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DESIGN AND DEVELOPMENT OF HIGH STORAGE CAPACITY COMPLEX HYDRIDES FOR REVERSIBLE HYDROGEN STORAGE IN VEHICLES

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ABSTRACT

In this thesis, we have developed and synthesized novel light weight complex hydrides for reversible hydrogen storage. Metal hydrides have a good hydrogen storage capacity but possess slow kinetics, irreversibility and high activation energy barriers. Therefore these metal hydrides often require very high temperatures ($>350^{\circ}\text{C}$) to release hydrogen. This behavior makes difficult for their wide usage in hydrogen storage applications. We have extensively employed a unique synthesis approach of solid state mechano-chemical process via high energy ball milling at a constant rotational speed of 400rpm but with varying milling durations. From this synthesis process, eight new complex hydrides have been prepared and each of them were characterized using the Pressure-Composition Isotherms (PCT), Residual Gas and/or Mass Spectrometric analysis (RGA/MS) and the Fourier Transform Infrared Spectroscopy (FT-IR) to determine their chemical and hydrogen sorption properties. The as-synthesized new complex hydrides developed from this work bearing light weight elements such as Lithium, Magnesium, Boron, Aluminum etc. in this present study, excel in physical and chemical behavior in terms of lower activation energies, higher reversible hydrogen storage capacity $\geq 6\text{wt}\%$ at operating temperatures below 350°C and faster reaction kinetics than the conventional metal hydride counterparts. Unfortunately, their residual gas analysis has revealed the evolution of some undesired and toxic gases such as ammonia (NH_3) and di-borane (B_2H_6) in addition to the release of hydrogen. But the release of these toxic gases was eventually suppressed by further synthesis in presence of catalysts and also by consecutive hydrogenation-dehydrogenation cycling. Among the various complex hydrides developed, two novel systems such as Li-nMg-B-N-H and $\text{BNH}_6\text{-nMgH}_2$ distinguish themselves as being efficient reversible hydrogen storage materials for on-board (fuel cell) vehicular applications.

Key Words:

Metal hydrides;

Hydrogen storage;

Complex hydrides;

Activation energy;

Mechano-chemical synthesis.

RESUME

Dans ce mémoire, nous avons procédé à la synthèse et à l'analyse des nouveaux hydrures complexes plus légers destiné au stockage réversible de l'hydrogène. Les hydrures métalliques ont une bonne capacité de stockage d'hydrogène, mais possèdent une cinétique lente, un problème d'irréversibilité et des barrières d'énergie d'activation élevée. Par conséquent, ces hydrures métalliques exigent souvent des températures très élevées (>350°C) pour libérer de l'hydrogène. Ce comportement rend difficile leur utilisation à grande échelle dans les applications de stockage d'hydrogène. Nous présentons dans cette étude, une approche unique qui est la synthèse du processus mécano-chimique des matériaux à l'état solide par le broyage à boulets à haute énergie. Elle se fait à une vitesse de rotation constante de 400 tr/min, mais avec différentes durées de broyage. De cette synthèse, huit nouveaux hydrures complexes ont été élaborés et chacun d'eux est caractérisé à l'aide du Pression-Composition isothermes (PCT), l'analyseur des gaz résiduels ou le spectromètre de masse (RGA/MS) et la Spectroscopie infrarouge à transformée de Fourier (FT-IR), afin de déterminer leurs propriétés chimiques et de sorption d'hydrogène. De cette étude, il résulte que les nouveaux hydrures complexes synthétisés à partir des éléments légers tels que le Lithium, magnésium, bore, aluminium etc. ont montré un comportement physique et chimique excellents. Ceci se démontre par des énergies d'activation plus basses, des plus grandes capacités réversibles de stockage d'hydrogène (supérieur à 6%) à des températures inférieures à 350°C et des cinétiques plus rapides que les hydrures métalliques conventionnelles. Cependant, l'analyse des gaz résiduels a révélé l'évolution de certains gaz indésirables et toxiques tels que l'ammoniac (NH₃) et le diborane (B₂H₆), en plus de l'hydrogène. La libération de ces gaz toxiques a été finalement supprimée en faisant plus de synthèse en présence de catalyseurs et aussi par des cycles consécutifs d'hydrogénation et de déshydrogénation. Des divers hydrures complexes développés, deux nouveaux systèmes tels que Li-nMg-B-N-H et le BNH₆-nMgH₂ se distinguent comme étant des matériaux de stockage d'hydrogène réversible et efficaces pour les applications automobiles (pile à combustible).

