorption and vacuum for desorption. After five cycles, a fine LaNi₅ powder was obtained.

3.2.2 Combustion-reduction method for LaNi⁵ production

The first step is to prepare lanthanum nickel oxide by self-combustion of nitrates precursors. In this process, glycine was added as a fuel to have a self-sustained reaction. In a typical synthesis, 0.500 g (1 mmol) $La(NO_3)_3 \cdot 6H_2O$, 0.165 g (5 mmol) $Ni(NO_3)_2 \cdot 6H_2O$ and 0.542 g (7.2 mmol) glycine were dissolved in MilliQ water under magnetic stirring. The amount of water added was optimised to 10 ml with considering nitrates and glycine solubility in water. The solution was then transferred into a crucible and evaporated at 100 °C in an oven to obtain a transparent gel. The combustion was ignited by increasing the temperature up to 500 °C and the product was calcined at this temperature for 2 h.

The black powder obtained was then finely mixed with CaH_2 and LiCl in a mass ratio of 1:2:0.9 and transferred into a tubular furnace. The furnace temperature increased from room temperature to 600 °C with a ramp of 5 °C min⁻¹ and kept at 600 °C for 5 h. At this temperature, the material was reduced by reduction-diffusion process under a H₂/Ar (10/90 by volume) flow of 10 mL.min⁻¹. The impurities in the sample were removed by washing with 5% acetic acid or ammonia chloride in absolute ethanol. Finally, the sample was dried in a vacuum oven at 50 °C for 4 h.

3.2.3 Preparation of carbon-supported LaNi5

Attempts were also made to prepare carbon-supported LaNi₅ material using combustion-reduction method.

Prior to the synthesis, carbon was treated with nitric acid to facilitate the loading of precursors by creating hydroxyl groups on the carbon. Carbon was reflux in 28% nitric acid at 80 $^{\circ}$ C for 4 h. Then, the carbon material was filtered and washed with distilled water until pH ~ 7 was reached. Finally, carbon was dried at 120 $^{\circ}$ C for 10 h and kept for coating.

The procedure for carbon-supported $LaNi_5$ is similar to the synthesis of $LaNi_5$. The only difference was the addition of pre-treated carbon in the solution before combustion. The $LaNi_5$ loading on carbon support was calculated to be 30 wt%.

3.3 Results

3.3.1 Products after combustion and their reduction

The reaction during the combustion will proceed as shown in equation 3.1 if La_2O_3 and NiO are assumed to be products after combustion.

$$La(NO_{3})_{3} \cdot 6H_{2}O + 5Ni(NO_{3})_{2} \cdot 6H_{2}O + \frac{65}{9}\varphi C_{2}H_{5}NO_{2} + \frac{65}{4}(\varphi - 1)O_{2} \Rightarrow \frac{1}{2}La_{2}O_{3} + 5NiO + \frac{130}{9}\varphi CO_{2} + \frac{973}{18}\varphi H_{2}O + \frac{13}{18}(5\varphi + 9)N_{2}$$
(3.1)

where φ is the fuel-oxidiser ratio. In a solution combustion reaction, the fuel-oxidiser ratio is an important factor that can affect the combustion temperature and the final products.

Deshpande et al's research on ferric nitrate-glycine system observed that the maximum combustion temperature decreased from 1200 °C for $\varphi = 1$ to 410 °C for $\varphi = 3$. [2] Jung et al investigated the fuel-oxidiser ratio effect on the combustion products during the

combustion of nickel nitrate-glycine system. They found that under fuel-rich conditions the combustion product was metallic nickel, while under fuel-lean and stoichiometric conditions the products were nickel oxide. In our experiment, the fuel-oxidiser ratio of φ = 1 was used.

The products after combustion were in the form of black powder. The crystal structure of the obtained powder were analysed by XRD and is shown in Figure 3-1. The main diffraction peaks of this material were attributed to NiO and La₂NiO₄. Xiao et al [3] used a similar combustion method to prepare LaNi₅ and after combustion the only phase was La_xNi_yO_z and they did not observe peaks of the single component NiO and La₂O₃. They assumed La_xNi_yO_z directly formed during the combustion. The difference in combustion products is possibly due to the fuel-oxidiser ratio, which led to different combustion temperatures.



Figure 3-1: XRD curve of product after combustion of La(NO₃)₃-Ni(NO₃)₂-glycine solution at a fuel-oxidiser ratio of 1.0 and calcinations at 500 °C for 2 h.

Different reduction methods were attempted to reduce NiO and La_2NiO_4 to form $LaNi_5$. The first attempt was to reduce them under a H₂/Ar flow at 800 °C and the reduced products were Ni and La₂O₃ according to XRD shown in Figure 3-2(a). Nickel oxide was reported to be reduced to metallic Ni in a temperature range of 200-400 °C. [4-6] However, to fully reduce $La_xNi_yO_z$ to Ni and La_2O_3 , a temperature higher than 700 °C will be required according to H₂-TPR profiles on La-Ni-O material. [7-9] It is difficult to further reduce La_2O_3 to metallic La by hydrogen due to the strong La-O bonds, which is indicated by the high enthalpy of formation of La_2O_3 (1792 kJ.mol⁻¹). [10] To the best of my knowledge, there is no report on La_2O_3 reduction by gaseous hydrogen to prepare metallic lanthanum, and lanthanum metal is obtained from La_2O_3 by reacting with NH₄Cl followed by reduction of $LaCl_3$ by lithium. [11] Therefore, it is reasonable that a mixture of Ni and La_2O_3 was obtained after reducing the combustion product in hydrogen at 800 °C.



Figure 3-2: XRD curves of combustion products after reduction and washing treatment (a) H_2 reduced, (b) CaH_2 reduced, (c) CaH_2 reduced and acid washed and (d) CaH_2 reduced and NH_4Cl washed.

Calcium hydride was reported to have the capability to reduce La_2O_3 to La, which has been applied to prepare LaNi₅ via a reduction-diffusion process. [12-14] CaH₂ was then attempted to reduce the combustion product and the reaction can be expressed as below:

$$18NiO + 2La_2NiO_4 + 13CaH_2 \rightarrow 4LaNi_5 + 13CaO + 13H_2O$$
(3.2)

After CaH₂ reduction, the XRD curve in Figure 3-2(b) showed clearly the formation of LaNi₅, which is in a hexagonal structure. The crystal size of LaNi₅ was estimated by Scherer equation to be 49 nm. Diffraction peaks from the by-product CaO were also observed as expected from equation (3.2), which indicated that occurrence of the reaction. The CaO by-product can be effectively removed to obtain pure LaNi₅ by washing with diluted acetic acid or NH₄Cl in absolute ethanol as shown in equation (3.3) and (3.4).

$$CaO + 2CH_3COOH \rightarrow Ca(CH_3COO)_2 + H_2O \tag{3.3}$$

$$CaO + 2NH_4Cl \rightarrow CaCl_2 + 2NH_3 + H_2O \tag{3.4}$$

The XRD curves of samples after washing are shown in Figure 3-2(c) and 3-2(d), which both showed pure LaNi₅ phase with the successful removal of CaO after washing with diluted acetic acid or NH_4Cl solution.

Therefore, LaNi₅ nanoparticles were successfully synthesised through a combustionreduction method and the pure phase was obtained by washing with acetic acid or NH₄Cl. Their crystalline size was estimated to be around 49 nm.

3.3.2 Morphology properties of LaNi₅ nanoparticles

The morphology of LaNi₅ nanoparticles was then checked by SEM and TEM. Firstly, SEM was carried out on LaNi₅ nanoparticles after washing with NH₄Cl solution in ethanol and the images are shown in Figure 3-3. For comparison purpose, SEM image of the activated commercial LaNi₅ from Aldrich was also shown in Figure 3-3(d). SEM images of LaNi₅ nanomaterial showed that it is a spongelike material composed of cross-linked small particles with a tremendous number of pores inside. These pores were generated during combustion due to the release of a huge amount of gases. According to reaction (3.1), if the fuel-oxidiser ratio was $\varphi = 1.0$ and respective metal oxides formed, there will be 78.6 moles of gases produced with each molar LaNi₅ production. The rapid release of such a huge amount of gases would generate a porous structure. Image at high magnification (Figure 3-3(c)) showed that the spongelike structure was composed of small particles in spherical or rod-like shape. Spherical particles have an average particle size of 250 nm with a range of 150-400 nm, while the rod-like particles have a diameter about 250 nm and a length of 400 nm. These LaNi₅ nanoparticles are much smaller than the activated commercial LaNi₅ (Figure 3-3(d)), which showed an irregular shape with a wide size distribution of 10-80 µm.



Figure 3-3: (a, b) Low magnification, (c) high magnification SEM image of LaNi₅ synthesised by combustion-reduction method and (d) SEM image of activated commercial LaNi₅.

Further investigation of particles shown in Figure 3-3 (c) by the coupled EDS are shown in Figure 3-4. The EDS result clearly showed the existence of La and Ni. Signal of C is from the SEM grid or possibly residual carbon after combustion and O is possibly due to oxidation during washing process. There was no peak of Ca at 3.69 kev on EDS spectrum, which proved that the CaO by-product was successfully washed away by NH₄Cl solution. EDS mapping analysis on La and Ni indicated that they both were homogeneously dispersed across the material.



Figure 3-4: (a) STEM image, (b) EDS spectrum, EDS mapping of (c) La and (d) Ni of LaNi₅ nanoparticles by combustion-reduction method and washed with NH₄Cl solution. The particle sizes of LaNi₅ were cross checked by TEM and the images are shown in Figure 3-5(a). Again, spherical and rodlike particles were observed in TEM images. The particle sizes were measured and they are in agreement with the values of SEM results. Round particles showed an average particle size of 220 nm and the rodlike particles had a diameter of about 250 nm and a length of 400-500 nm. After cycling, the

nanoparticles showed no change (Figure 3-5(b)). With a similar synthesis method, Xiao et al [3] also synthesised rod-shaped LaNi₅ with similar diameter, but the length of their products were reported to be 6-10 μ m, much larger than that of material reported in this study. We assumed that the difference possibly again originated from the fuel-oxidiser ratio, which would lead to a different combustion temperature and subsequently varied aggregation degree of small particles to form a rodlike shape. TEM images also showed areas with low contrast between the small particles. We assumed it corresponded to the residue carbon during combustion. EDS spectra again showed La and Ni peaks but no Ca peak, which proved again the formation of LaNi₅ phase and successful removal of CaO by-product.



Figure 3-5: TEM images and EDS spectra of (a) as synthesised and (b) cycled $LaNi_5$ nanoparticles prepared by combustion-reduction method and washed with NH_4Cl solution.

3.3.3 Kinetic properties of LaNi⁵ nanoparticles

In order to investigate the hydrogen storage properties of the synthesised $LaNi_5$ nanoparticles, samples after washing with acetic acid or NH_4Cl solution were cycled at room temperature under a hydrogen pressure of 40 bar for absorption and vacuum for desorption.

The sample washed with diluted acetic acid showed no hydrogen absorption and desorption at room temperature. Then the cycling temperature was increased to 80 °C with attempts to activate the sample. The kinetic curves for activation are shown in Figure 3-6. At 80 °C after activation, the storage capacity was still very low (0.35 wt%) and there was no significant improvement in storage capacity after nine cycles. This low storage capacity of the acetic acid treated sample was possibly due to the severe oxidation by acetic acid during washing process.



Figure 3-6: Kinetics curves of LaNi₅ washed with diluted acetic acid at 80 °C under 40 bar H_2 for absorption (abs) and vacuum for desorption (des).

Oxidation has been considered the main factor leading to the storage capacity decay. [15] The oxidation layer on the air-exposed LaNi₅ surface was composed of La₂O₃, La(OH)₃ and metallic nickel. This kind of oxide layer is considered to work as a protective barrier to further oxidation and the capacity decay due to this kind of oxidation can be reactivated. [16, 17] However, with prolonged severe oxidation, the loss of storage capacity cannot be recovered possibly because lanthanum oxide or hydroxide becomes even harder to reduce. [18] A linear relation was found between the degree of oxidation of the LaNi₅ powder and the decrease in hydrogen storage capacity. [19] We assumed that during washing with diluted acetic acid, the protective oxide layer was destroyed by acid and severe deep oxidation occurred to the bulk of the material, which caused unrecoverable loss of hydrogen storage capacity.

Changing the washing solution from acetic acid to NH₄Cl solution in absolute ethanol avoided the severe oxidation caused by acetic acid washing. The kinetics curves of LaNi₅ nanoparticles after washing with NH₄Cl (noted as nano-LaNi₅ hereafter) are shown in Figure 3-7. This material possessed good cyclability without pre-activation treatment and the storage capacity reached 1.0 wt%. This value is lower than the activated commercial LaNi₅ (1.4 wt%). The existence of residual carbon observed by TEM is a possible reason for the capacity difference to commercial LaNi₅. Nano-sizing may also lead to the decrease of hydrogen storage capacity of LaNi₅ as reported on ballmilled materials due to the formation of the amorphous phase. [20] The kinetics for nano-LaNi₅ was 0.4 min for absorption and 1.2 min for desorption at room temperature. Under same conditions, the time required for the commercial LaNi₅ is 1.4 min and 5.0 min for absorption and desorption, respectively. Therefore, nano-LaNi₅ showed much faster kinetics for both absorption and desorption than the commercial material.



Figure 3-7: Kinetics curves of nano-LaNi₅ at room temperature under 10 bar hydrogen H_2 for absorption (abs) and vacuum for desorption (des). Kinetics of activated commercial LaNi₅ under same test conditions were added as a reference.

3.3.4 Thermodynamic properties of LaNi₅ nanoparticles

Above kinetics investigations showed that LaNi₅ nanoparticles washed with NH₄Cl solution showed much better performance in both capacity and kinetics by avoiding severe oxidation from acetic acid washing. Thus, LaNi₅ nanoparticles washed with NH₄Cl solution (nano-LaNi₅) were chosen to study the thermodynamic properties for hydrogen storage. This thermodynamic study started by measuring PCI curves of nano-LaNi₅ as well as that of commercial material. PCI curves of nano-LaNi₅ and commercial LaNi₅ at 26, 50 and 80 °C are shown in Figure 3-8 and the plateau pressures are summarised in Table 3-1.

Sample	PCI Temp. (°C)	Plateau pressure (bar)		H _f	Enthalpy (kJ.mol ⁻¹ H ₂)		Entropy (J.K ⁻¹ .mol ⁻¹ H ₂)	
		abs	des		abs	des	abs	des
Nano-LaNi₅	26	3.82	1.06	1.28				
	50	8.83	3.26	1.00	28.7	36.9	107	124
	50	0.05	5.20	1.00	± 0.4	± 0.4	± 1	± 1
	80	22.29	10.28	0.77				
Commercial LaNi5	26	2.50	1.47	0.53				
	50	5 67	1 5 1	4 0.22	30.3	35.6	109	122
	50	3.07	4.34		±1.6	± 1.2	± 5	±4
	80	16.09	13.15	0.20				

Table 3-1: The plateau pressures, hysteresis factor (H_f), enthalpy and entropy of absorption and desorption of nano-LaNi₅ and commercial LaNi₅.

LaNi₅ nanomaterial showed more sloping plateau compared with commercial LaNi₅. Furthermore, the absorption plateau pressure of nano-LaNi₅ is much higher than that of commercial LaNi₅, while desorption plateau pressure is lower than that of commercial LaNi₅, especially at high temperature, e.g. 80 °C. For example, compared with commercial LaNi₅, nano-LaNi₅ increased the absorption plateau by 6.2 bar, while decreasing the desorption plateau by 2.87 bar at 80 °C. Subsequently, nano-LaNi₅ showed a significant hysteresis loop compared to commercial LaNi₅.

Hysteresis, showing a higher absorption plateau than the desorption plateau, is a common phenomenon of most of the metal hydrides. The extent of hysteresis can be evaluated by the hysteresis factor (H_f), which is deduced from $H_f = \ln(P_{abs}/P_{des})$, where P_{abs} and P_{des} refer to the plateau pressure of absorption and desorption, respectively. [21] The hysteresis factors of LaNi₅ and commercial LaNi₅ were calculated and they both decreased with the increase of PCI temperature (Table 3-1),

which is in agreement with previous reports on other alloys. [21] However, higher hysteresis factor values were observed on nano-LaNi₅ than commercial LaNi₅.



Figure 3-8: PCI curves of (a) nano-LaNi₅ and (b) commercial LaNi₅ absorption (abs) and desorption (des) at 26, 50 and 80 $^{\circ}$ C.

The cause of hysteresis is not fully understood; however, lattice expansion on hydrogenation is believed to be important. [22] The formation of the hydride phase seems to cause an irreversible dislocation in the lattice. These dislocations take up free energy, changing the thermodynamics of the process. [23] This process is lattice strain sensitive as proved by study on effects of lattice strain on the hysteresis for LaNi₅-H₂ system. [24] Therefore, we assume that the change of hysteresis of LaNi₅ is possibly due to the change of lattice strain due to the size reduction. It is also possible that it is

caused by a hindered nucleation hydriding at a pressure close to equilibrium. As reported by Gerasimov et al, a hysteresis was observed on nanocrystalline magnesium and they explained that the nucleation was hindered since the nucleation of each individual particle is proportional to a square of its linear dimension. [25] Therefore, according to their assumption, LaNi₅ nanoparticles have a smaller diameter than commercial LaNi₅ and thus they have a low probability of nucleation under the same pressure.

To further understand the size effects on thermodynamics of LaNi₅, van't Hoff plots of nano-LaNi₅ and commercial LaNi₅ were given in Figure 3-9, enthalpy and entropy for absorption and desorption were calculated and summarised in Table 3-1. Size reduction changed slightly the thermodynamic values for absorption and desorption. For absorption, the value decreased from 30.3 -kJ.mol⁻¹ H₂ and 109 J.K⁻¹.mol⁻¹ H₂ to 28.7 kJ.mol⁻¹ H₂ and 107 J.K⁻¹.mol⁻¹ H₂ for enthalpy and entropy, respectively. For desorption, the value increased from 35.6 kJ.mol⁻¹ H₂ and 122 J.K⁻¹.mol⁻¹ H₂ to 36.9 kJ.mol⁻¹ H₂ and 124 J.K⁻¹.mol⁻¹ H₂ for enthalpy and entropy, respectively.



Figure 3-9: The van't Hoff plots for hydrogen absorption (abs) and desorption (des) of nano-LaNi₅ and commercial LaNi₅.

Unlike the beneficial effects of nanosizing found in magnesium, the reported effects of nanosizing on LaNi₅ were in controversy. Zaluski reported that LaNi₅ nanocrystalline showed faster kinetics than polycrystalline LaNi₅. [26, 27] However, Joseph recently made an opposite conclusion based on increased energy barrier for absorption reaction on milled LaNi₅. [20] However, most attempts on LaNi₅ gave a low hydrogen storage capacity possible due to structural change, [20] or amorphous phase formation. [28, 29] Results of this study showed that nanosizing of LaNi₅ significantly increased the absorption and desorption kinetics, at the same time as it slightly altered the thermodynamics leading to a larger hysteresis.

3.3.5 Carbon-supported LaNi₅

To further reduce particle size of LaNi₅, an attempt to prepare carbon supported LaNi₅ was carried out. The structure of carbon supported LaNi₅ after reduction was checked with XRD (Figure 3-10(a)). As expected, strong peaks from LaNi₅ were detected, and at the same time La₂Ni₅C₃ was observed. Unfortunately, the main diffraction peaks from carbon at 26.4 and 54.5° did not show from this sample.



Figure 3-10: (a) Carbon supported LaNi₅ after reduction and (b) sample prepared with same procedure but no calcination at 500 °C after combustion.

The reaction with La, Ni precursors to form $La_2Ni_5C_3$ is possibly one reason that carbon was consumed during combustion or reduction. $La_2Ni_5C_3$ was reported to be synthesised at 900 °C using elemental components and graphite flakes. [30] Another sample prepared with the same procedure but no calcination after combustion showed the obtained material after reduction contained almost only $La_2Ni_5C_3$, which indicated that under the calcination condition the carbide can react with oxygen or undergo decomposition. Another possible reason for carbon consumption during combustion is directly burning to carbon oxides at high temperature.



Figure 3-11: TEM of carbon-supported LaNi₅ from combustion-reduction method.

Further investigation using TEM as in Figure 3-11 showed that the obtained LaNi₅ are mostly in a rodlike morphology. They have a diameter about 250 nm and length from 700 nm to 2 μ m, and they are separated from the remaining carbon, while for the particles supported on the remaining carbon, the particle sizes are approximately 150 nm, much smaller than the rodlike particles.

The attempt to support LaNi₅ on carbon support was unsuccessful due to consumption of carbon during the combustion or reduction process. Further study is required to avoid the oxidation of carbon support during the preparation process.

3.4 Discussion

3.4.1 Combustion-reduction is an effective method for LaNi⁵ nanoparticle synthesis

LaNi₅ nanoparticles were successfully synthesised by the combustion-reduction method. During the synthesis, La-Ni-O and NiO were firstly obtained by solution combustion of respective nitrates with glycine as a fuel. Then, the combustion products were reduced by CaH₂ to obtain LaNi₅ nanoparticles. The pure LaNi₅ phase can be obtained by washing with acetic acid or NH₄Cl solution. This method is an alternative to the conventional melting-casting method with easily accessible raw materials and less energy consumption. During the synthesis process, several factors can affect the final product and LaNi₅ properties.

(1) Fuel-oxidiser ratio during the solution combustion step

Fuel-oxidiser ratio (ϕ) is an important parameter to control the combustion process, which can lead to a varied adiabatic temperature and a reducing or oxidising environment during combustion.

Thermodynamic analysis was applied to predict the effect of fuel-oxidiser ratio on the adiabatic flame temperature in various combustion systems. [31-36] Calculation can be carried out using enthalpy of formation of the reactants and products and the heat capacity of products at constant pressure. Since the enthalpy of combustion can be expressed as:

$$\Delta H^{\theta} = \left(\sum n H_{p}^{\theta}\right) - \left(\sum n H_{r}^{\theta}\right)$$
(3.5)

and

$$\Delta H^{\theta} = \int_{T\theta}^{T} (\sum n C_p) dT$$
(3.6)

So,

$$T = T_{\theta} + \frac{\Delta H_r^{\theta} - \Delta H_p^{\theta}}{c_p}$$
(3.7)

where *n* is the number of the mole, H_r^{θ} and H_p^{θ} are the enthalpies of formation of the reactants and products, respectively, T the adiabatic flame temperature, T₀ the 298 K and C_p is the heat capacity of products at constant pressure. [37]

Compound	$\Delta H_{f} (kJ mol^{-1})$	$C_p \left(kJ \ mol^{\text{-}1} K^{\text{-}1} \right)$
La(NO ₃) ₃ ·6H ₂ O	-3065.0	-
Ni(NO ₃) ₂ •6H ₂ O	-2212.6	-
$C_2H_5NO_2$	-333.7	-
O ₂	0	0.039
La ₂ O ₃	-1794.5	0.109
NiO	-239.8	0.044
CO ₂	-393.7	0.061
H ₂ O	-241.9	0.051
N_2	0	0.024

Table 3-2: Thermodynamics data for the adiabatic temperature calculations.