Mots clés

Hydrures métalliques;

Stockage d'hydrogène ;

Hydrures complexes ;

Energies d'activation ;

Synthèse mécano-chimique.

**DESIGN AND DEVELOPMENT OF HIGH STORAGE CAPACITY COMPLEX
HYDRIDES FOR REVERSIBLE HYDROGEN STORAGE IN VEHICLES**

LIST OF ABBREVIATIONS

Al: Aluminum

Av: Average

B: Boron

B₂H₆ : Diborane

BET: Brunauer Emmett Teller

BNH₆: Amino Borane

CaH₂ -Calcium Hydride

CH₄ – Methane

cMgH₂: commercial Magnesium Hydride

Co: Cobalt

CO₂: Carbon dioxide

DOE – Department of Energy

EERE: Energy Efficiency and Renewable Energy

FC: Fuel cells

FC&FP: The Freedom Car and Fuel Partnership

Fe: Iron

FT-IR – Fourier Transform Infrared Spectrometer

GrC: Gravimetric Capacity

H₂: Hydrogen

HEBM – High Energy Ball Mill

ICE: Internal Combustion Engine

K: Potassium

KBr: Potassium Bromide

Li – Lithium

LiAlH₄ – Lithium Aluminum Hydride

LiBH₄ – Lithium Borohydride

DESIGN AND DEVELOPMENT OF HIGH STORAGE CAPACITY COMPLEX HYDRIDES FOR REVERSIBLE HYDROGEN STORAGE IN VEHICLES

LiH -Lithium Hydride

LiNH₂ – Lithium Amide

Max: maximum

Mg- Magnesium

MgH₂ – Magnesium Hydride

Na – Sodium

NH₃: Ammonia

Ni: Nickel

nMgH₂: Nano Magnesium Hydride

O₂: Oxygen

OH: Hydroxide

PCT: Pressure Composition Temperature

PEM: Proton Electron Membrane

RGA/MS: Residual Gas Analysis/ Mass Spectrometry

RTP: Room Temperature and Pressure

ScH₂ - Scandium Hydride

STP- Standard Temperature and Pressure

TBD: To Be Determined

TGA: Thermo Gravimetric Analysis

Ti: Titanium

TiH₂-Titanium Hydride

UHP: Ultra High Purity

US DOE: United States Department of Energy

VC: Volumetric Capacity

XRD: X- Ray Diffraction

Zr: Zirconium

TABLE OF CONTENTS

LIST OF TABLES.....	3 -
LIST OF FIGURES.....	4 -
INTRODUCTION.....	5 -
CHAPTER 1: STATE OF THE ART AND BACKGROUND.....	6 -
1. HYDROGEN- A CLEAN AND RENEWABLE FUEL.....	6 -
2. OBSTACLES FACING THE STORAGE OF HYDROGEN	6 -
3. COMPLEX METAL HYDRIDES	8 -
3.1. General Overview	8 -
3.2. Properties of chosen metal hydrides	8 -
3.3. Methods to improve kinetics and thermodynamic stability of starting hydrides	10 -
4. THESIS AIM AND SIGNIFICANCE.....	12 -
CHAPTER 2: EXPERIMENTAL APPROACH.....	13 -
1. MATERIALS AND EQUIPEMENT	13 -
2. SYNTHESIZING METHODS AND EQUIPMENT	13 -
2.1 Planetary high energy ball mill (HEBM).....	13 -
2.2 Nitrogen Filled Glove Box (<1 ppm O ₂ / moisture).....	15 -
3. CHARACTERIZATION METHODS AND EQUIPMENT	16 -
3.1 Fourier Transform Infrared Spectroscopy (FT-IR).....	16 -
3.2 Pressure-Composition Isotherms (PCT)	16 -
3.3 X-ray Diffraction (XRD)	17 -
3.4 Autosorb iQ Gas Sorption and Residual Gas Analyzer	18 -
4. GENERAL PROCEDURE.....	19 -
CHAPTER 3: RESULTS AND DISCUSSION.....	20 -
1. LINMGNH COMPLEX HYDRIDES.....	21 -
1.1. Mass Spectrometry, Ramping kinetics and TGA Analysis.....	22 -
1.2. FT-IR Spectroscopy	25 -
1.3. Analysis of scheme 1	25 -
2. LINMGALNH COMPLEX HYDRIDES	26 -
2.1. Mass Spectrometry, Ramping kinetics.....	26 -
2.2. Analysis of scheme 2	28 -
3. LINMGBNH COMPLEX HYDRIDES	28 -