Thermodynamics data for the reaction (3.1) were obtained from references and are summarised in Table 3-1. [31, 32, 38] The adiabatic flame temperatures at different φ values were calculated and plotted in Figure 3.1 against the fuel-oxidiser ratio. A slight change of φ from 0.9 to 1.1 will increase the adiabatic temperature from about 700 °C to 1,300 °C, which will most likely lead to a different aggregation degree affecting the particle size. The great dependence of particle size on fuel-oxidiser ratio has been

observed in various systems, e.g. Mg(NO₃)₂-Fe(NO₃)₃-glycine [39], Mg(NO₃)₂-starch [40] and Y(NO₃)₃-Eu(NO₃)₃-glycine [41].



Figure 3-12: Effect of fuel-oxidiser ratio (ϕ) on adiabatic temperature of solution combustion reaction of the La(NO₃)₃-Ni(NO₃)₂-glycine system.

Fuel-oxidiser ratio (φ) also affects the combustion products due to combustion temperature or combustion atmosphere. When $\varphi < 1$, there is an excess amount of oxygen in the reactant mixture and after combustion it will be an oxidative atmosphere. When $\varphi > 1$, oxygen from the ambient environment is required for complete oxidation of the fuel and after combustion there is a reductive atmosphere. Therefore, it is possible to obtain oxides or metals (alloys) by adjusting the fuel-oxidiser ratio. [42] An attempt to increase the fuel-oxidiser to $\varphi = 1.8$ led to the formation of La₂O₃ and NiO instead of La₂NiO₄ and NiO at $\varphi = 1.0$ (Figure 3-13(a)).



Figure 3-13: XRD curves of (a) product after combustion of $La(NO_3)_3$ -Ni $(NO_3)_2$ -glycine solution at a fuel-oxidiser ratio of 1.8 and calcinations at 500 °C for 2 h and (b) the above material after reduction by CaH₂ with LiCl as a melting agent at 600 °C.

(2) Reducing agent and reduction temperature during reduction process

Results of this study showed that hydrogen reduction of La_2NiO_4 and NiO at 1000 °C led to a mixture of Ni and La_2O_3 . CaH₂ was proved to be an effective reducing agent to reduce the combustion produce to $LaNi_5$. The actual reducing agent is Ca from the decomposition of CaH₂ at a temperature higher than 600 °C. [12] Tanabe and Asaki investigated the formation mechanism of $LaNi_5$ through the reduction of $La_2O_3 + Ni$ by CaH₂. [12] An intermediate CaNi₅ was observed and they proposed the formation mechanism as below:

$$Ca(l) + 5Ni(s) \to CaNi_5(s) \tag{3.8}$$

$$3Ca(l) + La_2O_3(s) \to 2La(l) + 3CaO(s)$$
 (3.9)

 $CaNi_{5}(s) + La(l) \rightarrow LaNi_{5}(s, l) + Ca(l)$ (3.10)

A temperature of 1000 °C was required to reduce $La_2O_3 + Ni$ mixture to $LaNi_5$ with CaH₂. [43] The addition of a melting agent (LiCl) can be used to reduce the reduction temperature. [3] The formation of La-Ni-O oxide is possibly another factor that led to a low reduction temperature of 600 °C in this study, because the attempt to reduce $La_2O_3 + NiO$ with LiCl as a melting agent at 600 °C led to a mixture of $La_2O_3 + Ni$ (Figure 3-13(b)), while under same condition La_2NiO_4 and NiO was reduced to $LaNi_5$.

(3) Oxidation problem during the washing step

Diluted acetic acid solution and NH₄Cl solution in absolute ethanol were proved efficient to remove the CaO by-product after reduction with CaH₂. However, samples after washing with these two solutions showed very different hydrogen storage properties. We assumed that acetic acid solution could lead to deep oxidation of LaNi₅ and loss of its hydrogen storage capacities. Therefore, NH₄Cl solution is a better choice than diluted acetic acid to LaNi₅ after reduction with CaH₂.

As discussed above, if these factors could be well controlled, the combustion-reduction method would be a good pathway to prepare LaNi₅ and the particle size can be in the range of nanoscale.

3.4.2 Size effects on hydrogen storage properties of LaNi5

Comparison of the storage properties of LaNi₅ nanoparticles with that of commercial LaNi₅ showed that nano-sizing greatly improved the absorption and desorption kinetics. At the same time, reaction thermodynamics also altered due to the size reduction.

The diffusion coefficient of LaNi₅ and LaNi₅H₆ are reported to be in the range of 10^{-8} - 10^{-9} cm².s⁻¹ at 25 °C. [44, 45] Therefore, it is reasonable to assume fast kinetics with shortened diffusion pathway with the particle size reduced from 10-80 µm for commercial LaNi₅ to around 250 nm for LaNi₅ nanoparticles. However, previous
investigation on ball-milled LaNi₅ nanomaterials showed that the kinetics depended on the treatment time. Short-time ball-milling, e.g. 1 min, improved the kinetics, [46] but 100 h-milled sample dramatically slowed down the kinetics and also reduced the storage capacity. [47] This was assumed to be due to the formation of amorphous nanoparticles since the milling of metallic La and Ni for 30 h produced amorphous LaNi₅ of 25 nm, which showed only 0.4 wt% hydrogen storage. [48]

Nanoparticles from the combustion method were usually well crystallised due to the high combustion temperature. Therefore, LaNi₅ nanoparticles from high temperature combustion-reduction method showed a well-defined hexagonal crystal structure, which is proved by the XRD results (Figure 3-2). With eliminating the negative effective from amorphous phase of ball-milled LaNi₅, the LaNi₅ nanoparticles from combustion-reduction showed clearly fast kinetics due to the size reduction (Figure 3-7).

LaNi₅ nanoparticles from the combustion–reduction reaction showed a lower absorption enthalpy and higher desorption plateau, which led to a larger hysteresis with increased absorption plateau and decreased desorption plateau. Similar to nanoparticles of this study, ball-milled LaNi₅ nanocrystalline also showed sloping absorption and desorption plateau, [29] but no enthalpy value and entropy value was reported due to poor storage properties of the ball-milled LaNi₅. This is the first time that detectable enthalpy and entropy change due to size effects was reported.

3.5 Conclusions

The solution combustion method is proved to be a feasible way to synthesise lanthanum nickel oxides with easily controlled component ratio. By reducing this oxide in hydrogen flow with the addition of CaH_2 , $LaNi_5$ nanomaterials with crystallite size of 49 nm were prepared. The by-product after reduction, CaO, was successfully removed by washing with diluted acetic acid or NH_4Cl in absolute ethanol. However, washing

with acetic acid led to severe oxidation to LaNi₅ and as a result it reversibly absorbed only less than 0.4 wt% hydrogen at 80 °C even after activation. Washing with NH₄Cl in absolute ethanol avoided the oxidation problem and the obtained material can reversibly store 1.0 wt% hydrogen at room temperature without activation procedure. Compared with the activated commercial LaNi₅, nanosizing showed very fast kinetics due to a short diffusion pathway. At the same time, it slightly decreased the absorption enthalpy but increased the desorption enthalpy.

Furthermore, the efforts to prepare carbon supported $LaNi_5$ were unsuccessful with the solution combustion method due to the consumption of carbon during combustion or reduction steps. Further investigations to protect carbon from consumption are required so that $LaNi_5$ can be well dispersed on it.

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CHAPTER 4 MAGNESIUM NANOPARTICLES SYNTHESISED BY SOLUTION REDUCTION METHOD

4.1 Introduction

The study on size effects with LaNi₅ as a model in Chapter 3 showed that size reduction improved the kinetics and altered the thermodynamics of LaNi₅. We will investigate the size effects on high capacity metal hydride, MgH₂, in this chapter.

The literature review about nano-sized magnesium for hydrogen storage in Chapter 2 indicated that solution reduction method is an effective way to generate magnesium nanoparticles with a high yield. Reduction of Mg salts using an alkali metal in solution was firstly developed by Rieke in the 1970s [1] for the preparation of organometallic compounds. [2, 3] Generally, Rieke magnesium is synthesized by reducing anhydrous MgCl₂, MgBr₂ or MgI₂ with alkaline metals in THF or diglyme in the presence of naphthalene as an electron carrier to lead to Mg particles with a size around 300 nm. [4] Through the reduction of organomagnesium, the method also led to Mg nanoparticles with physical properties depending upon the electron carrier type and organomagnesium used as well as the concentrations of reactants. [5, 6]

In this chapter, we report a facile synthesis of magnesium nanoparticles by a solution reduction method using di-*n*-butylmagnesium as precursor, which has proven to be an excellent starting material for the generation of MgH_2 nanoparticles by thermal hydrogenolysis. [7, 8] The effect of the type of reducing agent and its concentration on nanoparticles synthesised and their hydrogen storage properties were investigated.

4.2 Synthesis of magnesium nanoparticles

All operations of synthesis were carried out under inert atmosphere in an argon-filled LC-Technology glove box with oxygen and moisture level less than 1 ppm.

Lithium, potassium, naphthalene, and 1.0 M di-*n*-butylmagnesium solution in heptane were purchased from Aldrich. Tetrahydrofuran (THF) was purchased as HPLC grade from Fisher Scientific and dried using a LC Technology SP-1 Solvent Purification System. Naphthalene was dried by recrystallization under vacuum at 60 °C. Sodium from Merck and potassium were washed several times with fresh THF to remove mineral oils on their surface before use. Magnesium hydride from Merck was ball-milled for three times of 10 min at 20 Hz on a Retsch MM301 mill to use as a reference material. All other chemicals were used as received.

4.2.2 Synthesis method

The magnesium nanoparticles were synthesized by reducing di-*n*-butylmagnesium $(Mg(Bu)_2)$ in THF using an alkali metal as reducing agent. Naphthalene was added as an electron carrier in the synthesis medium as indicated in equations below.

$$M + \bigcup \longrightarrow M^{+} \left[\bigcup \right]$$
(4. 1)

$$Mg(Bu)_{2} + 2M^{+} \left[\swarrow + 2BuM \right] + 2W^{+} \left[\swarrow + 2BuM \right]$$
(4. 2)

where M is an alkali metal: lithium, sodium or potassium.

Firstly, the effect of different reducing agents was investigated by *in-situ* generation of alkali metal naphthalenides in the reaction system. To ensure all magnesium precursor could be converted to magnesium, excess alkali metals were added. The amount of alkali metal and Mg(Bu)₂ was kept constant at 9.2 to 1 in molar ratio. Since naphthalene can be cycled during the reaction, the amount of naphthalene in the system was only about 5 mol% of that of alkali metals. In a typical synthesis, naphthalene (0.436 g, 3.4 mmol) and di-*n*-butylmagnesium solution in heptane (7 mL, 7 mmol) were dissolved in

20 mL THF. This solution was then transferred into a 250 mL round-bottom flask containing some pieces of alkali metals (64.6 mmol) suspended in THF (30 mL) under vigorous stirring at room temperature. The reaction was left to proceed for 24 h and unreacted alkali metals were taken out before separating the product by centrifugation. The product was then washed with THF until the supernatant was clear. The powder obtained was finally dried under vacuum on a Schlenk line overnight leading to a black material.

After that, lithium was taken as an example to study the concentration effect of reducing agents on particle sizes. The synthesis process was the same but with varied amounts of alkali metals and naphathelene to get different concentrations of lithium naphthalenide. For all samples prepared with different concentrations of reducing agent, the amount of $Mg(Bu)_2$ was kept same at 7 mmol.

The materials are noted MgM_xNapht_y , where *x*, *y* represent molar ratio of alkali metals and naphthalene to di-*n*-butylmagnesium, respectively. These materials should be handled with care, because they are very pyrophoric materials once exposed to air.

4.3 Effects of different reducing agents

TGA-DSC-MS was firstly carried out on the as-synthesised materials. As shown in Figure 4-1, the as-synthesised samples started partial decomposition from 100 °C, and this was attributed to the decomposition of the alkali naphthalenide and the remaining *n*-BuM (*n*-butyllithium, *n*-butylsodium or *n*-butylpotassium). The decomposition of *n*-BuLi proceeded in the reaction (4.3) with the formation of LiH and the release of 1-butene as detected by MS. [9]

$$n - BuLi \rightarrow 1 - butene + LiH \tag{4.3}$$



Figure 4-1: TGA-DSC and MS of the as-synthesised magnesium nanoparticles (a) MgLi_{9.2}Napht_{0.5}, (b) MgNa_{9.2}Napht_{0.5} and (c) MgK_{9.2}Napht_{0.5}.

In the case of *n*-BuNa and *n*-BuK, the reaction follows the same route but leads to the respective metal because hydrogen pressures in excess of 10 bar are required to form the corresponding hydride. [10-12] In the case of lithium, hydrogen pressures below 1 bar is sufficient to form LiH, [13] and such an hydrogen pressure is generated during the decomposition process. Furthermore, the additional weight loss above 400 $^{\circ}$ C observed

by TGA for MgNa_{9.2}Napht_{0.5} and MgK_{9.2}Napht_{0.5} are assumed to be a result of partial sodium and potassium evaporation. Since sodium and potassium melt at 63.5 and 97.8 °C respectively, and have a high vapour pressure at 400 °C, [14] some evaporation can be expected during TGA measurement. Hence, upon a first heat treatment under vacuum at 100 °C, it should be possible to decompose the remaining alkali naphthalenide and *n*-BuM to generate an alkali coating at the surface of the magnesium nanoparticles.

4.3.1 Structure and morphology properties

The X-Ray Diffraction (XRD) was carried out to characterise the magnesium materials treated at 100 °C under vacuum before hydrogenation. The diffraction patterns are shown in Figure 4-2. All these three samples showed diffraction peaks mainly from the hexagonal Mg phase, which indicated the successful reduction of di-*n*-butylmagnesium with alkali naphthalenides.

The MgLi_{9.2}Napht_{0.5} also showed weaker peaks from LiH resulting from the partial decomposition of remaining *n*-butyllithium. As expected, samples synthesised with the sodium and potassium naphthalenide also showed diffraction peaks from metallic sodium and potassium. Such phases result from the decomposition of the remaining *n*-BuM as previously discussed as well as the decomposition of their respective naphthalenide on the magnesium surface at the end of the synthetic process. Indeed, spontaneous decomposition of the corresponding naphthalenide compound into naphthalene and metallic sodium has been reported at low pressure. [15] Furthermore, diffraction peaks of hydroxides were observed on the XRD patterns of MgNa_{9.2} Napht_{0.5}, which were most likely from the partial oxidation of Na or K with moisture during XRD measurement.

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Figure 4-2: XRD curves of magnesium nanoparticles (a) MgLi_{9.2}Napht_{0.5}, (b) MgNa_{9.2}Napht_{0.5} and (c) MgK_{9.2}Napht_{0.5}.

The morphology of these magnesium materials were checked by TEM. As shown in Figure 4-3, analysis by TEM revealed that the obtained magnesium nanoparticles displayed spherical morphology for all three samples but the particle size differed depending on the reducing agent. MgLi_{9.2}Napht_{0.5} and MgK_{9.2}Napht_{0.5} showed a mean particle size of 18 nm within a range from 8 to 40 nm, while MgNa_{9.2}Napht_{0.5} possessed a much broader size distribution from 7 nm to 52 nm and a slightly larger mean particle size at 24.4 nm.

Analysis by Energy Dispersive X-ray Spectroscopy (EDS) confirmed that the nanoparticles observed by TEM were composed of Mg. In agreement with the XRD analysis, signals from sodium and potassium were also detected on MgNa_{9.2}Napht_{0.5} and MgK_{9.2}Napht_{0.5}, respectively. Lithium from *n*-butyllithium in MgLi_{9.2}Napht_{0.5} cannot be detected with our EDS. Further elemental mapping also indicated the close proximity of

the magnesium nanoparticles and the coating elements suggesting the formation of an alkali coating (Figure 4-4). However, due to the relatively small size of the nanoparticles, it was difficult to achieve high resolution images on individual particles. Therefore, it is reasonable to assume that the reduction of di-*n*-butylmagnesium with an excess of Li, Na or K probably led to a mixture of isolated alkali and coated magnesium nanoparticles. Hence, the materials synthesised are most likely composed of magnesium nanoparticles surrounded by a Li, Na or K phase, especially when considering the low melting temperature of these alkali metals as compared to magnesium.



Figure 4-3: TEM images and the EDS spectra of magnesium nanoparticles (a) MgLi_{9.2}Napht_{0.5}, (b) MgNa_{9.2}Napht_{0.5} and (c) MgK_{9.2}Napht_{0.5}.





Figure 4-4: STEM images and elemental mapping of (a) $MgNa_{9.2}Napht_{0.5}$ and (b) $MgK_{9.2}Napht_{0.5}$. Due to the instrumental limitations, it was not possible for lithium mapping.

4.3.2 Hydrogen absorption and desorption properties

Hydrogen absorption and desorption investigations were started by carrying out HP-DSC measurements on these nanomaterials in order to determine the required temperature for hydrogen uptake and release. For absorption, all three samples showed three exothermic peaks with temperatures ramping up to 450 $^{\circ}$ C at a rate of 5 $^{\circ}$ C.min⁻¹ under 30 bar hydrogen pressure as shown in Figure 4-5.



Figure 4-5: HP-DSC curves of (a) $MgLi_{9.2}Napht_{0.5}$, (b) $MgNa_{9.2}Napht_{0.5}$, (c) $MgK_{9.2}Napht_{0.5}$ (1st cycle) and d) $MgK_{9.2}Napht_{0.5}$ (2nd cycle).

MgLi_{9.2}Napth_{0.5} displayed low temperature absorption events with peaks at 120, 167 and 284 °C that may reflect the uptake of hydrogen by Mg at different particle sizes. The kinetic measurements on this material at 120 °C and XRD measurement after absorption (Figure 4-6) proved a 0.9 wt% hydrogen uptake by Mg in less than 5 h, i.e. nearly 50% of the storage capacity of this material. In contrast to MgLi_{9.2}Napth_{0.5}, MgNa_{9.2}Napth_{0.5} was hydrogenated at much higher temperature with exothermic peaks at 200, 342 and 392 °C, and these exothermic events were once more attributed to the absorption of magnesium with different particle sizes or possibly reactions involving the remaining Na. MgK_{9.2}Napth_{0.5} showed a low temperature peak at 112 °C and the other two peaks at 193 and 337 °C. However, TGA-DSC-MS of the as-prepared material (Figure 4-3(c)) and the second HP-DSC cycle indicated the low temperature peak was from the thermal decomposition of the remaining *n*-butylpotassium in the fresh sample. The high temperature peaks were attributed to the hydrogenation of magnesium nanoparticles or possibly reaction involving the remaining K.



Figure 4-6: XRD curve of $MgLi_{9.2}Napth_{0.5}$ hydrogenated at 120 °C. The insertion showed the kinetics at 120 °C.

The hydrogen desorption behaviour was also checked by HP-DSC under a pressure of 0.5 bar. $MgLi_{9.2}Napth_{0.5}$ and $MgK_{9.2}Napth_{0.5}$ showed only one peak for hydrogen desorption situated at 373 and 337 °C, respectively, while $MgLi_{9.2}Napth_{0.5}$ showed two desorption peaks at 360 and 375 °C.

The materials were then cycled at 300 °C under a hydrogen pressure of 30 bar for absorption and 0.5 bar for desorption. The crystal structures after cycling were analysed by XRD and the results are shown in Figure 4-7. The peaks from the hexagonal Mg phase in the as-prepared materials (Figure 4-2) completely disappeared, which means that under the cycling conditions these magnesium nanoparticles can be fully hydrogenated.



Figure 4-7: XRD curves of hydrogenated samples after cycling at 300 °C: (a) MgLi_{9.2}Napht_{0.5}, (b) MgNa_{9.2}Napht_{0.5} and (c) MgK_{9.2}Napht_{0.5}.

MgLi_{9.2}Napth_{0.5} was fully converted β -MgH₂ with a LiH phase and a small Li₂C₂ phase possibly resulting from the decomposition of *n*-butyllithium. Interestingly, in addition to β -MgH₂, MgNa_{9.2}Napth_{0.5} also showed diffraction peaks from NaMgH₃ and NaH phase. The perovskite hydride NaMgH₃ possesses an orthorhombic structure and has a rapid H motion at an elevated temperature above 100 °C, [16] which has been suggested to be used to improve the slow hydrogenation kinetics of some strongly bound light-metalhydride systems, such as MgH₂. [17] Similarly, KMgH₃ in cube perovskite structure and potassium phase were detected in MgK_{9.2}Napth_{0.5}. Pure NaMgH₃ and KMgH₃ in the same crystal structure were prepared by ball-milling NaH or KH with MgH₂ in 1:1 molar ratio. [18] Herein we found these materials could be prepared by wet chemical method followed by hydrogenation.

To further investigate the desorption properties of these magnesium nanoparticles and the effect of perovskites, the hydrogenated materials were desorbed by TGA-DSC from room temperature to 500 °C and gas evolution was followed by MS (Figure 4-8). MgLi_{9.2}Napth_{0.5} showed two hydrogen desorption peaks at 355 and 470 °C, respectively. As proved by XRD of the hydrogenated sample, the former was assigned to the decomposition of MgH₂ and the latter to the decomposition of LiH. It is noteworthy that this decomposition temperature of LiH is significantly lower than the 688 °C necessary for the decomposition of bulk LiH. [19] This indicated that the LiH is in nanoscale, which supports the hypothesis of Mg nanoparticles fully coated or embedded in a LiH matrix.

MgNa_{9.2}Napth_{0.5} had three overlapped hydrogen desorption peaks in the temperature range of 350 to 390 °C. Since the hydrogenated sample showed three different phases, MgH₂, NaMgH₃ and NaH, each desorption peak is corresponding to the decomposition of one phase. Furthermore, the decomposition of NaMgH₃ was reported to process in the following two steps: [20, 21]

$$NaMgH_3 \rightarrow NaH + Mg + H_2$$
 (4-4)

$$NaH + Mg + H_2 \rightarrow Na + Mg + \frac{3}{2}H_2$$
(4-5)

Nanosized NaMgH₃ and NaH were found to decompose at 365 and 387 °C, respectively. [22] Therefore, in our results, the peak at 370 °C is believed to correspond to NaMgH₃ desorption and the one at 387 °C to NaH decomposition. Then the remaining peak at 351 °C was assigned to MgH₂ desorption. We can also assign these peaks according to their reaction enthalpy. The reported desorption enthalpy values are in the order MgH₂ (-74.1 kJ.mol⁻¹ H₂) [23] < NaMgH₃ (-86.6 kJ.mol⁻¹ H₂) [24] and NaH (-116 kJ.mol⁻¹ H₂) [18] and so the desorption temperature would follow the same trend.



Figure 4-8: TGA-DSC and MS of released hydrogen of the hydrogenated magnesium nanoparticles at 300 °C (a) $MgLi_{9.2}Napht_{0.5}$, (b) $MgNa_{9.2}Napht_{0.5}$ and (c) $MgK_{9.2}Napht_{0.5}$.

KMgH₃ was reported to decompose in one single step as shown in equation (4-6) with a desorption enthalpy of 110 kJ.mol⁻¹ H₂. [18, 25, 26]

$$KMgH_3 \rightarrow K + Mg + \frac{3}{2}H_2$$
 (4-6)

Therefore, the high temperature desorption peak of $MgK_{9.2}Napth_{0.5}$ at 403 °C should correspond to the release of hydrogen from KMgH₃ and the one at 342 °C to MgH₂ desorption.

4.3.3 Kinetics and thermodynamics

The hydrogen absorption and desorption kinetics (Figure 4-9) were measured on materials after heat treatment at 100 °C under vacuum. The magnesium nanoparticles prepared with lithium and potassium naphthalenide showed relatively fast absorption kinetics with full storage capacity reached in less than 10 min. For MgNa_{9.2}Napth_{0.5}, the absorption kinetics was slower and this may be due to the higher temperature required to form the NaMgH₃ phase as compared to the KMgH₃, i.e. 392 °C instead of 337 °C, respectively (Figure 4-5). The formation of NaMgH₃ was reported to occur upon heating NaH and MgH₂ for one week at 380 °C under 70 bar hydrogen pressure.[27] In this study, with the Mg/MgH₂ in nanometre scale, NaMgH₃ was formed in less than 2 h as proved by XRD (Figure 4-7) after hydrogenation at 300 °C.

Desorption kinetics were found to be relatively fast for MgLi_{9.2}Napht_{0.5} in comparison to MgNa_{9.2}Napht_{0.5}. It took less than 100 min to release hydrogen from MgLi_{9.2}Napht_{0.5}. For MgK_{9.2}Napht_{0.5}, the desorption kinetics drastically slowed down after the first 75 min and this is due to the slow decomposition of the perovskite phase at 300 °C. According to the TGA-DSC-MS measurements (Figure 4-8), desorption kinetics would correspond to the release of hydrogen from the MgH₂ core and then the perovskite phases. Hence, comparing MgNa_{9.2}Napth_{0.5} and MgK_{9.2}Napth_{0.5}, it would appear that KMgH₃ leads to faster hydrogen kinetics as compared to NaMgH₃. However, this difference in hydrogen kinetics may also be the result of the smaller sizes of the magnesium particles resulting from the potassium reduction.



Figure 4-9: Hydrogen absorption and desorption kinetics of magnesium nanoparticles (a) MgLi_{9.2}Napht_{0.5}, (b) MgNa_{9.2}Napht_{0.5} and (c) MgK_{9.2}Napht_{0.5}.

In the case of MgLi_{9.2}Napht_{0.5}, the LiH phase remains unchanged upon hydrogen release at 300 °C. Indeed, a temperature higher than 450 °C is required for the decomposition of LiH according to the TGA-DSC-MS analysis of MgLi_{9.2}Napht_{0.5} (Figure 4-8). Accordingly, a lower hydrogen storage capacity of 2 wt% was obtained for MgLi_{9.2}Napht_{0.5} in comparison to MgNa_{9.2}Napht_{0.5} and MgK_{9.2}Napht_{0.5} (Figure 4-9). More remarkably, TEM analysis of the cycled materials revealed that these coated nanoparticles remain stable upon cycling with little aggregation and sintering observed (Figure 4-10 and Table 4-1)



Figure 4-10: TEM images, EDS spectra and size distribution of magnesium nanoparticles after cycling at 300 °C (a) MgLi_{9.2}Napht_{0.5}, (b) MgNa_{9.2}Napht_{0.5} and (c) MgK_{9.2}Napht_{0.5}.

To determine the thermodynamics of these materials, pressure-composition isotherm (PCI) measurements were carried out at three different temperatures and the results for hydrogen sorption are plotted in Figure 4-11.



Figure 4-11: PCI curves of magnesium nanoparticles (a) MgLi_{9.2}Napht_{0.5}, (b) MgNa_{9.2}Napht_{0.5} and (c) MgK_{9.2}Napht_{0.5}.

All samples showed a single plateau pressure, which was attributed to the hydrogenation of Mg. The absorption plateau for NaMgH₃ and KMgH₃ formation could not be detected since their plateau pressures are too low at 300 °C, which was calculated to be 0.05 bar for NaMgH₃ and 0.0035 bar for KMgH₃ at 300 °C using van't Hoff equation and their reported enthalpy and entropy values. [24]

$$\ln p = \frac{\Delta H}{RT} - \frac{\Delta S}{R} \tag{4-7}$$

Calculations from the van't Hoff plots (Figure 4-12) indicated a large decrease of Δ H to -66.9 ± 2.5 kJ.mol⁻¹ H₂ for MgLi_{9.2}Napht_{0.5} and -63.2 ± 2.8 kJ.mol⁻¹ H₂ for MgK_{9.2}Napht_{0.5} in comparison to ball milled magnesium measured under the same conditions (Table 4-1). For MgNa_{9.2}Napht_{0.5} this value was closer to that of ball milled magnesium, i.e. -71.7 ± 0.8 kJ.mol⁻¹ H₂. The lower enthalpy values calculated for MgLi_{9.2}Napht_{0.5} and MgK_{9.2}Napht_{0.5} were also accompanied by a drop in entropy (Δ S). Hence, Δ S around -120 kJ.K⁻¹.mol⁻¹ H₂ was obtained for MgLi_{9.2}Napht_{0.5} and MgK_{9.2}Napht_{0.5} instead of the -139.0 kJ.K⁻¹.mol⁻¹ H₂ obtained for ball milled MgH₂.

Table 4-1: Property summary of magnesium nanoparticles prepared using different

1 * 1	C 1	•	
kinds	of red	ucing	agent.

Sample	Particle size (nm)		Thermodynamics		
	As- synthesised	After cycling	Enthalpy (kJ.mol ⁻¹ H ₂)	Entropy (J.mol ⁻¹ H ₂ .K ⁻¹)	
MgLi _{9.2} Napht _{0.5}	8-40 (18)	8-40 (19)	-66.9 ± 2.5	-122.1 ± 4.9	
MgNa9.2Napht0.5	7-52 (24)	9-46 (26)	-71.7 ± 0.8	-130.9 ± 1.4	
MgK9.2Napht0.5	8-32 (18)	8-29 (18)	-63.2 ± 2.8	-117.8 ± 4.6	
Ball milled MgH ₂	-	-	-75.2 ± 1.8	-139.0 ± 3.0	



Figure 4-12: van't Hoff plots of the magnesium nanoparticles.

Although a significant decrease in enthalpy was achieved, the corresponding entropic compensation resulted in overall less change in thermodynamic properties as compared to bulk magnesium than expected. The formation of perovskite structures was reported to have no influence on the thermodynamic properties of bulk MgH₂. [28] This may also be the case at the nanoscale considering the results obtained. Indeed, MgLi_{9.2}Napht_{0.5} and MgK_{9.2}Napht_{0.5} underwent thermodynamic changes while the thermodynamic properties of MgNa_{9.2}Napht_{0.5} remained closed to that of ball milled MgH₂. The shift in enthalpy and entropy measured for MgLi_{9.2}Napht_{0.5} and MgK_{9.2}Napht_{0.5} and MgK_{9.2}Napht_{0.5} may thus be the result of their smaller particles sizes only.

4.4 Effects of the concentration of reducing agent

Investigation of the effect of the reducing agent showed that all investigated alkali (Li, Na and K) naphthalenides could reduce di-*n*-butylmagnesium to generate magnesium nanoparticles, but magnesium from Na reduction showed larger particle size than that of

Li and K reduced materials. Furthermore, magnesium nanoparticles from Na and K reduction formed a perovskite structure upon cycling, which will affect the kinetics of magnesium nanoparticles. To investigate size effects without influence from these perovskite structures, lithium naphthalenide was thus chosen to study its concentration on the Mg particle sizes and their hydrogen storage properties.

4.4.1 Structure and morphology properties

Since naphthalene is necessary to enhance the electron transfer rate in the reduction of the organomagnesium by lithium, varied naphthalene concentrations should influence the number of Mg nuclei generated, the growth process and thus the final physical properties of the Mg synthesised. Hence, we investigated the influence of low and excessive naphthalene concentrations on the overall final properties of the Mg nanoparticles synthesised. Since excess lithium may keep lithium naphthalene concentration constant to have a narrow size distribution and also possibly prevent Mg aggregation, we also investigated the formation of Mg nanoparticles at excessive lithium content.

Four samples were prepared at different lithium/naphthalene ratio. Analysis by TEM revealed different morphologies for the four lithium/naphthalene ratios investigated. At low naphthalene concentrations, compared with MgLi_{9.2}Napht_{0.5}, decreasing the amount of lithium led to nanoparticles of similar shape and size. The MgLi_{4.6}Napht_{0.5} sample with half the amount of lithium displayed spherical Mg nanoparticles with a size ranging from 10 to 34 nm (Figure 4-13a). However, increasing naphthalene concentrations to ensure fast electron transfer and thus rapid growth resulted in bigger Mg particles with sizes ranging from 140 to 350 nm (Figure 4-13(c)). It is thus apparent that the concentration of the initial reagents can drastically influence the physical

properties of the final material and thus low lithium naphthalide concentrations lead to smaller particle sizes.





All four samples showed the same crystal structure corresponding to the hexagonal Mg phase mainly as shown by XRD patterns in Figure 4-14. Further analysis of the XRD patterns by the Rietveld method revealed relatively similar Mg crystallite sizes (~27 nm) for all the materials except for MgLi_{4.6}Napht_{4.6} having a slightly higher average crystallite size of 34 nm (Table 4-2). Nevertheless, as found in MgLi_{9.2}Napht_{0.5}, elemental analysis confirmed that the as-synthesised materials contained some residual lithium. The lithium content is within the range of 16.8 to 30.1 wt % with MgLi_{9.2}Napht_{0.5} showing the highest lithium content. This can be explained by the remaining *n*-butyllithium generated from (4.2) in THF and lithium naphthalenide as

discussed in section 4.3.1. The *n*-butyllithium could be removed upon heating above 100 °C. [9]

 Table 4-2: Particle size and crystallite size analysis of magnesium nanoparticles from

 different concentrations of reducing agent.

Sample	Particle size (nm)		Crystallite size (± 3 nm)		Content by ICP (wt %)	
	Fresh	Cycled	fresh	cycled	Mg	Li
MgLi _{4.6} Napht _{0.5}	8-34 (15)	8-34 (16)	27	42	58.5	16.8
MgLi9.2Napht0.5	8-40 (18)	8-40 (19)	23	39	23.0	30.1
MgLi _{4.6} Napht _{4.6}	140-350 (247)	129-360 (249)	34	47	63.3	14.9
MgLi _{9.2} Napht _{4.6}	70-130 (112)	71-442 (136)	26	40	42.8	28.7



Figure 4-14: XRD patterns of the as-synthesised magnesium nanoparticles with varied lithium/naphthalene ratio.

4.4.2. Hydrogen absorption and desorption properties

HP-DSC measurements were carried out on these nanomaterials to determine the hydrogenation temperature. Except for MgLi_{4.6}Napth_{4.6}, all the materials started to absorb hydrogen from relatively low temperatures below 150 °C with most of the hydrogen uptake completed by 300 °C (Figure 4-15). MgLi_{4.6}Napth_{4.6} absorbed hydrogen from 200 °C with a single peak at 295 °C (Figure 4-15 (c)). Such a hydrogen uptake at low temperatures sorption may be due to the formation of LiH. However, XRD analysis confirmed the partial conversion of Mg into the tetragonal β -MgH₂ phase for all the materials exposed to a hydrogen pressure of 30 bar at 200 °C (Figure 4-16). At 300 °C (Figure 4-17), all the materials were fully converted to β -MgH₂. In addition, all the materials contained a small LiH phase.



Figure 4-15: HP-DSC curves for hydrogen absorption and desorption of the assynthesised magnesium nanoparticles using different concentrations of lithium naphthalenide.



Figure 4-16: XRD patterns of the as-synthesised magnesium nanoparticles hydrogenated at 200 °C.



Figure 4-17: XRD patterns of the as-synthesised magnesium nanoparticles hydrogenated at 300 °C.

However, hydrogen release was not possible at temperatures below 150 °C and this would indicate no significant changes of the Mg/MgH₂ thermodynamics. It is noteworthy that once the material was heated to temperatures in excess of 300 °C, it was not possible to reproduce the low temperature sorption peaks (< 150 °C) by DSC and we believed that this is due to some sintering of the Mg nanoparticles or an alteration of the Mg surface reactivity. Since, the decomposition of *n*-butyllittium will lead to a partial organic contamination of the surface of the Mg nanoparticles and an embedment of the latter in a LiH matrix, higher or equivalent hydrogen desorption temperatures may result from this.



Figure 4-18: Hydrogen desorption followed by MS for the as-synthesised magnesium nanoparticles after hydrogen absorption at 200 °C.

Despite hydrogen uptake at low temperatures, HP-DSC measurements showed that hydrogen was released at high temperatures (> 300 °C) only. To confirm that this was not due to excessive heating/sintering of the Mg nanoparticles, hydrogen desorption was followed by MS on the materials absorbed at 200 °C (Figure 4-18) and once more the need for high temperatures in excess of 300 °C to release the hydrogen was observed. Accordingly, the thermodynamics of these Mg nanomaterials may be similar to that of bulk Mg since high temperatures are still required for hydrogen release.



Figure 4-19: Hydrogen desorption followed by MS for the as-synthesised magnesium nanoparticles after hydrogen absorption at 300 °C.

Furthermore, after hydrogen uptake at 300 °C, all the materials released hydrogen in a single peak (Figure 4-19). However, these peaks were shifted to slightly higher temperatures (by ~20 °C) as compared to the hydrogen release observed after hydrogen absorption at 200 °C and this may be due to some organic contamination of the Mg nanoparticles surface arising from the decomposition of *n*-butyllithium and the formation of LiH. MgLi_{9.2}Napth_{0.5} with the highest lithium content appeared to be an exception as the main hydrogen desorption peak remained at 355 °C. In this case, the formation of Li₂C₂ due to the large amount of organolithium remaining within the material is an indicator of residual carbon and carbides within the material. This may protect the Mg nanoparticles against sintering and their surface reactivity toward hydrogen. Indeed, a previous study found that the amorphous carbon generated during the thermal hydrogenolysis of di-n-butylmagnesium and the associated in-situ degradation of butane was an effective way to preserve the hydrogen sorption properties of Mg nanoparticles. [7] Konarova et al. have also reported around 1.5 wt % of residual carbon in Mg samples prepared through the thermal degradation of di-nbutylmagnesium. [29]

4.4.3 Kinetic and thermodynamics

As shown in Figure 4-20, all the materials displayed relatively fast hydrogen absorption kinetics at 300 °C. The fastest absorption was with MgLi_{9.2}Napth_{0.5} as the hydrogen uptake occurred in less than 10 min. Desorption kinetics followed the same trend with MgLi_{9.2}Napth_{0.5} showing the fastest desorption rate. It took less than 100 min to fully release hydrogen from the material, significantly faster than that reported for nanoconfined Mg particles. [30]



Figure 4-20: Absorption and desorption kinetics of the magnesium nanoparticles cycled at 300 °C.

However, the state of the Mg surface particle as well as a significant evolution in particle size during cycling may strongly influence the results. Kinetics will strongly depend upon a reduction of the activation barrier for splitting the hydrogen at the magnesium surface (432 kJ.mol⁻¹ H₂) and an enhancement of the hydrogen diffusion rate in magnesium hydride ($4 \times 10^{-13} \text{ m}^2.\text{s}^{-1}$). [31] If the latter can be improved by reducing particle size, such a positive effect can be counter balanced by poor hydrogen dissociation rates at the magnesium surface. Indeed, assuming similar chemical surface states for the Mg particles synthesised and the same surface planes (101) as observed by HRTEM (Figure 4-21), the trend in faster desorption kinetics observed with decreasing particle sizes, i.e. MgLi_{4.6}Napth_{4.6} < MgLi_{9.2}Napth_{4.6} < MgLi_{4.6}Napth_{0.5} < MgLi_{9.2}Napth_{0.5}, should be related to some extent to the shorter distances required for
hydrogen diffusion. However, for MgLi_{4.6}Napth_{0.5}, MgLi_{9.2}Napth_{0.5} of similar average particle sizes (16 and 19 nm, respectively, Table 4-2), different desorption rates were obtained (Figure 4-20). This would indicate a stronger contribution of the Mg nanoparticles surface state since similar diffusion rates should take place. Norberg et al. also observed variations in hydrogen kinetics for Mg nanoparticles of similar sizes that they attributed to an increase in defect density within 25 nm Mg nanoparticles. [6] Since vacancy defects have the potential to improve hydrogen kinetics in Mg, this hypothesis is plausible unless existing defects are annealed upon cycling.[31]



Figure 4-21: HRTEM of magnesium nanoparticles after cycling.

Analysis by TEM of the materials after the cycling (Figure 4-22) and the PCI measurement campaign revealed some minor agglomeration/sintering of Mg nanomaterials. In particular for MgLi_{4.6}Napth_{0.5} and MgLi_{9.2}Napth_{0.5} the morphology of the particles was found to be relatively intact despite prolonged hydrogen cycling. Hence, the various kinetic rates observed for the different materials may be related to differences in particle sizes and distinct chemical surface states. Another factor may be the influence of lithium since it has been predicted that doping Mg with 1 mol % lithium should enhance hydrogen diffusion. [32] However, it is difficult to separate such a potential effect from particle size effects, since all the materials contained more than a 1 mol % of lithium (Table 4-2). MgLi_{9.2}Napth_{4.6} with larger particle sizes than MgLi_{9.2}Napth_{0.5} but similar Li content displayed slower kinetics (Figure 4-20). Accordingly, particle size effects on kinetics are more prominent than Li content.



Figure 4-22: TEM images of cycled magnesium nanoparticles produced by reducing di*n*-butylmagnesium with different lithium/naphthalene ratios.

Evolution of the thermodynamic properties was determined by PCI measurements and cross checked for Δ H by HP-DSC measurements. Since the absorption kinetics were quite fast, only the PCI measurements (Figure 4-23) for absorption were used to determine the van't Hoff plot (Figure 4-24). Values of Δ H and Δ S for the different materials are reported in Table 4-3 as well as those determined by HP-DSC measurements.



Figure 4-23: PCI curves corresponding to the absorption of hydrogen in the synthesised magnesium nanoparticles.

Except for MgLi_{4.6}Napth_{4.6}, all the other materials displayed a significant reduction in enthalpy and entropy as compared to that of ball-milled MgH₂ determined by the same procedure. The highest decrease was obtained with MgLi_{4.6}Napth_{0.5} with a reduction of 11.7 kJ.mol⁻¹ H₂ for Δ H and 20.6 J.mol⁻¹ H₂.K⁻¹ for Δ S. This is equivalent to the reduction observed for 3 nm Mg particles confined within activated carbon nanofibers although the average particle size of $MgLi_{4.6}Napth_{0.5}$ is somewhat bigger (~16 nm).

 Table 4-3: Thermodynamics of magnesium nanoparticles prepared using different concentrations of reducing agent.

Sample	$\Delta H (kJ.mol^{-1}H_2)$		$\Delta S (J.mol^{-1}H_2.K^{-1})$
	PCI	HP-DSC	_
MgLi _{4.6} Napht _{0.5}	63.5 ± 1.8	62.1 ± 1.6	118.4 ± 3.1
MgLi _{9.2} Napht _{0.5}	66.7 ± 2.4	66.1 ± 2.1	122.2 ± 3.9
MgLi _{4.6} Napht _{4.6}	71.7 ± 2.0	73.4 ± 2.2	130.3 ± 4.0
MgLi _{9.2} Napht _{4.6}	70.9 ± 1.9	70.4 ± 1.7	128.7 ± 3.5
Ball milled MgH ₂	75.2 ± 1.8	75.1 ± 1.0	139.0 ± 3.0



Figure 4-24: The van't Hoff plots of the magnesium nanoparticles.

4.5 Discussion

4.5.1 Synthesis of Mg nanoparticles

The chemical reduction method proved to be an effective pathway to produce magnesium nanoparticles using the alkaline metal naphthalenide. Investigations of this chapter showed that all the alkali (Li, Na and K) naphthalenide successfully reduced di*n*-butylmagnesium to metallic magnesium, but the mean particle size and the size distribution depended on the reducing agent and more importantly on its concentration.

The variation in particle sizes of magnesium nanoparticles from different alkali naphthalenides is supposed to derive from its redox potential. As shown in Table 4-2, Li⁺/Li, Na⁺/Na and K⁺/K have much negative reduction potentials than Mg(Bu)₂, and this is the reason that they can reduce Mg(Bu)₂ to metallic magnesium. However, the reduction potential of Na⁺/Na (-2.71 V) is lower than that of Li⁺/Li (-3.04 V) and K⁺/K (-2.93 V), which will affect the nucleation rates of magnesium seeds and finally lead to larger particle size. According to La Mer's model of nucleation and growth, [33] strong reducing agents promote formation of small particles because rapid reduction favours nucleation over diffusion-limited growth of larger particles. [34]

Table 4-4: Redox potentials E of the reducing agents used for the synthesis of the magnesium nanoparticles and magnesium particle sizes. [14] The value for di-*n*-butylmagnesium is estimated from cyclic voltammetry measurements. [35] Numbers in

parentheses are mean particle sizes.

	Mg(Bu) ₂	Naphthalene	Li ⁺ /Li	Na ⁺ /Na	K ⁺ / K
E (V vs NHE)	-1.39	-2.15	-3.04	-2.71	-2.93
Particle size (nm)	-	-	8-40 (18)	7-52 (24)	8-32 (18)

The effect of a reducing agent on particle size was also reported in the preparation of other materials. [36-39] For example, the particle sizes of gold nanoparticles reduced with NaBH₄ (-1.37 V), citrate (+0.699 V) and hydroquinone (+1.2 V) are in the same order as the reduction potentials of reductant, which is 5 nm, > 5 nm and 10-20 nm, respectively. [36]

However, it seemed that the reducing agent type showed less influence on the particle size of magnesium compared with its concentration. With the low concentration of naphthalene that was adapted in this study, magnesium nanoparticles showed particles about 20 nm, while at the high concentration that was used the particles were observed to be larger than 100 nm. The same trend was reported by Norberg et al. on crystallite size of Mg by reducing magnesocene with different concentrations of reducing solutions. With the concentration of reducing solution increased from 0.02 M, 0.04 M to 0.08 M, the crystallite size increased from 25 nm, 32 nm to 38 nm. [6]

Therefore, the low concentration we used in this study is an optimal concentration compared to the high concentration. At the low concentration, a suitable amount of nuclei were formed, while at high concentration an excess amount of nuclei formed and large particles were formed due to the Ostwald ripening, that is a phenomenon by which smaller particles are essentially consumed by larger particles during the growth process. [40] In previous research, stabilisers were reported to be used to minimise the Ostwald ripening to obtain small magnesium nanoparticles. For example, tetrabutylammonium bromide was used to protect magnesium nanoparticles during electrochemical magnesium synthesis and magnesium particles about 5 nm were prepared. [41] Magnesium nanoparticles of similar size were also obtained by the chemical reduction method with poly(methyl methacrylate) as a stabilizer. [42] In this study, no additional protecting agent was added, but excess alkali naphthalenide and the by-product butylM

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could possibly act as a protecting agent to some extent as proved by the alkali metal/hydride coating layer on magnesium surface.

Thus, magnesium nanoparticles could be synthesized by the solution reduction method without the addition of a stabilizer. The particle size can be controlled by the concentration of a suitable reducing agent.

4.5.2 Size effects on kinetics of magnesium

The investigation of hydrogen storage properties of magnesium nanoparticles from different reducing agents showed that Na- and K-reduced samples formed perovskite structures upon cycling, which influenced the kinetics of these materials. It is difficult to separate the size effects from the catalytic effects of the formed perovskite structure. Therefore, the following discussion on size effects will mainly focus on lithium-reduced magnesium nanoparticles.

Magnesium nanoparticles prepared by the solution reduction method showed hydrogen absorption starting from about 100 °C. Such low temperature hydrogen absorption never happened on bulk magnesium due to kinetic limitation. In fact, the absorption of hydrogen by Mg is an exothermic reaction, hence it should occur at room temperature if the Mg surface is clean, the barrier for splitting hydrogen is sufficiently low and the surface to volume ratio large enough for enabling fast kinetics. [31] Therefore, for small Mg particles close to room temperature, hydrogen sorption should occur under the right synthetic conditions, i.e. with a clean Mg surface. Indeed, a few reports in the literature have demonstrated low temperatures hydrogen uptake for Mg nano-objects. [41, 43] The same achievements seem possible for Mg nanoparticles generated by the solution reduction method. For desorption kinetics, the trend in faster desorption kinetics was observed with decreasing particle sizes due most likely to the reduced diffusion distance, but it still took about 100 min for the magnesium nanoparticles with the smallest particle size (MgLi_{9.2}Napht_{0.5}) in this study to fully release hydrogen (Figure 4-20). This kinetics is even slower than the ball-milled MgH₂ under the same cycling conditions (Figure 4-25).



Figure 4-25: Absorption and desorption kinetics of the ball-milled MgH_2 cycled at 300 °C.

Slow kinetics was also observed on magnesium nanostructures in previous studies. It took 3 h for MgH₂ of 7 nm embedded in a LiCl salt matrix to release hydrogen at 300 °C, and 6 h for MgH₂ of 3 nm infiltrated in a carbon scaffold to reach a full desorption at 290 °C. [30, 44] This study showed that the reason for slow kinetics of magnesium nanoparticles is possibly due to the benefits on desorption kinetics of reduced diffusion distance was possibly counter balanced by a poor hydrogen dissociation rate on magnesium nanoparticle surface. Further study is required to activate the surface of magnesium nanoparticles to obtain fast hydrogen desorption kinetics.

4.5.3 Size effects on thermodynamics of magnesium

An alteration of the Mg/MgH₂ thermodynamics was also achieved with these magnesium nanoparticles, which are much larger than previously thought. Theoretical calculations have predicted evolution of enthalpy for relatively small particles < 3 nm. [45-47] However, these calculations are often performed under ideal environments, e.g. vacuum and 0 K that do not reflect experimental conditions and the chemical/physical environments of the Mg nanoparticles experimentally synthesised. Alteration of thermodynamics may depend on the stabilisation of specific surface planes [48] but more broadly on the stability of specific nanostructures. Indeed, modification of thermodynamics has also been found for 7 nm MgH₂ nanoparticles with surface planes 020. [44] Additional plots of the enthalpy and entropy of the Mg nanoparticles synthesised versus their size clearly show this trend with a significant drift from the thermodynamics of bulk Mg as particle size decreases below 50 nm (Figure 4-26). This further indicates the possibility of modifying the thermodynamic of the Mg/MgH₂ system with relatively large nanoparticles.



Figure 4-26: The evolution of enthalpy and entropy versus the size of the magnesium nanoparticles.

However, an enthalpy-entropy compensation was observed, which counteracted on the desorption temperature leading to the drop of desorption temperature less than expected. For bulk Mg, the reaction entropy upon hydrogen uptake is determined as followed: ΔS (-131.4 J.K⁻¹.mol⁻¹ H₂) = S_{Mg} (-32.5 J.K⁻¹.mol⁻¹ H₂) + S_{H2} (-130 J.K⁻¹.mol⁻¹ H₂) - S_{MgH2} (-31.1 J.K⁻¹.mol⁻¹ H₂). S_{H2} should not be affected by the particle size, but it is possible that at the nanoscale upon hydrogen uptake and release, Mg nanostructures undergo greater entropic changes for MgH₂ than Mg. This might arise from a different interaction of hydrogen with Mg at the nanoscale. Indeed, similar effects have been observed with Pd nanoparticles and were attributed to a weaker Pd-H bond and thus a higher level of freedom for the hydrogen atom in nanosized Pd as compared to bulk Pd. [49] Thus, the challenge in using such nanosized effects to improve the hydrogen sorption properties of Mg is a better understanding of the $\Delta S/\Delta H$ interdependent relationship and the determination of any critical limits beyond which ΔS (and/or ΔH) does not evolve.

4.6 Conclusions

In this chapter, the study of size effects was extended from LaNi₅ to a high capacity hydride, MgH₂. The method for magnesium synthesis with controllable particle sizes was developed and size effects on kinetics and thermodynamics were evaluated.

This study showed that the solution reduction method using alkali metal naphthalenide as a reducing agent is an effective way to reduce di-*n*-butylmagnesium to prepare magnesium nanoparticles. Varying the reducing agent slightly changed the particle sizes of magnesium, but it led to a different coating layer (LiH, Na or K) on Mg surface. The Na and K coating layer was converted to a perovskite structure, NaMgH₃ or KMgH₃, upon cycling. These perovskite structures influenced the kinetics of magnesium although they most likely had no effect on thermodynamics. Thus it was difficult to separate the size effects from the catalytic effects of the perovskite structure. Therefore, the study of size effects was carried out on magnesium nanoparticles with controllable sizes by varying the concentration of lithium naphthalenide.

The amount of lithium and naphthalene were varied to study their effects on magnesium nanoparticles and their hydrogen storage properties. By adjusting the reactants' ratio, the nucleation and growth process could be controlled to some extent for the synthesis of magnesium nanoparticles with varied sizes from 8 to 350 nm. At low naphthalene concentration, nanoparticles with mean particle size of 18 nm were obtained and they grew to about 250 nm with high naphthalene concentration.

Size effects were then studied on these magnesium nanoparticles. Remarkably, the nanoparticles generated at low naphthalene concentration were capable of absorbing hydrogen at low temperatures (<150 °C), which means a great increase in absorption kinetics due to size reduction. For hydrogen desorption, the kinetics followed the trend as the particle sizes were due most likely to the reduced diffusion pathway. However, these desorption kinetics are slower than that of ball-milled MgH₂ and we assume this was caused by a poor hydrogen dissociation rate on magnesium nanoparticle surface.

Further investigation showed that smaller magnesium nanoparticles showed lower desorption temperature and all materials can be cycled at 300 °C. The determination of the hydrogen thermodynamics of these materials revealed a significant evolution of both enthalpy and entropy with decreasing particle sizes. Hence, a ΔH of -63.5 ± 1.8 kJ.mol⁻¹ H₂ and ΔS of -118.4 ± 3.1 J.mol⁻¹ H₂. K⁻¹ was measured for MgLi_{4.6}Napth_{0.5} with an average particle size of 18 nm instead of the -75.2 ± 1.8 kJ.mol⁻¹H₂ and -139.0 ± 3.0 J.mol⁻¹H₂.K⁻¹ for bulk magnesium. Such an evolution of enthalpy appears to occur with nanoparticles of Mg much larger than previously thought. Following early theoretical calculations it has been commonly accepted that only very small particles < 3 nm would

undergo thermodynamic alterations. Since larger nanoparticles are easier to handle this opens new perspectives for the use of particle size effects to control both Mg thermodynamics and kinetics. However, the enthalpy-entropy compensation phenomena counteracted on desorption temperature so that it was not as low as expected. Thus, the remaining question is how to effectively control such evolutions of thermodynamics.

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CHAPTER 5 EFFECTS OF ELEMENTAL COATING BY TRANSMETALATION ON HYDROGEN STORAGE PROPERTIES OF MAGNESIUM NANOPARTICLES

5.1 Introduction

In Chapter 4, we noticed that the reduction in enthalpy was accompanied by an entropy decrease when the magnesium particle sizes reduced below 20 nm. We assume that the more weakly bonded hydrogen in magnesium nanoparticles would result in a higher freedom of hydrogen atoms. As a result, the enthalpy-entropy compensation effect, which was also reported by other researchers on magnesium nanoparticles, [1, 2] significantly weakened the size effects on plateau pressure and desorption temperature. Therefore, the thermodynamics of magnesium nanoparticles need to be finely tuned to obtain low temperatures hydrogen desorption.

A correlation of hydrogen desorption kinetics with magnesium particles sizes was found in Chapter 4, but desorption times longer than one hour at 300 °C were still required for a full H₂ release. This is not the first time that slow kinetics was observed on magnesium nanostructures. MgH₂ of 7 nm embedded in a LiCl salt matrix was reported to decompose in 3 hours at 300 °C. [1] MgH₂ of 3 nm infiltrated in a carbon scaffold required about 6 hours to reach a full desorption at 290 °C. [2] Magnesium of 40 nm prepared by acetylene plasma metal reaction desorbed the stored hydrogen at 287 °C in more than two hours. [3] Among numerous factors that contribute to the kinetics, molecular hydrogen dissociation and hydrogen diffusion are two factors of primary concern. [4] Reducing particles sizes to nanometres does not seem to speed up the kinetics as expected. It therefore appears that molecular hydrogen dissociation on Mg surfaces is a more important factor. To increase the kinetics, the magnesium surface needs to be modified and the addition of catalysts has been proposed in a feasible way as discussed in Chapter 2.

Thus, we report in this chapter on the possibility of significantly altering the properties of magnesium at the nanosize by coating individual magnesium nanoparticles with Co, Fe, Ni, Si and Ti. Following theoretical calculations, the coating of magnesium nanoparticles with transition metals should result in a weaker Mg-H bond, [5, 6] whereas Si and Ti may lead to lower desorption temperatures through the formation of intermediate/metastable phases. [7, 8]

5.2 Experimental

All operations were performed in an argon-filled glove box (LC Technology) with oxygen and moisture levels less than 1ppm.

5.2.1 Chemicals

Lithium, naphthalene, di-*n*-butylmagnesium solution in heptane (1.0 M), nickel chloride anhydrous (NiCl₂), silicon tetrachloride (SiCl₄), and titanium tetrachloride (TiCl₄) were purchased from Sigma-Aldrich. Iron (II) chloride anhydrous (FeCl₂) was from Alfa Aesar and cobalt chloride hexahydrate (CoCl₂) from Ajax Finechem. Tetrahydrofuran (THF) was purchased as HPLC grade from Fisher Scientific and dried using a LC Technology SP-1 solvent purification system. Naphthalene was dried by recrystallization under vacuum at 60 °C and cobalt chloride hexahydrate was heated at 100 °C under vacuum overnight to obtain the anhydrous form. All other chemicals were used as received.

5.2.2 Preparation of coated magnesium nanoparticles

Magnesium nanoparticles were prepared using a chemical reduction method reported in Chapter 4 with a di-*n*-butylmagnesium: lithium: naphthalene ratio of 1:4.6:0.5. This material is noted as Mg in this chapter. The coating of these magnesium nanoparticles was performed via a transmetalation method. In this process, the surface of the magnesium nanoparticles was used as the reducing agent leading to the reduction of the metallic salts onto the magnesium surface. [9] Typically, magnesium nanoparticles (0.171 g) were suspended in 10 mL THF. To this suspension, a 5 mL solution or suspension of CoCl₂, FeCl₂, NiCl₂, SiCl₄ or TiCl₄ in THF was added dropwisely under stirring. After 24 h reaction, the products were separated by centrifugation followed by three times washing with THF. The black powder was dried under vacuum on a Schlenk line overnight. The coated nanoparticles are described as Co/Mg, Fe/Mg, Ni/Mg, Si/Mg and Ti/Mg for CoCl₂, FeCl₂, NiCl₂, TiCl₄ or SiCl₄, respectively.

5.3 Results

Elemental coated magnesium nanoparticles were formed in a pathway as shown in Figure 5-1. Firstly, magnesium nanoparticles were generated by reducing di-*n*-butylmagnesium with lithium naphthalenide. Then M (M = Co, Fe, Ni, Si or Ti) was coated on magnesium nanoparticles by a transmetalation reaction between MCl_x and Mg nanoparticles.



Step 1: Generation of Mg nanoparticles Step 2: Coating of Mg nanoparticles

Figure 5-1: Synthetic pathway of the elemental coated magnesium nanoparticles.

Standard reduction potentials of redox couples M^{x+}/M and Mg^{2+}/Mg are summarised in Table 5-1. It is obvious that the standard reduction potential of Mg^{2+}/Mg is much lower

than that of M^{x+}/M , so M in this study can be readily reduced to its metallic form and deposited on the magnesium surface. Magnesium on the original nanoparticle surface is partially consumed to form MgCl₂. This strategy was previously reported to be adapted to form a metallic shell on NaBH₄ core. [9, 10] The reduction rate of the coating precursors was reported to be an important factor to form a uniform shell since sufficient time is required for individual nuclei to grow on the Mg surface. [9]

Standard redox Elemental composition potential (V) as determined by ICP (%) Mg Li **Element coated** Mg^{2+}/Mg -2.372 58.5 16.8 Co²⁺/Co -0.280 40.4 15.5 8.2 Fe²⁺/Fe -0.447 34.9 13.1 9.2 Ni²⁺/Ni -0.257 55.2 14.7 5.3 SiCl₄/Si 59 12.6 Ti²⁺/Ti -1.630 54.9 14.2

Table 5-1: Standard reduction potentials of the coating elements and elemental composition of the uncoated and coated magnesium nanoparticles as determined by ICP.

5.3.1 Physical properties of the coated Mg nanoparticles

The uncoated magnesium nanoparticles as reported in Chapter 4 possessed a spherical morphology with a particle size ranging from 7 to 32 nm. TEM images of the coated samples are shown in Figure 5-2 and their particle sizes were calculated and listed in Table 5-2. The coated samples showed much smaller particle size due to the sacrificial oxidation of magnesium nanoparticles and this suggested the occurrence of the transmetalation process. TEM image of Co/Mg revealed darker areas suggesting the effective deposition of Co at the surface of the Mg nanoparticles. After coating, the

coated particles retained a spherical shape, which indicated a uniform coating of metallic Co, Fe, Ni, Si or Ti on the magnesium surface.



Figure 5-2: TEM images of the as-synthesised uncoated and coated magnesium nanoparticles. Insertions correspond to the associated EDS analysis.



Figure 5-3: Elemental mapping of the as-synthesised coated magnesium nanoparticles.

The EDS analysis coupled with TEM measurement as insertion in Figure 5-2 indicated that nanoparticles shown in the TEM images are composed of magnesium and the respective metal of coating precursors. We tried to observe isolated particles to prove the core-shell structure by EDS mapping (Figure 5-3), but it was difficult to achieve due to too small nanoparticles and instrumental limitations. However, the mapping images

showed that there is always the respective coating metal detected where there are magnesium particles, which could prove indirectly the formation of a core-shell structure. Thus, based on the above results, it is reasonable to assume that the coating process led to the formation of a core-shell structure as well as some isolated respective metal particles.

Table 5-2: Summary of the physical properties of the uncoated and coated magnesium nanoparticles. Particle size was determined by TEM. Values in the brackets are the mean values. ΔH and ΔS value of Ni/Mg was determined for the 1st plateau attributed to

Mg/	Mg.	H_2 .
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	Particle size (nm)		ΔH	ΔS	Ea
	As-synthesised	Cycled	(kJ.mol ⁻¹ H ₂)	(J.K ⁻¹ .mol ⁻¹ H ₂)	(kJ.mol ⁻¹)
Mg	7-32 (15)	8-34(16)	-63.5 ± 1.8	-118.1 ± 3.1	167 ± 1
Co/Mg	7-16 (11)	6-16 (10)	-68.5 ± 1.0	-126.4 ± 1.0	156 ± 4
Fe/Mg	3-10 (5)	4-20 (7)	-59.9 ± 1.9	-112.3 ± 3.1	137 ± 6
Ni/Mg	3-10 (6)	3-11 (5)	-71.6 ± 3.8	-130.7 ± 6.4	124 ± 6
Si/Mg	2-9 (4)	3-9 (5)	-68.8 ± 1.0	-126.5 ± 1.4	136 ± 1
Ti/Mg	2-5 (3)	2-5 (3)	-70.7 ± 3.5	-129.6 ± 6.8	142 ± 5

Like the uncoated sample, the coated magnesium nanoparticles showed a hexagonal structure of Mg as revealed by XRD analysis (Figure 5-4). However, there were no diffraction peaks from the coated metals detected. To prove the transmetalation reaction occurred, ICP analysis (Table 5-1) was carried out and results showed most of the respective precursor salts were reduced to a metallic form. We assumed the absence of diffraction peaks of respective metals was most likely because there is a layer of isolated nuclei formed on the magnesium surface instead of the isolated metallic crystals. Indeed, a full shell was reported to form upon heat treatment due to the growth of the

isolated nuclei. [9, 11] Small peaks of LiH were also detected on the coated samples by XRD, which was also detected in the uncoated sample. As reported in Chapter 4, the formation of LiH was attributed to the partial decomposition of *n*-butyllithium, which was formed during reduction of di-*n*-butylmagnesium by lithium naphthalenide. ICP results in Table 5-1 showed all samples show a lithium content more than 10 wt%.



Figure 5-4: XRD patterns of the as-synthesised uncoated and coated magnesium nanoparticles.

TGA-DSC-MS was carried out on the freshly prepared samples and results are shown in Figure 5-5 and Figure 5-6. The fragment ions of m/z 2, 27, 41 and 56 on mass spectra are corresponding to 1-butene, which was from *n*-butyllithium decomposition. [12] TGA curves showed that its decomposition started from below 100 °C and mostly

decomposed between 250 - 350 °C. LiH from *n*-butyllithium decomposition was further decomposed by releasing its hydrogen at a temperature higher than 450 °C as proven by mass spectrometry, where only m/z = 2 detected. Therefore, after M coating, the TGA-MS results further proved that *n*-butyllithium remained as a by-product of the reaction.



Figure 5-5: TGA-DSC of the as-synthesised uncoated and coated magnesium nanoparticles.



Figure 5-6: Gas evolution as determined by mass spectrometry during the TGA-DSC of the as-synthesised uncoated and coated magnesium nanoparticles.

5.3.2 Hydrogen sorption behaviour

Hydrogen absorption and desorption properties of the coated magnesium nanoparticles were checked by HP-DSC first. The curves are plotted in Figure 5-7. It is interesting to notice that all the coated samples started to absorb hydrogen at temperatures below 100 °C. Especially for Co/Mg and Ni/Mg, they showed an exothermic peak corresponding to hydrogen absorption at 140 and 124 °C, respectively.

The main absorption peak of all the coated samples appeared at about 240 °C, which was assumed to correspond to a full conversion of Mg to MgH₂ since the uncoated sample showed an absorption peak at nearly the same temperature. Another exothermic peak in the range of 355 to 361 °C was detected on coated samples only (Si/Mg is an exception). This is possibly due to additional hydrogen absorption of the intermediate phase leading to Mg₂CoH₅, Mg₂FeH₆, Mg₂NiH₄ and TiH₂, respectively.



Figure 5-7: HP-DSC curves for hydrogen absorption and desorption of synthesised uncoated and coated magnesium nanoparticles.

All the coated samples showed hydrogen desorption peaks at a temperature still higher than 300 °C. However, compared with the uncoated sample, the desorption temperatures were lower, especially for Ni/Mg, Si/Mg and Ti/Mg. Their desorption temperatures shifted from 382 °C for an uncoated sample to 330, 341 and 330 °C, respectively. It was noticed that Ti/Mg showed two clearly separated endothermic events at 330 and 358 °C, which attributed to the decomposition of MgH₂ and TiH₂, respectively.

To prove the reactions related to the HP-DSC peaks, samples were hydrogenated at different temperatures and then checked by XRD measurement. Firstly, we checked the low temperature hydrogen absorption with Co/Mg and Ni/Mg as examples, which were hydrogenated at 140 and 120 °C, respectively, according to HP-DSC. XRD results in Figure 5-8 (a) showed a partial conversion of Mg to MgH₂ for Ni/Mg and a nearly full conversion for Co/Mg under low temperature hydrogenation conditions. This result proved that the low temperature hydrogenation proceeded as indicated by HP-DSC. Hydrogenation at the main HP-DSC absorption peak of about 240 °C fully converted magnesium nanoparticles to MgH₂ (Figure 5-8 (b)).

Further increase of the hydrogenation temperature to 300 °C was investigated (Figure 5-9 (a)). A Mg₂Si phase, but no complex hydride phase, was observed on Si/Mg, which explains why there was only one exothermic peak during HP-DSC measurement for this material. This indicated the difficulty of hydrogenation of Mg₂Si even at the nanoscale. Previous attempts to hydrogenate Mg₂Si particles of 10 nm under a high pressure of 1,200 bar failed;[13, 14] accordingly it is not surprising that no hydrogenation occurred for Mg₂Si at 300 °C and under the 30 bar hydrogen pressure. However, the hydrogenation at 300 °C led to the formation of Mg₂CoH₅, Mg₂NiH₄ and TiH₂ on Co/Mg, Ni/Mg and Ti/Mg, respectively. These results are in agreement with the hypothesis of complex hydride formation based on HP-DSC absorption peaks higher than 350 °C. However, an Mg₂FeH₆ phase was not observed on hydrogenated Fe/Mg possibly because it remained amorphous at this temperature due to the lack of miscibility of magnesium and iron. [15] It is noteworthy that these transition metal complex hydride phases were formed under much milder conditions due to size effects than those required for bulk materials. For example, Mg₂CoH₅ is usually prepared by coupling mechanical milling and long-time sintering processes under pressure higher than 80 bar and 500 °C. Therefore, the coating method by transmetalation could be an alternative way for the synthesis of transition metal complex hydrides.



Figure 5-8: XRD patterns of (a) Ni/Mg hydrogenated at 120 °C and Co/Mg hydrogenated at 140 °C and (b) all coated magnesium nanoparticles hydrogenated at 240 °C.

The reversibility of the coated magnesium nanoparticles was investigated at 300 °C by desorbing the hydrogenated samples. XRD results (Figure 5-9 (b)) indicated Mg phases were fully recovered and no MgH₂ detected. This demonstrated their good reversibility. The complex hydride phase also decomposed into Mg₂Co, Mg₂NiH_{0.3} respectively. However, XRD of the desorbed Ti/Mg did not show Ti phase, possibly Ti was well dispersed after decomposition of TiH₂ on magnesium surface as the fresh sample.



Figure 5-9: XRD patterns of the uncoated and coated magnesium nanoparticles (a) after hydrogen absorption and (b) after hydrogen desorption at 300 °C.

The hydrogen desorption behaviour also cross checked by TGA-DSC (Figure 5-10) coupled with MS (Figure 5-11). In agreement with HP-DSC results, the main hydrogen desorption occurred at temperatures higher than 300 °C as shown from the TGA-DSC curves. It is noteworthy that Ni/Mg showed the lowest desorption temperature, about 30 °C lower than that of uncoated magnesium nanoparticles. MS spectra demonstrated that the only gas desorbed was hydrogen and the onset temperatures of desorption were about 200 °C and even lower for Fe/Mg and Ni/Mg.



Figure 5-10: TGA-DSC of the uncoated and coated magnesium nanoparticles after cycling at 300 °C.



Figure 5-11: Hydrogen evolution as determined by mass spectrometry during TGA-DSC analysis of the uncoated and coated magnesium after cycling at 300 °C.

Analysis by TEM (Figure 5-12) showed that the morphology of the coated Mg nanomaterials did not significantly evolve upon hydrogen cycling, although the nanoparticles may appear agglomerated in some cases and possibly sintered for Fe/Mg. Further elemental mapping (Figure 5-13) also confirmed the close proximity of Mg with the coated elements, proving once more the stability of the nanostructures synthesised with particle sizes remaining relativity constant (Table 5-2).



Figure 5-12: TEM images of the uncoated and coated magnesium nanoparticles after cycling at 300 °C. Insertions correspond to the associated EDS analysis.





5.3.3 Kinetic properties of the coated magnesium nanoparticles

The hydrogenation and dehydrogenation kinetics of uncoated and coated magnesium nanoparticles were measured by cycling these materials at 300 °C. The kinetic curves

are shown in Figure 5-14. All the nanomaterials displayed relativity fast hydrogen absorption kinetics at 300 °C. The fastest kinetics was obtained on Ni/Mg with 90 % of hydrogen uptake achieved in less than 10 min. The superior catalytic effect of Ni on hydrogen storage properties of Mg was proved by previous reports. [16, 17] Whereas, the coating with Ti showed almost no effects on Mg hydrogenation possibly due to a "passive" role of Ti in the absorption process because it is not miscible with Mg. [7]



Figure 5-14: Hydrogen absorption and desorption kinetics of the uncoated and coated magnesium nanoparticles cycled at 300 °C.
Desorption kinetics showed the same trend, with Ni/Mg showing a significant enhancement of desorption rates. Less than 50 min was spent to fully release stored hydrogen from Ni/Mg, which is much faster than that of uncoated magnesium nanoparticles. Whereas all other elemental coating, e.g. Co, Fe, Si and Ti possessed slower desorption rates compared with the uncoated nanoparticles.



Figure 5-15: (a) Kissinger plots and (b) van't Hoff plots of the uncoated and coated magnesium nanoparticles.

The apparent desorption activation energy of the uncoated and coated magnesium nanoparticles were then calculated using the Kissinger method (Figure 5-15(a) and Table 5-2). Attempts to link the calculated activation energy with the desorption kinetics showed that there is no direct correlation between the measured activation energy E_a and the desorption kinetics. However, all coated samples showed reduced activation energy and Ni/Mg showed the lowest value of 124 \pm 6 kJ.mol⁻¹ compared with that of uncoated magnesium nanoparticles of 167 ± 1 kJ.mol⁻¹. Hence, to some extent, the coated elements may provide some catalytic effect in improving hydrogen desorption. Several factors have been reported to affect the hydrogen release rate, such as hydrogen diffusion rates, defect density, growth mechanism of the Mg phase, surface area, catalytic effects and the desorption pressure. [18] Since all samples are in nanoscale, the diffusion rate should not prove a problem for hydrogen desorption any more. Then, the surface reactivity will become the rate limiting factor. However, it appears from our finding and previous reports [1, 2, 19-21] that desorption kinetics are rather slow even upon catalytic addition possibly due to the formation of other phases, e.g. complex hydride.

5.3.4 Thermodynamic properties of the coated magnesium nanoparticles

The coating effects on thermodynamics were investigated by measuring the pressurecomposition isotherms at three different temperatures as shown in Figure 5-16. Except for Ni/Mg, all samples showed one equilibrium plateau pressure (P_{eq}) in agreement with the literature, [22-24] which corresponds to the MgH₂ formation. In the case of Ni/Mg, the low plateau was assigned to the formation of MgH₂ while the second plateau at higher pressures was attributed to the formation of Mg₂Ni in accordance with previous reports on Mg rich Mg-Ni composites. [24, 25]



Figure 5-16: PCI corresponding to the absorption of hydrogen within the uncoated and coated magnesium nanoparticles.

The van't Hoff plots are shown in Figure 5-15(b) by plotting $ln(P_{eq})$ against 1000/T and ΔH , ΔS values (Table 5-2) were calculated based on the van't Hoff equation. Surprisingly, both ΔH and ΔS evolved upon coating the Mg nanoparticles with the various elements investigated. ΔH and ΔS for Co/Mg, Ni/Mg, Si/Mg and Ti/Mg both increased. While for Fe/Mg a decrease occurred leading to -59.9 ± 1.9 kJ.mol⁻¹ H₂ and -112.3 ± 3.1 J.K-1.mol⁻¹ H₂, for ΔH and ΔS respectively. Hence, despite a significant decrease in enthalpy and thus a weaker Mg-H bond, the resulting entropic compensation led to relatively high desorption temperatures for Fe/Mg. The reasons for such thermodynamic evolutions are not clear. Assuming an effective clamping effect due to a full coating of the Mg nanoparticles with the elements investigated, weaker H-H interactions leading to lower desorption temperatures should be expected. [26, 27] However, since many of the coated elements reacted with Mg to form intermediate phases subject to dilation upon hydrogen ab/desorption such a clamping effect is unlikely to occur.

Furthermore, theoretical reports have often simulated evolutions of ΔH assuming no variation in ΔS . Several experimental results and results in Chapter 4 have shown that both ΔH and ΔS are affected upon particle size reduction. [1, 28] Hence, the likewise evolution of ΔS upon particle size reduction may not lead to significant overall modifications of the temperature for the release of hydrogen.

5.4 Discussions

5.4.1 Transmetalation as a method to coat magnesium nanoparticles

Metals and Si layers were successfully coated on the surface of magnesium nanoparticles by a transmetalation method. It was difficult to directly check the coreshell structure of isolated particles by EDS mapping due to too small nanoparticles and the instrumental limitations. However, the following results indirectly proved the occurrence of transmetalation reactions and the formation of an elemental coating layer. Firstly, the EDS mapping during TEM measurement always showed a close proximity of magnesium and the respective coating elements, which would indicate the possible formation of a coating layer on the surface of the magnesium nanoparticles. Secondly, TEM measurements observed much smaller particle sizes of the coated samples, which proved the occurrence of the transmetalation reactions and indicated the formation of coated magnesium nanoparticles as well as isolated coating elements. In addition, ICP measurements proved that most of the precursors were reduced to their elemental form, which further proved that the transmetalation proceeded as expected. Finally, XRD patterns of the fresh sample did not show any phases from the precursors or coating elements but after cycling at 300 °C the coating elements appeared in the form of hydrides, complex hydride or alloys, which illustrated the presence of well-dispersed layers of coating elements on the magnesium surface after the transmetalation reaction. All the above results proved the success of coating the surface of magnesium nanoparticles with an elemental layer via transmetalation reaction.

5.4.2 Coating effects on kinetics of magnesium nanoparticles

Hydrogen absorption investigation by HP-DSC showed that the starting temperature for hydrogen absorption of magnesium nanoparticles were further reduced to below 100 °C by elemental coating, especially for Co/Mg and Ni/Mg. Such promising lowtemperature hydrogen absorption is due to the improvement on absorption kinetics upon elemental coating because hydrogen absorption is a thermodynamically favourable process but it never happens to bulk magnesium below 100 °C due to the limitation of absorption kinetics. The measurement of absorption kinetics proved this with the coated magnesium nanoparticles showing fast kinetics, especially for Ni/Mg with 90% hydrogen release in less than 10 min.

However, desorption kinetics measurements showed only Ni/Mg significantly improved desorption kinetics to less than 50 min, while other elemental coatings slowed down the desorption rate. An attempt to explain this was tried by linking the desorption kinetics with activation energy but no correlation was found. Thus, it was assumed that this was caused by the formation of a complex hydride from the coating elements during cycling.

Based on the synthesis mechanism and EDS mapping, a core-shell structure has been proposed on the coated materials. Thus the absorption and desorption kinetics could be controlled by the shell since the coated layer has a different hydrogen diffusion rate and varied hydrogen splitting/recombination ability. To investigate the relations between the coating layer and the kinetics, apparent decomposition activation energy (E_a) was summarised in Table 5-3. As shown in Figure 5-15 (a), the plotting of desorption kinetics against the apparent decomposition activation energy of complex hydrides, MgH₂+TiH₂ and MgH₂+Si showed a good correlation between them. Hence, hydrogen desorption kinetics as observed may be related to the ability of the shell structure in recombining hydrogen atoms. Further hydrogen diffusion and bonding within the shell structure may also affect kinetics and similar trends can be deduced considering thermodynamic parameters reported for transition metal complex hydrides (Table 5-3).

Table 5-3: Thermodynamic properties and activation energy (E_a) of magnesium alloyed

with transitions metals or destabilised with Si. E_a refers to the dehydrogenation

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Reaction		ΔH (kJ.mol ⁻¹ H ₂)	ΔS (J.K ⁻¹ .mol ⁻¹ H ₂)	E _a (kJ.mol ⁻¹)
MgH ₂	\iff Mg + H ₂	-75 ± 1[29]	-135 ± 2[29]	120-213[18, 30]
Mg ₂ CoH ₅	\iff Mg _x Co + Mg + H ₂	$-79 \pm 4[29]$	$-134 \pm 4[29]$	114[31]
Mg ₂ FeH ₆	$\iff 2Mg + Fe + 3H_2$	$-82.4 \pm 5.8[32]$	$-140.2 \pm 8.7[32]$	165[32]
Mg ₂ NiH ₄	\iff Mg ₂ Ni + H ₂	$-64.5 \pm 4.2[24]$	-122.3 ±6.3[24]	43-88[33]
$MgH_2 + 1/2S_2$	$i \iff 1/2Mg_2Si + H_2$	-38.9[34]	_	162[30]
$MgH_2 + TiH_2$	\iff Mg + TiH ₂ + H ₂	$-75.8 \pm 0.7[7]$	$-135 \pm 1[7]$	107-118[35]



Figure 5-17: (a) Evolution of the time for hydrogen desorption from the coated magnesium nanoparticles as a function of E_a for the corresponding complex hydrides, $MgH_2 + TiH_2$ and $MgH_2 + Si$ reactions reported in Table 5-3; (b) Evolution of the equilibrium plateau pressure (P_{eq}) of the coated magnesium nanoparticles as a function of the electronegativity of the corresponding coating elements.

5.4.3 Coating effects on thermodynamics of magnesium nanoparticles

Hydrogen desorption investigation of the coated magnesium nanoparticles by HP-DSC (Figure 5-7) showed that the elemental coating decreased the hydrogen desorption temperature, especially for Co/Mg, Ni/Mg and Ti/Mg, which indicated the change in thermodynamics of magnesium nanoparticles upon elemental coating. Their thermodynamics were then studied by PCI measurements and van't Hoff plots and results showed that the elemental coating affected the plateau pressure as well as reaction enthalpy and entropy.

Plotting the evolution of P_{eq} as a function of the electronegativity of the element coated (Figure 5-17(b)) showed a clear decrease of P_{eq} for the more electronegative elements. However, for Ni/Mg, its higher overall thermodynamic stability is possibly due to an electronic back donation. Theoretical calculations of model systems have often predicted a local destabilisation of the Mg-H bond strength upon transition metal doping and electronic donation from Mg-H to the d-band. [5, 36] However, in such model systems Ni was assumed to remain at Mg surface sites despite the good miscibility of both elements.

It is remarkable that coating Mg nanoparticles with various electronegative elements has such an effect on thermodynamics. A similar amount of transition metal on bulk or monocrystalline Mg only led to improvement of kinetics without any alteration of thermodynamics. [7, 17, 37] This would imply for the first time the possibility of directly tuning the thermodynamic properties of Mg at nanoscale by coating suitable elements. Our findings suggest that an element less electronegative than Mg would be required to effectively destabilise nanosized Mg by such a coating strategy, assuming an adequate shift of both Δ H and Δ S. However, the challenge remains in a better understanding of the compensation effects of enthalpy and entropy evolution.

5.5 Conclusion

The need to finely tune the thermodynamics of magnesium nanoparticles due to enthalpy-entropy compensation and the requirement to activate the magnesium nanoparticle surface due to slow kinetics of magnesium nanoparticles drives the research in this chapter. Elemental coating on the surface of magnesium nanoparticles was applied to solve these problems.

Transmetalation was found to be an effective process to deposit various elements at the surface of magnesium nanoparticles. Upon coating with Co, Fe, Ni, Si and Ti, smaller coated magnesium particles were obtained due to the sacrificial oxidation of the magnesium.

The coated magnesium nanoparticles absorbed hydrogen at low temperatures with improved absorption kinetics. In particular, Co- and Ni- coated magnesium nanoparticles were almost fully hydrogenated at 140 °C. Furthermore, all the coated materials were fully converted to MgH_2 at 240 °C.

Hydrogen absorption at temperatures above 350 °C led to the formation of intermediate phases, i.e. Mg_2CoH_5 , Mg_2FeH_6 , Mg_2NiH_4 and TiH_2 , respectively. These intermediate phases probably surrounding the magnesium core slowed down the dehydrogenation kinetics with Ni-coated magnesium as an exception. Hence, the hydrogen desorption kinetics were found to strongly correlate with the reported values of E_a of transition metal complex hydrides, MgH_2/Si and MgH_2/Ti systems. The Ni-coated magnesium nanoparticles significantly improved the desorption kinetics to less than 50 min due possibly to the back-donation effects from nickel.

More importantly, the coating process altered the thermodynamic properties of MgH₂. The enthalpy and entropy of Fe/Mg significantly decreased to -59.9 ± 1.9 kJ.mol⁻¹ H₂ and -112.3 \pm 3.1 J.K-1.mol⁻¹ H₂, respectively. However, for all other coated magnesium nanoparticles Δ H and Δ S were both found to increase above the values of "naked" magnesium nanoparticles, i.e. -63.5 \pm 1.8 kJ.mol⁻¹ H₂ and -118.1 \pm 3.1 J.K-1.mol⁻¹ H₂ for Δ H and Δ S, respectively. For all the materials, a compensation effect between Δ H and Δ S was observed. Hence, any increase or decrease of Δ H led to a similar evolution of Δ S. The reasons for the observed increase in Δ H and Δ S are not clear but the equilibrium plateau pressure of the coated magnesium nanoparticles was found to be correlated to the electronegativity of the coating elements. Hence, coating magnesium nanoparticles with Ni resulted in a significant decrease of the equilibrium plateau pressure and thus an apparent stabilisation of the Mg-H bond. This demonstrates the possibility of altering the properties of magnesium at the nanoscale through appropriate coating/doping and provides new tools to achieve an effective alteration of the kinetics and thermodynamic properties of magnesium at the nanoscale.

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CHAPTER 6 GAS-PHASE ELECTROCHEMICAL CHARGING AND DISCHARGING OF LANI5

6.1 Introduction

As discussed in Chapter 2, to achieve room-temperature hydrogen storage, one pathway is through the synthesis of low-temperature hydrogen storage material, another pathway is to develop a novel hydrogen charging/discharging method. The material-based studies have been discussed in previous chapters; the development of the novel gasphase electrochemical charging/discharging method will be discussed in this and the following chapter.

The conventional electrochemical charging method uses an alkaline solution as electrolyte; this limits application to materials with good corrosion resistance and the cycling causes severe decay in the charging capacity of hydrogen storage material, e.g. LaNi₅. In this chapter, the feasibility of replacing the alkaline solution electrolyte with a solid electrode was investigated for electrochemical hydrogen storage. Based on this concept, a novel method, gas-phase electrochemical charging/discharging, was developed. This method is expected to be universal to most materials and to combine advantages of the electrochemical and gas-phase hydriding/dehydriding method. Following the concept setting-up, an electrochemical cell was designed and built up with a proton conductive membrane (PEM) as electrolyte. LaNi₅ was then tested as a model material in this electrochemical cell and an electrochemical Pressure-Composition Isotherm (PCI) curve was plotted by charging LaNi₅ at different potentials. The effect of this novel method on the cycle life of LaNi₅ is studied compared to conventional gas hydrogenation method and electrochemical method. Finally, the possible application of this method in a metal hydride-air battery is discussed.

6.2 Setting-up the concept

The concept of gas-phase electrochemical charging/discharging method is based on the use of electrolytic potential to drive a chemical reaction to form a metal hydride with H source from gaseous hydrogen. Its principles are illustrated in Figure 6-1, which can be simply divided into three steps. Taking electrochemical charging as an example, gaseous hydrogen firstly is dissociated into protons (H⁺) and electrons (e⁻) over the catalyst layer. The formed protons then diffuse through the solid electrolyte to the other side of the solid electrolyte and at the same time electrons reach LaNi₅ by flowing through an external circuit. Finally, the recombination of protons and electrons within LaNi₅ generate LaNi₅H_x (x = number of H incorporated). For electrochemical discharging, the process will be reversed.



Figure 6-1: Principles of the gas-phase electrochemical charging of LaNi₅.

The involved electrochemical reactions can be expressed as equation (6.1) and (6.2). Therefore, we can obtain the overall reaction of the gas-phase electrochemical method as shown in equation (6.3). The standard cell potential was calculated to be -0.004 V for hydrogen absorption using Faraday Law (equation 6.4) and the reported $\Delta_f G_m^{\theta}$ value of LaNi₅ (-160.1 kJ.mol⁻¹) and LaNi₅H₆ (-157.4 kJ.mol⁻¹).[1]

Anode
$$3H_2 \leftrightarrow 6H^+ + 6e^ E^0 = 0.00$$
 (6.1)

Cathode
$$LaNi_5 + 6H^+ + 6e^- \leftrightarrow LaNi_5H_6$$
 $E^{\theta} = -0.004 V$ (6.2)

Overall
$$LaNi_5 + 3H_2 \leftrightarrow LaNi_5H_6$$
 $E_{cell} = -0.004 V$ (6.3)

It is obvious that the overall reaction is the same as that of the normal gas-phase hydrding/dehydriding method. Indeed, considering Faraday Law (equation (6.4)) and Gibbs free energy (Δ G) (equation (6.5)), the equilibrium potential (Δ E) of gas-phase electrochemical charging/discharging can be directly linked to plateau pressure (P_{H2}) of the gas-phase method as shown in equation (6.6).

$$\Delta G = -nF\Delta E \tag{6.4}$$

$$\Delta G = RT ln P_{H2} \tag{6.5}$$

$$\Delta E = -\frac{RT}{nF} \ln(P_{H2}) \tag{6.6}$$

where *n* is the mole of electrons transferred during the reaction; F is the Faraday constant; R is the gas constant and T is the absolute temperature. This relationship has been reported to be applied to generate hydride, e.g. AlH₃, which requires a hydrogen pressure up to 2.7×10^5 bar to form if gas hydrogenation method is used. [2, 3] However, only 0.16 V equivalent electrochemical potential in theory is needed to drive the formation of AlH₃. Experiment results showed that AlH₃ was electrochemically prepared at -1.5 V with NaAlH₄ in THF as electrolyte, Al sheet as anode and Pt foil as cathode. [4]

Similarly, the calculation using equation (6.6) showed that the LaNi₅H₆ formation would only require about -0.003 V of potential difference to achieve the equivalence of the needed 2.2 bar of hydrogen pressure.[5] This potential difference is near the value of the standard cell potential calculated based on Faraday law, which confirmed that the hydrogen plateau is equivalent to an electrochemical potential. Therefore, it is theoretically feasible to charge LaNi₅ by the gas-phase electrochemical method.

6.3 Experimental

The following are required to perform this proof-of concept:

6.3.1 A proton conductive membrane

Nafion membrane was selected as the solid electrolyte due to its wide application as a proton conductive membrane in fuel cells. The chemical structure of Nafion consists of a tetrafluoroethylene backbone bearing sulfonate-terminated perfluorovinyl ether branches. [6] Its structure offers thermo-mechanical stability and at the same time allows for the formation of hydrophilic domains that can accommodate hydrated protons. The underlying theories of proton migration have two competing mechanisms, e.g. vehicle mechanism [7] and Grotthuss hopping mechanism [8]. In the vehicle mechanism, protons diffuse together with a "vehicle", such as H_3O^+ , whereas in the hopping mechanism protons transfer within hydrogen bonds from "vehicles" to "vehicles". In both models, water plays an important role for proton migration and water content in the membrane affects proton conductivity. [9] Sone and co-workers [10] measured proton conductivity of Nafion 117 by AC impedance method and found conductivity of Nafion 117 at room temperature increased with relative humidity (Figure 6-2). The conductivity value was about 10^{-3} S.cm⁻¹ at 20% relative humidity and increased up to about 0.1 S.cm⁻¹ at 100% relative humidity.

The Nafion 117 membrane from Aldrich was used in this study. It was cut into a disk of 30 mm in diameter, then boiled in 6 M HNO_3 for 1 h followed by a similar treatment in Milli-Q water for 1 h to activate it before use.



Figure 6-2: Conductivity dependence of Nafion 117 on relative humidity at room temperature. [10]

6.3.2 Pt catalyst for hydrogen splitting

Pt was chosen as a catalyst for hydrogen splitting. A very fast kinetics for hydrogen splitting has been reported on Pt electrode with the exchange current density of 10^{-3} A.cm⁻², and the over-potential required to split hydrogen is relatively limited, usually below 0.02 V. [11, 12]

The Pt catalyst was coated on Nafion membrane using the previous method described in the literatures. [13, 14] In a typical deposition process, the membrane was exposed to an aqueous solution of 1 M NaBH₄/1 M NaOH and 0.01 M H₂PtCl₆ as shown in Figure 6-3. The reducing agent, BH_4^- continuously penetrates the membrane and comes into contact

with $PtCl_6^{2-}$ ions on the opposite membrane face, at which point the platinum ions are reduced to platinum metal at the membrane surface according to the redox reaction: [14]

$$BH_4^- + 3H_2O \to BO_3^{3-} + 2H_2 + 6H^+ + 4e^- \qquad E^{\theta} = -0.481V \qquad (6.7)$$

$$PtCl_6^{2-} + 4e^- \to Pt + 6Cl^ E^{\theta} = 0.742V$$
 (6.8)

to give the overall process:

$$PtCl_6^{2-} + BH_4^- + 3H_2O \to Pt + BO_3^{3-} + 6Cl^- + 2H_2 + 6H^+ \quad E^{\theta} = 1.223 \text{ V}$$
(6.9)



 H_2 PtCl₆ solution NaBH₄/NaOH solution

Figure 6-3: Schematic diagram of the cell used to deposit Pt on a Nafion 117 membrane.

This reaction generated a large amount of hydrogen which needed to be removed to ensure a homogeneous Pt coating. This was achieved by manually shaking the holder. A continuously conductive layer was formed after 20 min of reaction. The coated membrane was rinsed in Milli-Q water to remove any remaining reactants and byproducts. The other side of the membrane was coated in the same way.

6.3.3 LaNi₅ electrode

LaNi₅ alloy from Aldrich was used as the electrode material and the as-received material was activated by cycling it at 80 °C under 40 bar hydrogen pressure for

hydrogenation and vacuum for desorption. After five cycles, a fine powder was obtained. The properties of the activated LaNi₅ were characterised by XRD and pressurecomposition isotherm (PCI) measurement prior to the gas-phase electrochemical charging/discharging.

The electrode was then prepared by a cold-press method. 100 mg of activated LaNi₅ was finely mixed with 15 mg carbon using an agate mortar and pestle. Carbon was used to increase the conductivity and bind the electrode. A pellet electrode was prepared by pressing on a stainless steel mesh of the LaNi₅/C mixture at 200 tons/m² pressure for 15 min.

6.3.4 Electrochemical cell

The cell for the gas-phase electrochemical charging was designed as shown in Figure 6-4. The Pt-coated membrane, sitting on a sealing o-ring, worked as a separator as well as a proton conductor. On one side of the membrane, hydrogen was flown through the chamber by an inlet and outlet valve and split into electrons and protons on Pt surface, and a stainless steel mesh on a support block was connected as a current collector, which was also used to maintain the membrane in position. On the other side of the membrane, the pelletised LaNi₅ and carbon mixture was pressed against the membrane with a spring-connected copper disk, which also acted as a current collector. A release valve on this side was used to avoid any hydrogen pressure built-up inside the cell. Hence, the hydrogen pressure of this side was kept as 1 bar.

The electrochemical cell was mounted in an argon filled glove box with the Pt-coated Nafion membrane as a working electrode and the pelletised mixture of LaNi₅ and carbon as a counter electrode. The electrochemical tests were performed on a multichannel potentiostat from BioLogic Scientific Instrument, which was controlled by a EC-lab software.

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Figure 6-4: Scheme of the cell for gas-phase electrochemical charging of LaNi₅.

Firstly, the cyclic voltammetry (CV) measurement with a scan rate of 50 mV/s was carried out to characterise the cell and LaNi₅. The electrochemical charging and discharging was then conducted at set potential values and the charged materials were characterised by XRD and TGA-DSC-MS. The cycle life test was carried out by electrochemically charging and discharging up to 100 cycles. Between each transition of the applied potential, five minutes rest was permitted. After 50 cycles and 100 cycles, the charging/discharging capacity of electrode material was checked by TGA-DSC-MS and compared with that of the first charging-discharging cycle.

6.4 Results

6.4.1 Pt-coated Nafion membrane

Platinum was successfully coated on the surface of the membrane and the examination using a multimeter indicated the formation of a continuous conductive layer with a negligible resistivity.

Surface morphology of the Pt-coated Nafion membrane was then checked by SEM (Figure 6-5). Low magnification SEM images (Figure 6-5 (a) and (b)) showed that the Nafion membrane is almost fully covered with Pt coating. There are several uncoated

small areas which were formed most likely due to the hydrogen gas bubbling during the coating process. The platinum layer was made of small Pt particles in the range of 100-500 nm as shown on the image at higher magnification (Figure 6-5 (c)).



Figure 6-5: (a, b) Low magnification and (c) high magnification SEM images of Ptcoated Nafion membrane.

6.4.2 Properties of LaNi5

Prior to the electrochemical tests, the properties of LaNi₅ were checked by XRD and PCI measurements. The activated LaNi₅ showed a well-defined hexagonal structure, which was converted to hexagonal LaNi₅H₆ after hydrogenation under 5 bar hydrogen pressure at room temperature (Figure 6-6). Its storage capacity was proved to be 1.37 wt% at room temperature by PCI measurement with a plateau at 2.5 bar and 1.5 bar for absorption and desorption, respectively (Figure 6-7).



Figure 6-6: XRD curves of the activated commercial LaNi $_5$ in (a) desorbed form and (b) absorbed form.



Figure 6-7: PCI curves of the activated commercial LaNi5 at 26 $^\circ C$

6.4.3 Cyclic voltametric measurement

Firstly, cyclic voltametric measurements were carried out to characterise the behaviour of the electrochemical cell and LaNi₅ electrode. Prior to the measurement, the membrane was humidified by flowing argon or hydrogen through a humidifier for at least 30 min. Before the CV measurement in argon flow, the cell was charged in hydrogen flow for 10 min at 1.5 V and then purged with argon for 30 min.

In a reversible process, the reduction of H^+ should be symmetrical to that of the oxidation. Indeed, $\Delta E = 0.035$ V have been found in the literature on Pt electrode. [15] The CV results under argon are very symmetrical. As shown in Figure 6-8 (a), with argon flow over Pt catalyst coating, the cyclic voltammogram showed a reduction-oxidation couple at 0.3 V and -0.3 V. This can possibly be attributed to the reduction and re-oxidation of the residual protons in the membrane. [16] To prove this, CV was carried out on the cell with membrane but without a LaNi₅ pellet. The CV result also showed a symmetric reduction-oxidation couple (Figure 6-8(a)), but the peak shifted to 0.17 V and -0.17 V due to the resistance change with and without LaNi₅. This proved that the reduction-oxidation couple is from protons remaining in the membrane.

When changing flow gas to H₂, the hydrogen oxidation reaction started from near 0 V and finished at 1.0 V with the oxidation peak centred at 0.6 V. In the reduction scan, a broad peak showed from -0.5 to -1.5 V with the maximum current appearing at -1.2 V. These additional peaks were attributed to H₂ oxidation into H⁺ and reduction into H₂, respectively. The large ΔE between oxidation and reduction would suggest that the low reduction value corresponds to the insertion of H⁺ and recombination with e⁻ in the LaNi₅ phase. This overpotential may also be explained by the relatively low diffusion of H⁺ in the membrane and LaNi₅.

a) CV in Ar flow without LaNi,



Figure 6-8: Cyclic voltammogram of reactions on Pt-coated Nafion membrane (a) without $LaNi_5$ in an argon flow (b) with $LaNi_5$ in an argon flow and (c) with $LaNi_5$ in a hydrogen flow.

Cyclic voltammetry of hydrogen oxidation reaction (HOR) and hydrogen evolution reaction (HER) on membrane electrode assembly were usually measured ex-situ in a H₂SO₄ or HClO₄ solution using three electrode configurations. [17-19] The typical voltammogram of ex-situ CV showed two hydrogen adsorption peaks between 0 to 0.4 V if a reversible H₂ electrode was used as a reference electrode. [20] It was reported that measurement conditions significantly affected the overpotential values of voltametric peaks due to the difference in diffusion rate of electro-active species, bulk resistance and other factors. [21, 22] In the Nafion membrane, protons are transported in the form of H_3O^+ and its diffusion coefficient was measured in the order of 10^{-7} cm²/s. [23] The H diffusion coefficients were even smaller within LaNi₅, which was reported to be 2.0×10^{-9} m²/s. [24] The slow H diffusion in the Nafion membrane and LaNi₅ are not comparable with that of H^+ in aqueous solution, which is in the order of 10^{-5} cm²/s. [25] The slow H diffusion would generate greater over-potential during in-situ CV measurement. Furthermore, the contact surfaces, Nafion membrane, LaNi₅ pellet and all connections are expected to bring electrical resistance to the CV measurement and increase the overpotential values of the H oxidation-reduction couple.

Hence, CV proved that it should be possible to charge $/discharge LaNi_5$ electrochemically.

6.4.4 Gas-electrochemical charging of LaNi₅

A typical charging curve is shown in Figure 6-9. The electrochemical charging was started by increasing the applied potential from low value to the required value to avoid excessive strain/stress upon H_2 absorption and a decrepitation of the pelletised electrode. Indeed, we observed that under high voltage the electrode would become decrepit because of the rapid H_2 uptake resulting in large lattice expansion.



Figure 6-9: Evolution of charging current versus time when charging LaNi₅ at 1.5 V.

When charging at 1.5 V, the starting current was about 20 mA and gradually increased to about 100 mA within 150 min (Figure 6-9). The change in charging current is most likely caused by the formation of hydride since its resistivity is different from that of LaNi₅. Adachi et al. observed a decrease in resistivity when hydride formed on the LaNi₅ film since its hydride is more conductive than LaNi₅.[26, 27] The decrease in resistivity undoubtedly led to the current rise and then it levelled off when all the LaNi₅ was converted into hydride.

To find out the suitable potential that should be applied and plot an electrochemical PCI, different potentials were applied to charge the LaNi₅ electrode. Samples after charging were immediately checked by TGA-DSC-MS and XRD Figure 6-10 (insert) to check if hydrogen is charged inside. Samples charged at 0.5 and 1.0 V showed the same diffraction peaks as LaNi₅. Referring to TGA results, we assigned them to hydrides with low hydrogen concentration, e.g. α phase, which has the same crystal structure as LaNi₅. Diffraction peaks from LaNi₅H₆ or LaNi₅H_{6.8} appeared after charging at 1.25 V and 1.50 V, which further proved the success of hydrogen charging by the gas-phase electrochemical method. On a sample charged at 1.50 V, metallic Ni was also observed,

which was possibly from the slight disproportionation of LaNi₅ into LaH_x and Ni. Ni metal and LaH₂ formation was reported by Bowman et al [28] on cycled LaNi₅ and LaNi_{4.9}Sn_{0.1}. We did not detect the LaH₂ phase on XRD, but a small hydrogen release above 300 °C from a sample charged at 1.25 V and 1.50 V possibly from LaH₂ since its bulk material releases hydrogen at high temperature.[29] The LaNi₅ phase observed on these two samples was most likely from the hydride decomposition during XRD sample preparation, transportation and measurement.

The mass loss obtained from TGA was normalised to the mass of LaNi₅ here and hereafter. Upon an initial charging at 0.5 V and 1.0 V, less than 0.2 wt% of H₂ was charged in LaNi₅ sample. After applying a potential of 1.25 V, the material was charged to 1.50 wt% (Figure 6-10). The capacity reached up to 1.56 wt% when LaNi₅ was charged 1.50 V. This excess capacity may be explained by the oxidation of the LaNi₅ due to the humidified membrane. However, no water was detected on MS. Furthermore, XRD did not show any oxides phase after charging. This means hydrogen charged inside LaNi₅ is 1.50 wt% and 1.56 wt% at 1.25 V and 1.50 V, respectively, which is much higher than that of LaNi₅H₆ (1.37 wt%). [30]

This means more than six H were charged into LaNi₅ and the molecular formula will be LaNi₅H_{6.85} based on 1.56 wt% H₂ charged at 1.50 V. The formation of LaNi₅H_{6.5} and LaNi₅H_{7.2} has been reported by Oesterreicher et al [31] after LaNi₅ hydrogenation at room temperature and 77 K, respectively. Although a nine-atom absorption was predicted, the highest hydrogen content was reported to form LaNi₅H_{8.35} at a 1,650 atm hydrogen pressure. [32] In gas-phase electrochemical charging, it is possible to form a hydride phase that contains more than six hydrogen atoms because a low electrochemical potential could be equivalent to a high hydrogen pressure as illustrated in Faraday's equation (6.6). [33]

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Figure 6-10: Electrochemical PCI curves derived from $LaNi_5$ charging at (a) 0.5 V, (b) 1.0 V, (c) 1.25 V and (d) 1.50 V. Insert corresponds to the TGA-DSC-MS and XRD for individual voltage used for charging.

Similar to gas-phase PCI, an electrochemical PCI (Figure 6-10) was obtained by plotting the applied potential versus hydrogen percent charged in LaNi₅. Since there is a significant change in hydrogen content when increasing the applied potential from 1.0 to 1.25 V, it is obvious that the potential plateau is between 1.0 and 1.25 V. This plateau potential is much higher than the value (-0.004 V) calculated from Faraday's equation (6.6) due possibly to a slow diffusion rate of H^+ and/or large internal resistance of the electrochemical cell.

As previously discussed, the over-potential can be generated from limitation of ion conductivity of the Nafion membrane, internal resistance of the circuit connection and interfacial resistance between the LaNi₅ pellet, current collector and Pt layer. Electrical resistance of LaNi₅ seemed to have less impact on over-potential since its resistance was reported to be in the order of $10^{-4} \Omega$ for a 300 nm LaNi₅ film at 50 °C. [27] The conductivity of the Nafion 117 membrane depends on humidity and temperature. It was reported to be 0.07 S/cm at 25 °C and a 100% relative humidity; [34] this value doubled if the membrane was immersed into 1 M H₂SO₄. [35] Interfacial resistance is possibly one of the main causes of the over-potential since there are several contact surfaces and the force applied to press them together will affect the resistance. In fuel cells, contact (interfacial) resistance has been considered to be more important than internal (bulk) resistance since it may be several times higher. [36] Therefore, to reduce the over-potential, strategies are required to minimise the contact resistance.

6.4.5 Gas-phase electrochemical discharging of LaNi₅H_{6.8}

Gas-phase electrochemical discharging of $LaNi_5H_{6.8}$ was then performed to check the reversibility of this novel electrochemical method. The curve of discharging current versus time is given in Figure 6-11. The current decreased from -70 mA to -50 mA in

30 min, which is supposedly due to the resistance rise due to LaNi₅ formation as we discussed above, which possess higher resistance than its hydride form.



Figure 6-11: The gas-phase electrochemical discharging curve of LaNi₅ at -2.0 V.



Figure 6-12: TGA curves of (a) electrochemical discharged $LaNi_5H_{6.8}$ at -2.0 V for 6 h, (b) self-discharged $LaNi_5H_{6.8}$ without applying potential for 6 h and (c) $LaNi_5H_{6.8}$ after electrochemical charging at 1.50 V for 5 h.

The discharged pellet was measured by TGA and the result is shown in Figure 6-12 (a). Compared with $LaNi_5H_{6.8}$ (Figure 6-12 (c)), hydrogen was almost fully released with

hydrogen content less than 0.3 wt% after electrochemical discharging. As comparison, a TGA curve of the self-discharged sample (Figure 6-12 (b)) showed that there was still about 0.74 wt% hydrogen inside the material after six hours self-discharging. Therefore, the process for gas-phase electrochemical charging is reversible and it provides an effective way to discharge LaNi₅ hydride.

To further prove the success of gas-phase electrochemical discharging of LaNi₅, the sample after charging was discharged at -2.0 V to a different depth and the remaining hydrogen inside LaNi5 electrode was checked by TGA after discharging for 0 h, 0.5 h, 3 h and 6 h (Figure 6-13). The electrochemically discharged sample released most of its hydrogen (68%) in the first 30 min, then the hydrogen release rate slowed down till less than 0.3 wt% was left after 6 h discharging. As a comparison, another charged sample was kept in the cell to allow self-discharge for the same time span as electrochemical discharging under the same conditions and their hydrogen content was also checked by TGA. The self-discharged sample only released about 30% of the stored hydrogen in the first 30 min and further released to about 50% in 3 h.



Figure 6-13: The evolution of hydrogen content with time of the charged LaNi₅ during electrochemical discharging and self-discharging.

Therefore, the electrochemical charging of LaNi₅ is reversible and the LaNi₅ hydride can release most of its hydrogen in the first 30 min. The discharging process can be easily performed by reversing the applied potential.

6.4.6 Cyclability improvement

The cyclability was tested at a discharging depth of about 70% by applying a potential of 1.5 V for 120 min for charging and -2.0 V for 30 min for discharging, respectively. The samples after 50 cycles and 100 cycles were checked by TGA-DSC-MS to determine their charging capacity and the results are shown in Figure 6-14. DSC curves showed electrochemical cycling had no effect on the hydrogen desorption temperature and the position of two endothermic peaks remained at 90 °C and 150 °C, which are the same as the first cycle (Figure 6-10). The main hydrogen desorption on MS for all electrochemically charged samples are in the temperature range of room temperature to 250 °C. The only difference are their charging capacities, which is 1.56 wt% (Figure 6-10), 1.36 wt% and 1.30 wt% for the first cycle, 50th cycle and 100th cycle, respectively. The decrease in charging capacity is supposed to be caused by the disproportionation of LaNi₅ under the formation of the high pressure phase LaNi₅H_{6.8}, which was proved by XRD result of the first cycle (Figure 6-10).

Based on the charging capacity of the first cycle, 50^{th} cycle and 100^{th} cycle, the cycle life curve of LaNi₅ cycled by gas-phase electrochemical method was plotted with relative capacity (capacity/capacity theoretical) versus cycle number (Figure 6-15). Cycle life data for gas-phase hydrogenation/dehydrogenation cycling and electrochemical charging in alkaline solution, which are taken from reference [37, 38], were also plotted for comparison purposes.



Figure 6-14: TGA-DSC-MS curves of electrochemically charged LaNi₅ hydride after (a) 50 cycles and (b) 100 cycles.



Figure 6-15: Cycle life curves of LaNi₅ charged by gas-phase electrochemical method with cycle number versus relative capacity, capacity/capacity _{theoretical}. Cycle life data for gas hydrogenation was taken from references [38] and data for electrochemical charging in alkaline solution from reference [37].
The results showed that only LaNi₅ cycled by gas-phase electrochemical method showed a relative capacity above 110% and it decreased to about 100% after 50 cycles. Then its decay rate in capacity in the following cycles is similar to that of gas hydrogenation/dehydrogenation cycling by comparing the slope of cycle life after 50 cycles. Therefore, after 100 cycles, its relative capacity at 95.5% is still slightly higher than that of gas hydrogenation/dehydrogenation cycling. In the same cycling range, the capacity of LaNi₅ electrochemically cycled in alkaline solution decreased significantly to only about 40% and continued decreasing at a fast decay rate. Therefore, it can be concluded that the gas-phase electrochemical method significantly improved the cycling performance of LaNi₅ compared with electrochemical charging in alkaline solution.

6.5 Discussion

6.5.1 Gas-phase electrochemical charging/discharging of LaNi₅

The novel concept of gas-phase electrochemical charging/discharging was developed and its feasibility was tested through LaNi₅ charging/discharging in this chapter. Results showed that this novel method is an effective way to charge and discharge LaNi₅ at room temperature and ambient pressure without the use of a corrosive electrolyte.

The first proof was from the CV measurement under hydrogen flow, which showed an additional redox couple at high overpotentials in comparison with CV under argon flow. The asymmetric redox peaks and high overpotential indicated the possibility of H^+ insertion to LaNi₅ due to slow H diffusion rate inside LaNi₅. Then the charging/discharging current indirectly proved the occurrence of hydrogenation and dehydrogenation of LaNi₅ due to the conductivity difference between LaNi₅ and its hydride. Direct proofs are from the TGA-DSC-MS and XRD results of electrodes after charging. At charging potential higher than 1.25 V, TGA-DSC-MS clearly showed a

hydrogen release more than 1.50 wt% and XRD patterns gave obvious diffraction peaks from the hydride phase.

Therefore, it is proved that LaNi₅ could be hydrogenated or dehydrogenated by the gaselectrochemical method. However, according the evolution of phase to charging/discharging current, there are possible side reactions, which can contribute to the detected overall charging/discharging current. For example, if there are no other reactions except for the hydriding reaction (equation (6.3)) during charging, the current is expected to decrease when most of LaNi₅ is converted to hydride. However, no current drop was observed even after a full charge of LaNi₅, which indicated there are other reactions proceeding in the cell. The main reaction needing to be considered is a proton-electron direct recombination $(2H^+ + 2e^- \rightarrow H_2)$, which has indeed applied to purify or compress hydrogen in an electrochemical way. [39-42] In the cell of this study, Pt catalysts are coated on both sides and it is thus possible that hydrogen directly formed over the catalyst layer. This reaction did not affect the electrochemical charging of LaNi₅ since the hydrogen pressure was always below 1 bar (lower than the absorption plateau of LaNi₅ (Figure 6-7)) on the LaNi₅ side with a releasing valve. However, this side reaction needs to be minimised to increase the charging efficiency. One aspect is to decrease the resistance between the Pt layer and the LaNi₅ electrode so that it is easier for protons to reach the electrode surface. The other aspect will be to increase the proton conductivity of the LaNi₅ electrode using Nafion coated LaNi₅ [43] so that LaNi₅ is more accessible for protons.

Therefore, the gas-phase electrochemical method provides another way to charge/discharge LaNi₅ and its efficiency can be improved if the proton-electron direct recombination $(2H^+ + 2e^- \rightarrow H_2)$ reaction can be minimised.

6.5.2 Application of this novel charging method

The gas-phase electrochemical method avoids the use of a corrosive electrolyte to charge and discharge LaNi₅. This method has the potential to develop a rechargeable all-solid metal hydride-air battery. As shown in Figure 6-16, in charge mode electrical energy is stored in LaNi₅ hydride in the form of hydrogen via the gas-phase electrochemical method. Then the stored energy is released through the reaction of oxygen with protons and electrons, which are from the electrochemical decomposition of LaNi₅ hydride. The electrochemical reactions inside this battery during discharging are:

Anode
$$LaNi_5H_6 \to LaNi_5 + 6H^+ + 6e^ E^{\theta} = -0.004 V$$
 (6.10)

Cathode
$$O_2 + 4H^+ + 4e^- \to 2H_2O$$
 $E^0 = 1.229 V$ (6.11)

Overall
$$2LaNi_5H_6 + 3O_2 \rightarrow 2LaNi_5 + 6H_2O$$
 $E_{cell} = 1.233 \text{ V}$ (6.12)



Figure 6-16: The proposed structure of the MH-air battery based on the gas-phase electrochemical method.

On the anode, $LaNiH_6$ is oxidised to $LaNi_5$ with producing protons and electrons. On the cathode, O_2 is reduced to water by combining protons and electrons. Therefore, the overall reaction is the oxidation of $LaNi_5H_6$ with oxygen gas to produce $LaNi_5$ and water. According to their standard reduction potentials, [44] the cell potential is calculated to be 1.223 V. The calculation of the cell potential using Faraday's equation (equation (6.4)) gave the same value, where the Gibbs free energy of formation is - 157.4 kJ.mol⁻¹,[1] -160.1 kJ.mol⁻¹ [1] and -237.14 kJ.mol⁻¹ [45] for LaNiH₆, LaNi₅ and H₂O, respectively. Thus, this battery has the same single cell voltage as a commercial Ni-MH battery, but longer cycle life is expected without the use of an alkaline electrolyte.

6.6 Conclusions

In this chapter, the feasibility of gas-phase electrochemical charging and discharging of LaNi₅ was studied and an electrochemical cell was designed. This cell avoided alkaline solution which is used in conventional electrochemical charging method. This technique uses a Nafion membrane as a solid electrolyte and hydrogen gas at normal pressure as H source. During charging, protons from hydrogen dissociation pass through the Nafion membrane to combine with electrons from the external circuit inside the LaNi₅ pellet electrode to form a hydride. CV measurements indicated the possibility of hydrogen insertion into LaNi₅. TGA-DSC-MS and XRD investigations of the LaNi₅ samples charged showed that hydrogen was successfully charged inside the material and LaNi₅H_{6.8} formed at high applied potential. The electrochemical PCI plot indicated that to charge LaNi₅ using this method a potential higher than 1.25 V is required. The charged hydrogen was successfully discharged at a potential of -2.0 V. The cycle life test showed that this novel method greatly inhibited capacity decay compared to electrochemical charging in alkaline solution. The cycling properties of LaNi₅ are similar to or even better than gas hydrogenation/dehydrogenation cycling. This method opens the possibility to hydride hydrogen storage material without an alkaline electrolyte at room temperature and under ambient hydrogen pressure. It can also been applied to develop a metal hydride-air battery with LaNi₅ to store and release hydrogen.

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CHAPTER 7 GAS-PHASE ELECTROCHEMICAL CHARGING AND DISCHARGING OF MAGNESIUM

7.1 Introduction

In Chapter 6, the feasibility of charging and discharging of LaNi₅ using gas-phase electrochemical method has been discussed, and experiment results showed that this method is an efficient way to electrochemically charge and discharge LaNi₅ at room temperature and ambient temperature without the use of an alkaline electrolyte. In this chapter, we attempted to extend the use of this method to magnesium. Magnesium has a much higher storage capacity than LaNi₅, but its hydrogenation and dehydrogenation by a conventional gas-phase method requires harsh conditions, e.g. temperature higher than 350 °C, hydrogen pressure > 10 bar for hydrogenation and vacuum for dehydrogenation. Also, it cannot be hydrided or dehydrided electrochemically in alkaline solution electrolyte due to its high reactivity to the electrolyte. Therefore, if this gas-phase electrochemical method is proved to be successful in Mg hydriding and dehydriding, it will greatly promote magnesium application in hydrogen storage.

However, when applying this gas-phase electrochemical method to Mg/MgH₂, several challenges need to be considered. Oxidation is the first challenge since Mg/MgH₂ is very active toward moisture, which is used to humidify the Nafion membrane. Friedrichs et al [1] showed that a thin amorphous magnesium hydroxide, Mg(OH)₂, layer can form on the surface of nanocrystalline MgH₂ powder after even a relative short exposure to air, e.g. 5 min. Obviously, moisture can easily react with the surface of Mg/MgH₂ according to the following reactions:

$$Mg + 2H_2O \to Mg(OH)_2 + H_2$$
 (7.1)

$$MgH_2 + 2H_2O \to Mg(OH)_2 + 2H_2$$
 (7.2)

The Mg(OH)₂ formed on the surface can inhibit the dissociation of molecular H₂ on the surface and diffusion of atom H into the bulk.[2] Even on MgNi alloys, a Mg(OH)₂ phase was reported after 15 charge/discharge cycles in KOH electrolyte, which caused the loss of 59% of the original electrochemical capacity.[3] Therefore, measures should be adopted to avoid Mg/MgH₂ oxidation during gas-phase electrochemical charging-discharging. Fluorite treatment of the surface of MgNi alloys was reported to significantly restrict corrosion during electrochemical charging/discharging in KOH or NaOH electrolyte. [4, 5] Accordingly, the following strategies were adopted: a) fluorinate the surface of Mg by ammonium fluoride treatment and b) add LaNi₅ to the Mg powder to provide more sites for hydrogen splitting.

Considering this gas-phase electrochemical charging/discharging approach, the state of hydrogen in MgH₂ needs also to be considered. There are four states of hydrogen: H₂, proton (H⁺), protium (H^o) and protide (H⁻). Hydrogen exists in the form of H^o in LaNi₅ hydride but in the form of H⁻ in MgH₂. [6] An indirect proof of this is H⁻ formation from gaseous hydrogen at the outer surface of Mg, which provides the possibility of producing NaBH₄ from a NaBO₂/MgH₂ mixture. [7, 8] A protide is a hydrogen atom with an extra electron, which makes it very active and unstable. Therefore, the generation and transport of protides like protons with Nafion is very challenging. Protides were reported to be produced from the dissolution of a saline hydride like LiH in molten alkali halides at high temperature and such molten salts systems have been studied as electrolytes for electrochemical reaction involving protides. [9-12] Protides were required to form and migrate in substituted strontium titanate (SrTiO₃) under reducing conditions, [13, 14] but like molten salts high temperature protide generation and transport of room toom-temperature protide generation and transport of norms.

during hydriding is still unclear. However, electrochemical charging of MgNi alloys would indicate that protons can effectively be transported to some extent within Mg at least within the first subsurface layer prior to the recombination of protons with electrons.

In this chapter, different strategies were investigated to allow the electrochemical charging/discharging of Mg/MgH₂. In the first attempt, a humidified Nafion membrane was used for proton transportation, but Mg/MgH₂ oxidation due to the water permeation across the membrane was observed to hinder the charging/discharging. To minimise the Mg/MgH₂ oxidation, fluorinated Mg/MgH₂ was used as the electrode material and LaNi₅ was added to enhance the proton conductivity in the second attempt. However, Mg/MgH₂ oxidation still occurred during the electrochemical charging/discharging. In order to fully eliminate the Mg/MgH₂ oxidation, the electrochemical charging was then performed under anhydrous conditions with a dry Nafion-polybenzimidazole membrane as the proton conductor and the fluorinated Mg/MgH₂ plus LaNi₅ as the electrode material, which solved the oxidation problem and increased the charging capacity significantly. Based on the results, the advantages of this novel method, its potential application and possible improvements will also be discussed in this chapter.

7.2 Experimental

7.2.1 Electrodes preparation

Magnesium hydride was purchased from Merck. Ammonium fluoride was from Aldrich and used as received. LaNi₅ from Aldrich was activated by cycling it at 80 °C and 40 bar H₂ pressure for hydrogenation and vacuum for dehydrogenation.

For the first attempt, magnesium hydride without any treatment was used as electrode material for electrochemical discharging. The material for electrochemical charging was

obtained by desorbing magnesium hydride at 400 °C under argon flow until no hydrogen was detected by mass spectrometry. They are noted as *untreated* M_gH_2 and *untreated* M_g in the following sections, respectively.

To improve the corrosion resistance and provide more sites for hydrogen dissociation, fluorinate treatment of Mg/MgH₂ surface and addition of LaNi₅ was then performed. This process started by ball-milling magnesium hydride with 10 wt% of activated LaNi₅ and 10 wt% of NH₄F for three times 10 min at 20 Hz on a Retsch MM301 mill. A 15 min waiting period was permitted between each milling. The ball-milled material was then cycled at 350 °C under vacuum for desorption and 30 bar for absorption. The obtained materials were noted as *F-treated Mg/MgH₂* or *fluorinated Mg/MgH₂*. The Ftreated Mg or F-treated MgH₂ were then used to prepare electrodes for electrochemical charging and discharging, respectively.

Electrodes were prepared by a cold-press method in an argon-filled glove box. Firstly, electrode material of 30 mg was finely mixed with 10 or 50 wt% carbon using an agate mortar and pestle. Then, a pellet was prepared by pressing on a stainless steel mesh of the Mg/C mixture at 200 tons/m² pressure for 15 min.

7.2.2 Membrane activation and catalyst layer preparation

In this chapter, two kinds of membrane were used. One is Nafion 117 for electrochemical charging/discharging under humidified conditions and the other one is Nafion-polybenzimidazole (PBI) composite membrane for charging under dry conditions. Nafion 117 is extensively studied for proton transport in fuel cells but its proton conductivity depends greatly on the relative humidity with about 0.1 S.cm⁻¹ achieved under 100% relative humidity. [15-17] To transfer proton in a water-free environment, Nafion-PBI composite membrane is a good candidate since it was reported to have a reasonable proton conductivity and good durability at temperature

higher than 100 °C. [18] The proton conductivity of the composite membrane with 94% Nafion was reported to be 0.001 S.cm⁻¹ after doping with 19% phosphic acid. [19] The activation process of Nafion and Nafion-PBI membrane and catalyst layer preparation are described below.

The Nafion membrane was activated and coated with Pt catalyst using the same procedure as described in Chapter 6. In a typical process, a Nafion 117 membrane was activated by boiling in 6 M HNO₃ for 1 h followed by similar treatment in Milli-Q water for 1 h. The activated membrane was coated with Pt catalyst using a two-chamber cell with the membrane sitting between the two compartments of the cell. Each side of the membrane was then exposed to an aqueous solution of 1.0 M NaBH₄/1.0 M NaOH and 0.01 M H₂PtCl₆. After 20 min of reaction, a conductive Pt layer was formed on the H₂PtCl₆ solution side. The other side of the membrane was coated in the same way.

The activation of the Nafion-PBI composite membrane was achieved by boiling it in 85 wt% H_3PO_4 for 2 h and excess acid was removed with a filter paper. The activated Nafion-PBI composite membrane was then stored in glovebox to keep it dry. The Pt catalyst layer for the Nafion-PBI composite membrane was supported on a carbon cloth. The latter was prepared as follows: the carbon cloth was submerged in 1.5 ml (4 wt%) H_2PtCl_6 solution for 2 h. It was then dried in air at 60 °C for 2 h before H_2PtCl_6 decomposition at 430 °C for 2 h in argon flow and reduction at 480 °C for 4 h in H_2 flow.

7.2.3 Electrochemical charging/discharging

The electrochemical charging and discharging was carried out in a cell with a twoelectrode configuration, similar to the electrochemical cell for the LaNi₅ electrochemical charging/discharging.



Figure 7-1: Scheme of the electrochemical cell for the electrochemical charging/discharging of Mg.

As shown in Figure 7-1, the Pt catalyst layer plus proton conductive membrane was used as the working electrode and Mg/MgH₂ as the counter electrode. During charging, a hydrogen flow of 15 mL.min⁻¹ was passed through the Pt catalyst surface. The electrochemical tests were performed on a multi-channel potentiostat from BioLogic Scientific Instrument, which was controlled by an EC-lab software.

7.3 Results

7.3.1 Properties of the electrode materials

For comparison purpose, properties of the electrode materials were characterised by TGA-DSC-MS and XRD prior to the electrochemical test. These materials include untreated Mg, untreated MgH₂, F-treated Mg and F-treated MgH₂. TGA-DSC-MS results of untreated Mg and F-treated Mg proved that there was no hydrogen in these two materials after desorption at 400 and 350 °C, respectively.



Figure 7-2: TGA-DSC-MS of (a) untreated MgH₂ and (b) F-treated MgH₂.

Untreated MgH₂ gave an endothermic peak at about 434 °C on DSC, which corresponded to the MgH₂ desorption at this temperature with a mass loss about 7.2 wt% (Figure 7-2a). There is also another mass loss of 0.7 wt% at low temperature range from 150 to 300 °C, which was possibly due to surface oxidation. [20] Fluorite treatment by cycling MgH₂ with LaNi₅ and NH₄F at 350 °C made the decomposition of MgH₂ more complex (Figure 7-2(b)). The TGA curve of the F-treated MgH₂ showed a three-step hydrogen release up to 6.4 wt% at 201, 348 and 395 °C, respectively. The values for mass loss here and hereafter are normalised to Mg. Considering 10 wt% LaNi₅ and 10 wt% NH₄F (5 wt% after NH₃ and H₂ release according to equation 7.3), the theoretical capacity of F-treated MgH₂ is 6.1 wt%, which is near the value from TGA (6.4 wt%). It is believed that this 0.3 wt% difference was due to the reaction of NH₄F with MgH₂ [21] and Mg(OH)₂ as shown in equation (7.3) and (7.4).

$$MgH_2 + 2NH_4F \rightarrow MgF_2 + 2NH_3 + 2H_2$$
(7.3)

$$Mg(OH)_2 + 2NH_4F \rightarrow MgF_2 + 2NH_3 + 2H_2O$$
 (7.4)

The reaction between MgH₂ and NH₄F can occur readily due to its large thermodynamic driving force ($\Delta_r G_m^{\theta} = 369.6 \ kJ. mol^{-1}$) [22] and we assumed that MgF₂ formed after the ball-milling and cycling process. Ma et al [21] proved the formation of MgF₂ by XRD examination on a ball-milled mixture of MgH₂ and NH₄F. Furthermore, hydrogen desorption started from 300 °C which is lower than the 400 °C required for the untreated MgH₂. This is due to the catalytic effect of fluorites as reported in the literatures. [23-25] Most importantly, MgF₂ formation was reported to inhibit the generation of magnesium oxide and hydroxide during F-treatment of MgP₂ in an F-containing aqueous solution. [25] The oxidation test proved that F-treated MgH₂ is more resistant to oxidation. As shown in Figure 7-3, there are broad diffraction peaks of MgO on the XRD pattern of the ball-milled MgH₂ but not for F-treated MgH₂ after 24 h exposure to air.



Figure 7-3: XRD patterns of F-treated and ball-milled MgH₂ after 24 h air exposure.



Figure 7-4: XRD patterns of the electrode materials for electrochemical charging and discharging of Mg.

Next the electrode materials were checked by XRD. Untreated MgH₂ showed a tetragonal structure as shown by XRD (Figure 7-4). Tiny peaks from hexagonal Mg were also detected. After hydrogen desorption at 400 °C, this material was fully converted to hexagonal Mg. XRD measurements on F-treated Mg/MgH₂ confirmed the formation of MgF₂, which was assumed to form upon ball-milling and cycling. Material in absorbed form also showed MgH₂, Mg₂NiH₄, LaNi₅, and LaH₃ phases, and in the desorption process MgH₂, Mg₂NiH₄ were converted to Mg and Mg₂Ni, respectively. LaH₃ and Mg₂NiH₄ formation was reported after mechanical milling of MgH₂ + LaNi₅ mixture. [26]

7.3.2 Charging/discharging of untreated Mg/MgH_2 with humidified Nafion membrane as solid electrolyte

The first attempt to charge Mg was carried out in the same way for LaNi₅ charging as stated in Chapter 6. The electrochemical cell was connected as described in Figure 7-5 (insert). The Pt coated Nafion membrane was used as a solid electrolyte and was humidified by a 10 mL.min⁻¹ H₂ flow bubbling through a humidifier. Figure 7-5 showed the evolution of the charging current with time when the applied potential rose stepwise from 0 to 3.5 V.



Figure 7-5: Evolution of the charging current versus time when charging untreated Mg with the humidified Nafion membrane as solid electrolyte. Insertion is the scheme of the electrochemical cell connection.

To check the electrochemical reaction involved during charging, the untreated Mg electrode was removed from the electrochemical cell after 10 h charging and characterised by TGA-DSC-MS (Figure 7-6). For reference, the material before electrochemical charging was also plotted in Figure 7-6.



Figure 7-6: TGA-DSC and MS of untreated Mg before and after electrochemical charging at 3.5 V with the humidified Nafion membrane as solid electrolyte.

TGA-DSC and MS indicated that there was no hydrogen in the Mg material before charging. After electrochemical charging, Mg showed a total weight loss of 3.7 wt%.

The weight loss (0.8 wt%) at a temperature lower than 150 °C was due to surface adsorbed moisture since a weak ion peak from m/z = 18 was detected at about 100 °C. The main decomposition process occurred at temperatures ranging from 150 to 275 °C and a corresponding endothermic peak appeared at 225 °C with release of water and H₂ as detected by mass spectrometry. This H₂ release possibly originated from the thermal decomposition of Mg(OH)₂ [20] and further H₂ release was observed above 400 °C. We thus assume that all decomposition below 275 °C was mainly due to the degradation of a Mg(OH)₂ phase, whereas the 0.7 wt% mass loss observed after 300 °C was due to the decomposition of MgH₂ into several steps as observed by MS. This was corroborated by the endothermic peak at 443 °C observed on DSC.



Figure 7-7: XRD patterns of the untreated Mg electrode before and after charging at 3.5 V with the humidified Nafion membrane as solid electrolyte.

Further check by XRD analysis showed that Mg remained as the main phase after charging although very small peaks from tetragonal MgH₂ were observed (Figure 7-7).

However, the $Mg(OH)_2$ and MgO phases were clearly shown. Accordingly, XRD analysis confirms the formation of the $Mg(OH)_2$ phase, which is in agreement with the TGA-DSC-MS results.

The influence of H_2O on oxidation of Mg nanoparticles was investigated using the Mg K-edge NEXAFS technique by Ogawa and co-workers [27]. Their results proved that water vapour is the main factor for MgH₂ oxidation, which led to the formation of Mg(OH)₂. In this experiment, water was from the moisture of the Nafion membrane. As we have discussed in Chapter 6, the relative humidity of the Nafion membrane is critical to its proton conductivity because molecular water acts as a "vehicle" for the transport of protons. However, the water moisture inevitably led to the oxidation of Mg. For gas hydrogenation, MgO and /or Mg(OH)₂ oxidation layer on Mg surface are inactive as hydrogen storage media and led to decreased storage capacity. More severely, they actively block the penetration of H₂ molecules and H atoms, which slows down hydrogenation kinetics and increases the temperature for hydrogenation. [28] Hence, the low charging capacity obtained in this experiment, 0.7 wt% based on Mg, indicates that the oxidation layer prevented further hydriding during the gas-phase electrochemical charging.

An attempt to discharge untreated MgH_2 was also performed. The electrochemical cell for discharge was connected as illustrated in Figure 7-8 (insert) and a discharging potential of -3.5 V was applied. The current evolution with time was shown in Figure 7-8.

After electrochemical discharging, TGA-DSC and MS measurement was performed on the electrode materials and results are shown in Figure 7-9. For reference, TGA-DSC-MS of MgH₂ before discharging were also plotted. The main mass loss for the materials before and after electrochemical discharging happened in a temperature range of 350 to 500 °C with a corresponding endothermic peak at 434 °C, which can be attributed to MgH_2 decomposition. The weight loss due to MgH_2 decomposition is 7.2 wt% and 6.4 wt% for material before and after discharging, respectively. The difference in hydrogen content of 0.8 wt% could come from electrochemical discharging as well as partial oxidation of MgH_2 . MgH_2 oxidation was proved by mass loss at temperature lower than 350 °C with H_2O detected on MS.



Figure 7-8: Evolution of discharging current versus time when discharging untreated MgH₂ with the humidified Nafion membrane as solid electrolyte. Insertion is the scheme of the electrochemical cell connection.

The XRD investigation (Figure 7-10) of the discharged material and initial material proved the formation of MgO and Mg(OH)₂ phases after discharging. Since both materials showed diffraction of Mg, quantification analysis of the XRD results was carried out. The quantification analysis of XRD results showed that the Mg phase increased from 7% to 15% after discharging at -3.5 V. This proved that a small part of MgH₂ was discharged by the gas-phase electrochemical method.



Figure 7-9: TGA-DSC and MS of the MgH_2 material before and after electrochemical discharging at -3.5 V with the humidified Nafion membrane as solid electrolyte.

Above results showed that hydrding/dehydriding of untreated Mg electrochemically using a wet Nafion membrane has its limitations due to surface oxidation of Mg/MgH₂.

The formation of an oxidation layer prevented further hydrding/dehydriding with charging/discharging capacity less than 0.6 wt%.



Figure 7-10: XRD patterns of the MgH_2 electrode before and after discharging at -3.5 V with the humidified Nafion membrane as solid electrolyte.

7.3.3 Charging/discharging of F-treated Mg/MgH_2 with humidified Nafion membrane as solid electrolyte

F-treated Mg/MgH_2 was then used as electrode material for electrochemical charging/discharging, expecting to minimise oxidation reaction of Mg/MgH_2 .

TGA-DSC-MS results of F-treated Mg after electrochemical charging with humidified Nafion as solid electrolyte (Figure 7-11(a)) showed a weight loss of 2.1 wt% and 0.5 wt% before and after 350 °C, respectively. According to MS, the mass loss before 350 °C was attributed to water moisture and Mg(OH)₂ decomposition since water was also detected with the hydrogen release and the mass loss after 350 °C corresponded to MgH₂ decomposition. Therefore, the fluorite treatment did not fully prevent the oxidation reaction of Mg during electrochemical charging and the hydrogen content charged inside is about 0.5 wt%.



Figure 7-11: TGA-DSC and MS of (a) F-treated Mg after electrochemical charging with humidified Nafion membrane as solid electrolyte and (b) F-treated MgH₂ after electrochemical discharging with humidified Nafion membrane as solid electrolyte.

TGA-DSC-MS of the electrode material after discharging are shown in Figure 7-11(b). Similarly, water from Mg(OH)₂ decomposition was recorded on the mass spectrum of electrode material after discharging. The mass loss from remaining MgH₂ was 4.6 wt%, and the difference to the mass loss of starting electrode material (6.4 wt%) will be 1.8 wt%. This value contains discharged hydrogen via electrochemical discharging as well as the capacity loss from MgH₂ oxidation. Furthermore, the MgH₂ decomposition temperature after electrochemical discharging all shifted to a much higher temperature due to MgO/Mg(OH)₂ formation.

Above results showed that the oxidation of Mg/MgH_2 still occurred when charging/discharging using the F-treated Mg/MgH_2 , although the fluorite treatment has proved to be effective to prevent the oxidation of MgH_2 to some extent (Figure 7-3). Other methods are required to avoid the oxidation problem.

7.3.4 Charging of F-treated Mg with dry Nafion-PBI membrane as solid electrolyte

Since the fluorite treatment did not fully prevent Mg/MgH₂ oxidation under the humidified charging or discharging conditions, we attempted to use dry Nafion-PBI composite membrane as a proton conductor to charge F-treated Mg in a water-free environment. A stepwise potential will also be applied to enable a slow nucleation and growth of the MgH₂ phase and thus avoid the formation of a hydride "front" slowing down hydrogen diffusion.



Figure 7-12: Evolution of charging current versus time when charging F-treated MgH₂ with dry Nafion-PBI membrane as a proton conductor. Insertion is the scheme of the electrochemical cell connection.

The electrochemical cell was connected as shown in Figure 7-12 (insert). For an effective proton transportation inside a Nafion-PBI composite membrane, the electrochemical charging was carried out at 120 °C. Figure 7-12 shows the evolution of charging current when the applied potential increased stepwisely from 0.125 V to 3 V in 24 h.



Figure 7-13: TGA-DSC and MS of the F-treated Mg before and after electrochemical charging up to 3.0 V with a dry Nafion-PBI membrane as a proton conductor.

TGA-DSC-MS were carried out on the electrode material after electrochemical charging and the results are shown in Figure 7-13. Results of material before charging were also plotted as a reference. TGA and MS results showed that the initial material before charging had almost no hydrogen desorption (< 0.1 wt%) when the temperature was increased from 20 to 500 °C. After electrochemical charging up to 3.0 V, the TGA curve showed a mass loss of 2.53 wt% in the temperature range 175 °C-500 °C with several endothermic peaks. Hydrogen was detected as the only desorbed gas by mass spectrometry. Hydrogen was desorbed through a broad peak at a temperature slightly lower than that of the commercial MgH₂ used, i.e. 400 °C (Figure 7-13).

XRD measurements were then carried out on fluorinated Mg after electrochemical charging under dry conditions. The results are plotted in Figure 7-14. The XRD pattern of the fluorinated Mg before charging proved that there were no diffraction peaks from MgH_2 before charging. Under dry conditions of charging, diffraction peaks from MgH_2 at 35.9, 39.9 and 54.7 ° were clearly seen, which further proved that hydrogen was successfully charged into Mg under dry conditions.



Figure 7-14: XRD patterns of the F-treated MgH₂ before and after electrochemical charging under dry conditions.

The above results showed that electrochemical charging in dry conditions successfully prevented Mg/MgH₂ oxidation and subsequently the charging capacity increased greatly to 2.53 wt%, which is almost half of that of fluorinated MgH₂. Attempts to fully charge the material were however unsuccessful and the problem may be due to 1) formation of a hydride layer blocking the absorption since MgH₂ is insulating and 2) slow diffusion of H^+ into Mg/MgH₂ phase.

7.4 Discussion

The use of a gas-phase electrochemical method to charge/discharge hydrogen storage material was extended to the high capacity hydride, MgH₂, in this chapter. Hydrogen was successfully charged into magnesium with high capacity when the process was carried out under water-free conditions. The challenges of this method and possible solution of this method are discussed in the following sections.

(1) Mg/MgH₂ oxidation

When the humidified Nafion membrane was used as the solid electrolyte, hydrogen was successfully charged into Mg or discharged MgH₂, but the capacity was very limited. The main problem was the oxidation of Mg/MgH₂ by the moisture of the membrane. The study of water transport in the Nafion 117 membrane showed that the net water transport across the membrane was low with a value of 0.2 H₂O/H⁺. [29] This is possibly one reason that no water was detected for LaNi₅ charging/discharging. However, since Mg/MgH₂ is too reactive to moisture, the reaction between them will possibly drive more water across the membrane due to the diffusion force. Thus the oxidation layer formed prevented the formation of MgH₂ during charging or MgH₂ decomposition during discharging.

Although fluorite treated Mg/MgH_2 can prevent the oxidation to some extent, $MgO/Mg(OH)_2$ were still observed after charging/discharging. The successful pathway was the use of the Nafion-PBI composite membrane, which can conduct protons under water-free conditions.

(2) Side reactions

When a humidified membrane was used, several side reactions were involved during charging and discharging, for example, proton-electron direct recombination, water splitting, Mg/MgH₂ oxidation. When the Nafion-PBI composite membrane was used, the main side reaction remaining is the proton-electron direct recombination. As we already discussed in Chapter 6, the proton-electron direct recombination proceeds on Pt or electrode surface with protons and electrons directly recombined to form hydrogen gas instead of the recombination inside Mg to form MgH₂. Indeed, this side reaction has been applied for hydrogen purification and compression. [30, 31] However, in this study, this reaction needs to be minimised to increase the charging efficiency. The addition of LaNi₅ is expected to increase the proton conductivity of the electrode so as to minimise this side reaction. The deposition of a Nafion layer on the metal hydride surface was also reported to increase the proton conductivity of metal hydride to minimise the proton-electron direct recombination. [32]

(3) Kinetic limitation

During gas-phase electrochemical charging, the charging capacity was limited by the hydriding kinetics. After 24 h charging under water-free conditions, magnesium was not fully charged, which is most likely due to the slow diffusion rate of hydrogen in Mg and MgH₂. The diffusion coefficient of hydrogen in Mg and MgH₂ is 4×10^{-13} m².s⁻¹ and

 1.5×10^{-16} m².s⁻¹, respectively. A stepwise potential has been applied in this study to enable a slow nucleation and growth of the MgH₂ phase and thus avoid the formation of a hydride "front" slowing down hydrogen diffusion. Furthermore, nanomaterials have the potential to improve the kinetics with a short H diffusion pathway.

(4) Anhydrous proton conductive membrane

A Nafion-PBI composite membrane can transport protons under water-free conditions, but it requires temperatures higher than 100 °C to have reasonable proton conductivity. Compared with the humidified Nafion membrane (about 0.1 S.cm⁻¹ at 100% relative humidity), its conductivity (0.001 S.cm⁻¹) is very low for proton transportation. New membranes that have high proton conductivity at room temperature need to be developed.

Therefore, the gas-phase electrochemical method is a promising method to charge and discharge Mg at room temperature and ambient pressure. Future studies on minimising the side reactions, increasing the H diffusion kinetics and using a new anhydrous membrane will possibly greatly improve its charging/discharging properties.

7.5 Conclusions

In this chapter, gas-phase electrochemical charging/discharging of Mg/MgH₂ was investigated. TGA-DSC-MS and XRD results on untreated Mg/MgH₂ after electrochemical charging or discharging with a humidified Nafion membrane as solid electrolyte proved that this technique has the ability to charge H into Mg or discharge it from MgH₂. However, the water, which is used to humidify the Nafion membrane, transported through the membrane and reacted with Mg and MgH₂ to form a MgO/Mg(OH)₂ layer. These oxidation layers prevent further charging and discharging. Therefore, only very low charging/discharging capacities of < 0.6 wt% were obtained. An attempt to prevent Mg/MgH₂ oxidation by the use of F-treated Mg/MgH₂ surface was not successful. Then, the fluorite treatment of Mg/MgH₂ was combined with the use of a dry Nafion-PBI membrane as a proton conductor to charge Mg in a water-free environment. Under dry conditions, the problem of Mg/MgH₂ oxidation was solved and the charging capacity increased significantly to 2.53 wt%. TGA-DSC-MS identified the hydrogen charged inside Mg and XRD results proved the formation of the MgH₂ phase. Further work is needed to be undertaken on MgH₂ discharging under dry conditions.

For the Nafion-PBI composite membrane, its working temperature for proton exchange under dry conditions is above 100 °C. Further study on the gas-phase electrochemical method should be focused on the use of a room temperature conductive non-hydrous membrane. Furthermore, Mg was not fully hydrided to MgH₂ using dry-state electrochemical charging and slow hydrogen diffusion rate in Mg/MgH₂ is possibly one reason. Nano-sized magnesium can be used to replace bulk magnesium for future work to reduce diffusion distance so as to fully hydride Mg.

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CHAPTER 8 CONCLUSIONS AND FUTURE PERSPECTIVES

Storage of hydrogen in metal hydrides is safer and more efficient compared with conventional storage methods, e.g. compressed gas and liquefaction. However, for high capacity hydride, e.g. Mg, it suffers problems of high temperature and pressure for cycling. This research aimed to solve problems of metal hydrides for hydrogen storage from two aspects: nanosized storage materials and a novel hydriding/dehydriding technique. On the material aspect, LaNi₅ and magnesium in nanoscale were targeted for investigation. LaNi₅ nanoparticles were synthesised in an energy efficient way, combustion - reduction method, and their storage properties and size effects were studied. Magnesium nanoparticles were synthesised by a chemical reduction method and modified with elemental coating with all the efforts to increase kinetics and alter the thermodynamics of Mg for hydrogen storage. On the aspect of the novel hydriding/dehydriding method, a universal gas-phase electrochemical technique was developed to charge/discharge hydrogen storage materials to avoid high temperatures and pressure in gas hydriding/dehydriding and the use of a corrosive electrolyte in electrochemical charging/discharging. Based on each aspect, the following conclusions were drawn and future perspectives were proposed.

8.1 Nanomaterials for hydrogen storage

Firstly, size effects were investigated with LaNi₅ as a model. LaNi₅ nanoparticles were synthesised via an energy effective procedure, which involved La₂NiO₄ + NiO synthesis by a solution combustion method followed by reduction with CaH₂ and wash with NH₄Cl in ethanol solution. This material showed a sponge-like porous structure with crystallite size of 49 nm and average particle size of 250 nm. To further reduce their particle size, we attempted to support LaNi₅ nanoparticles on carbon but consumption of carbon with the formation of LaNi₅C₃ was observed. Hydrogen storage investigation on

LaNi₅ nanoparticles showed this material can be cycled at room temperature without an activation process. Compared with activated commercial LaNi₅, LaNi₅ nanoparticles showed a great improvement in kinetics for absorption and desorption but without a significant change in thermodynamics.

Next, the synthesis of magnesium nanoparticles was investigated and size effects on hydrogen storage properties were studied. A chemical reduction method was used for magnesium nanoparticles synthesis by reducing di-n-butylmagnesium with alkali naphthalenide. Changing the reducing agent from Li to Na and K during synthesis generated Mg nanoparticles with mean particle size of 18 nm, 24 nm and 18 nm, respectively. LiH was formed on Li reduced material and metallic Na and K phases were detected respectively on Na and K reduced magnesium nanoparticles when excess alkali naphthalenides were used. LiH and metallic Na and K were from the decomposition of alkali naphthalenides or butylM on the surface of magnesium nanoparticles and this process generated a LiH, Na or K shell with magnesium nanoparticles as a core. The Na or K shell was then converted to perovskite hydride, NaMgH₃ or KMgH₃, after hydrogenation at 300 °C. Fast kinetics were observed on the K-coated Mg nanoparticles due to a higher catalytic effect of KMgH₃ or smaller Mg particles size. More importantly, K coated Mg nanoparticles decreased the reaction enthalpy and entropy for hydrogen hydrogenation to $-61.8 \pm 1.7 \text{ kJ} \cdot \text{mol}^{-1} \text{ H}_2$ and -113.6 \pm 3.0 J. K⁻¹.mol⁻¹ H₂, respectively.

Then size effects were investigated on Li reduced magnesium nanoparticles, which can avoid the effects from the perovskite structure. By varying the reactants' ratio, the particle sizes can be controlled in the range from 8 nm to 350 nm. Nanoparticles synthesised at high lithium/naphthalene had small particle sizes and were capable of absorbing hydrogen at temperatures lower than 150 °C. All magnesium nanoparticles

could be fully cycled at 300 °C and the sorption kinetics to a great extent depended on their particle size. The fastest kinetics were observed on nanoparticles of 18 nm mean particle size with full absorption in less than 10 min and full desorption in less than 100 min at 300 °C. As expected, particle sizes of magnesium also greatly influenced the reaction thermodynamics. Magnesium nanoparticles with mean particle size of 16 nm reduced the reaction enthalpy by a value of 11.7 kJ mol⁻¹ H₂. However, the phenomenon of entropy – enthalpy compensation effects also caused a reduction of entropy by 20.6 J K⁻¹ mol⁻¹ H₂, which weakened the effect from enthalpy reduction with an overall reduction in desorption temperature of 24 °C compared to bulk magnesium.

As the core-shell structured materials showed improved hydrogen storage properties, other elemental M (Co, Fe, Ni, Si and Ti) shells were also successfully formed on magnesium nanoparticles using a transmetalation reaction between MCl_x and Mg to active the magnesium surface and further alter their thermodynamics. The coated materials showed smaller particle sizes due to the sacrificial oxidation of surface magnesium. The hydrogen storage investigation showed that elemental coating improved their hydrogenated at 140 °C only and all coated samples were fully hydrogenated at 240 °C. Upon hydrogenation at 350 °C, a shell of complex hydrides was formed around the MgH₂ core, which controlled hydrogen desorption kinetics to some extent with Ni coated material showing the best kinetics of less than 50 min for full desorption at 300 °C. More importantly, the coating altered the thermodynamics and the plateau pressures were correlated with the electronegativity of the coating elements.

It can be concluded that the combustion-reduction method and chemical reduction method used in this thesis are effective approaches for the preparation of LaNi₅

nanoparticles and Mg nanoparticles, respectively. Size reduction showed effects on kinetics and thermodynamics. For LaNi₅, nano-sizing led to significantly improved kinetics. For Mg nanoparticles, smaller particles generally showed faster kinetics but a Ni catalyst was still needed to reduce desorption time to less than 60 min at 300 °C. Nanosizing also altered thermodynamics and decreased hydrogenation temperature for Mg to near 100 °C, but a temperature of 300 °C was still required for hydrogen desorption due to the entropy – enthalpy compensation effects.

8.2 Gas-phase electrochemical charging/discharging

Nano-sizing and elemental coating of magnesium lowered the hydrogenation and dehydrogenation temperature to some extent and accelerated its kinetics with Ni coating. However, a temperature above 100 °C was still required for hydrogenation and a temperature above 300 °C for dehydrogenation. Therefore, a new concept of gas-phase electrochemical charging/discharging was proposed and developed to hydride and dehydride Mg at or near room temperature and ambient pressure. In this concept, taking charging as an example, firstly hydrogen is split into protons and electrons with the help of a catalyst. Then protons pass through a membrane and electrons flow via an external circuit to combine inside Mg or LaNi₅ to form a hydride on the other side of the membrane.

LaNi₅ was used as a model again to develop this method. Pt was used as a catalyst for hydrogen splitting and Nafion 117 was used as a proton conductive membrane. Pt was successfully coated on the Nafion membrane in a two chamber cell. Then an electrochemical cell was designed and the novel concept was tested. The CV measurement provided the first evidence of hydrogen splitting on Pt catalyst and H charging into LaNi₅. TGA-DSC coupled with MS and XRD measurement of the charged electrode then proved that LaNi₅ was successfully hydrogenated using this method and a high-pressure phase was formed with the storage capacity up to 1.56 wt%. After charging at different potential, an electrochemical PCI curve was plotted and the potential plateau was proved to be at 1.25 V. The reversed process, electrochemical discharging, was proved to be successful as well when discharging at -2.0 V.

After successfully charging/discharging LaNi₅ using the gas-phase electrochemical method, an Mg electrode was used to replace LaNi₅ to check if this method is universal. TGA-DSC coupled with MS showed that hydrogen could be charged into Mg or reversibly discharged, but the charge/discharge capacity was low due to Mg(OH)₂/MgO formation when the electrode reacted with water, which is essential for proton conductivity of Nafion membrane. Several modifications were then made to solve the oxidation problem and improve hydrogen splitting and diffusion. These modifications included the F-treatment of Mg surface and the use of PBI composite as a dry membrane. After these modifications, the electrode was charged at 120 °C up to 3.0 V and TGA-DSC coupled with MS proved that the charging capacity was successfully increased up to 3.2 wt% and MgH₂ was formed as detected by XRD.

Successful charging and/or discharging of LaNi₅ and Mg proved that the gas-phase electrochemical method is a potential method to hydride/dehydride metal hydrides at or near room temperature and ambient pressure. This method can also be extended to develop rechargeable fuel cells.

8.3 Future perspectives

Results of this project proved that Mg nanomaterials combined with a suitable catalyst can lower hydrogenation/dehydrogenation temperature and increase the sorption kinetics. However, the temperature was still too high for practical on-board application. The development of a gas-phase electrochemical hydriding/dehydriding method provided a possible way to store and release hydrogen in metal hydrides near room temperature and ambient pressure. However, further investigations are required to optimise the properties of hydrogen storage materials and understand the gas-phase electrochemical hydriding/dehydriding method.

The following four directions could be carried out:

- Improving the synthesis conditions for the synthesis of magnesium nanoparticles to minimise the content of impurities since their storage capacity was lower than the theoretical value although magnesium nanoparticles were successfully synthesised and size effects were evaluated.
- Fine tuning the enthalpy and entropy to minimise the compensation effect between them. Finely controlling particle size and adding suitable additives could reach this aim.
- 3. Taking measures to reach high capacity dehydriding of MgH₂ since Mg showed low discharging capacity although the charging/discharging process was observed to be reversible. One possible solution is to find an anhydrous membrane with high proton conductivity at room temperature.
- Understanding of the mechanism for gas-phase electrochemical charging/discharging method by electrochemistry analysis.

Nanosizing, the gas-phase electrochemical hydriding/dehydriding method and their combination are promising approaches to lower sorption temperature and/or accelerate sorption kinetics for metal hydrides. Their thorough investigation would lead to the wide application of hydrogen for on-board purposes.

APPENDIX I CHARACTERISATION TECHNIQUES

The materials synthesised in this thesis were characterised by various techniques before the test of their hydrogen storage properties. These techniques include x-ray diffraction (XRD) for structural information, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) coupled with energy-dispersive x-ray spectroscopy (EDS) for morphology and compositional information, x-ray photoelectron spectroscopy (XPS) and inductively coupled plasma/optical emission spectrometry (ICP/OES) for compositional information.

(1) XRD

X-ray diffraction is a powerful technique to identify the crystal phase of crystalline materials. Its working principle is based on constructive interference of X-rays with a crystalline sample. The interactions between the incident x-rays and the crystalline structure generate scattered x-rays, which produce constructive interference when the conditions satisfy Bragg's law (Equation A.1) (Figure A-1). The constructive interference then results in a reflected wave of significant intensity and is recorded as peak in the diffraction pattern.

$$n\lambda = 2d\sin\theta$$
 (A.1)

where *n* is the integer number of wavelengths; λ is the wavelength of x-ray; d is the repeating distance between reflecting planes and θ is the scanning angle.



Figure A-1: Schematic diagram of the principle of X-ray diffraction.

In this study, XRD patterns were recorded on a Philips X'pert Multipurpose XRD system operated at 40 mA and 45 kV with a monochromated Cu K α radiation ($\lambda = 1.541$ Å) with step size = 0.01, 0.02 or 0.05, time per step = 10 or 20 s/step. The XRD samples were prepared inside a glovebox and they were protected against oxidation from air by a Kapton foil during transport and measurement.

The obtained XRD patterns were then analysed with database software of X'pert Highscore from Panalytical. The crystalline size of materials was estimated using a Scherrer equation:

$$D = \frac{\kappa\lambda}{\beta\cos\theta} \tag{A.2}$$

where D is the average size of the crystallites; K is the Scherrer constant; λ is the wavelength of radiation; β is the peak width at half height (in rad) and θ corresponds to the Bragg angle.

(2) SEM

SEM is a widely used technique to image the surface of samples. The principle of SEM is based on the interaction of an incident electron beams and the solid specimen. Their interaction generates a wide variety of emissions from the specimen, including backscattered electrons, secondary electrons, Auger electrons and x-rays. Secondary electrons and backscattered electrons are detected for SEM images and x-rays are used for EDS analysis of the elemental composition of the sample.

SEM was performed on a FEI Nova NanoSEM 230 FESEM with a Bruker Silicon Drift Energy Dispersive X-ray microanalysis system at an acceleration voltage of 10.0 kV and a working distance of 5-10 mm. SEM samples were dispersed on a carbon tape on a SEM stub.

(3) TEM

TEM is an advanced technique where electron beams are transmitted through an ultrathin specimen, and then an image is formed, magnified and detected by a sensor. In TEM images, contrast is formed due to the interaction of the electron beam with the sample. Combined with EDS, the properties of nanoparticles, such as the shape, size and composition are characterised.

TEM was imaged on a FEI Tecnai G2 microscope operated at 200 kV. High resolution TEM and Scanning Transmission Electron Microscopy (STEM) mapping was performed on a Philips CM200 microscope. The materials were dispersed in THF, dropped onto a carbon coated copper grid and dried before transferring to the microscope.

(4) XPS

XPS is a powerful tool for surface analysis of solid materials. During the XPS experiment, photoelectrons are ejected when the solid sample is irradiated by monochromatic X-rays under ultrahigh-vacuum condition. Photoelectrons from different atomic shells possess characteristic kinetic energy. Their binding energy can be obtained according to the following equation:

$$KE = hv - BE - \varphi_{sp} \tag{A.3}$$

where KE is the kinetic energy; hv is the energy of incident X-ray; BE is the binding energy and φ_{sp} is the spectrometer work function.

The chemical environment of an element can also affect the binding energy, leading to so-called "chemical shift" that can provide information on the oxidation states of elements on the surface.

In this thesis, XPS were carried out on a Thermo Scientific VG-ESCALAB 220-iXL spectrometer with a monochromated Al-K α radiation at 1486.60 eV and a power source

of 120 W. A spot size of 0.5 mm in diameter with pass energy of 100 eV was used for wide scans and pass energy of 20 eV was used for narrow scans of particular elemental peaks. The materials were exposed to air during transfer to the instrument.

(5) ICP/OES

ICP/OES is used to characterise the chemical composition of bulk material. Solid materials need to be dissolved in solution by acid digestion before measurement. Then the sample is introduced into an ICP source and a complete atomization of the sample is achieved producing characteristic optical emissions at different wavelengths. The concentration of the sample is obtained by comparing the measured intensity to intensities of standards of known concentration.

ICP-OES was measured on an OPTIMA 7300 instrument from Perkin–Elmer. Prior to the analysis, 50 mg of material was digested in concentrated nitric acid at 60 $^{\circ}$ C for 12 h and then the solution was diluted with high purity water to 10 mL for measurement.

APPENDIX II HYDROGEN STORAGE PROPERTY TEST

The hydrogen storage properties were tested by thermogravimetric analysis- differential scanning calorimetry - mass spectrometry (TGA-DSC-MS), high pressure differential scanning calorimetry (HP-DSC), and kinetics-pressure-composition isothermal (PCI) measurements.

(1) TGA-DSC-MS

TGA-DSC-MS of hydrogenated samples gives information about storage capacity, desorption temperature and related thermodynamics. This measurement was performed at 10 °C.min⁻¹ under an Argon flow of 25 mL.min⁻¹ using a Mettler Toledo TGA/DSC 1 coupled with an OmniStar (Pfeiffer) Mass Spectrometer. The TGA/DCS was hosted in an Argon filled glove box (< 1 ppm O₂ and H₂O) to avoid any oxidation of the materials and masses between m/z = 2 and 100 were followed by MS.



Figure A-2: Instrument for TGA-DSC-MS.

(2) HP-DSC

HP-DSC is used to characterise the thermodynamic change during hydrogen absorption and desorption, and give information about reversibility of hydrogen storage materials. HP-DSC was performed on a Sensys Evo DSC apparatus (Setaram) equipped with a 3D sensor and a calibrated high pressure cell. Typically 50 mg of material was used and measurements were performed at 5 °C.min⁻¹ under 30 bar hydrogen pressure for absorption and 0.5 bar for desorption.



Figure A-3: Instrument for HP-DSC.

(3) Kinetics and PCI

Kinetics and PCI were measured by volumetric method, which gave information about storage capacity, absorption/desorption rate and plateau pressure. Plateau pressures at different temperature can then be applied to calculate the reaction enthalpy and entropy. The instrument used is an automatic Sieverts apparatus (Advanced Materials Corporation). For the kinetic measurements, a hydrogen pressure of 30 bar was used for absorption and pressures of 0.5 bar for desorption. Prior to PCI measurements the materials were cycled 3 times at 300 °C. The PCI measurements were then performed with a step size of 0.4 bar at three different temperatures.



Figure A-4: Instrument for kinetics and PCI.