**DESIGN AND DEVELOPMENT OF HIGH STORAGE CAPACITY COMPLEX
HYDRIDES FOR REVERSIBLE HYDROGEN STORAGE IN VEHICLES**

3.1.	X-Ray Diffraction	- 28 -
3.2.	FT-IR Spectroscopy	- 29 -
3.3.	Mass Spectrometry and Kinetics of LinMgBNH.....	- 30 -
3.4.	Analysis of scheme 3	- 31 -
4.	BNH ₆ .MGH ₂ COMPLEX HYDRIDES.....	- 32 -
4.1.	Mass Spectrometry and Kinetics of all BNH ₆ Complex hydrides	- 32 -
4.1.1.	Hydrogen release in complexes.....	- 32 -
4.1.2.	Toxic gas release in complexes	- 33 -
4.1.3.	Kinetics of BNH ₆ .2nMgH ₂	- 34 -
4.2.	FT-IR Spectroscopy	- 35 -
4.3.	Analysis of scheme 4	- 35 -
CONCLUSION.....		- 36 -
RECOMMENDATIONS		- 37 -
REFERENCES		- 38 -
ANNEXURES		- 41 -
ANNEX 1: COMPARISM OF HYDROGEN FUEL TO OTHER HYDROCARBON FUELS		- 41 -
ANNEX 2: US DOE DETAIL TARGETS FOR ONBOARD HYDROGEN SYSTEMS		- 42 -
ANNEX 3: THE PRINCIPAL COMPONENTS OF THE GLOVE BOX AND ITS FUNCTIONS		- 43 -
ANNEX 4: DESCRIPTION OF VALVE OPERATIONS OF THE PCTPro E&E INSTRUMENT		- 44 -
ANNEX 5: EXAMPLE OF EXCEL PAGE USED FOR RATIO CALCULATION FOR COMPLEX HYDRIDES.....		- 45 -
ANNEX 6: SUMMARY OF THE CHARACTERISTIC ABSORPTION LINES FOR THE FT-IR		- 46 -
ANNEX 7: SUMMARY OF RESULTS OBTAINED FROM THE VARIOUS MATERIALS		- 47 -

**DESIGN AND DEVELOPMENT OF HIGH STORAGE CAPACITY COMPLEX
HYDRIDES FOR REVERSIBLE HYDROGEN STORAGE IN VEHICLES**

LIST OF TABLES

TABLE 1 COMPARISON OF SOME HYDROGEN STORAGE METHODS	- 7 -
TABLE 2 US DOE AND FREEDOM CAR HYDROGEN STORAGE TEAM TECHNICAL TARGETS	- 8 -
TABLE 3 THEORETICAL HYDROGEN STORAGE CAPACITIES OF SOME COMPLEX HYDRIDES.....	- 9 -
TABLE 4 HYDROGEN SORPTION PROPERTIES OF STARTING MATERIALS.....	- 9 -
TABLE 5 STARTING MATERIALS, CHEMICAL COMPOUNDS AND GASES.....	- 13 -
TABLE 6 SUMMARY OF SCHEME 1 RESULTS.....	- 25 -
TABLE 7 HYDROGEN SORPTION PROPERTIES OF LINMGALNH MATERIAL SYNTHESIZED VIA SCHEME 2....	- 28 -

DESIGN AND DEVELOPMENT OF HIGH STORAGE CAPACITY COMPLEX HYDRIDES FOR REVERSIBLE HYDROGEN STORAGE IN VEHICLES

LIST OF FIGURES

FIGURE 1 HYDROGEN ABSORPTION (LEFT) AND DESORPTION (RIGHT) OF MgH_2 AT $300^{\circ}C$ AND 10BARS	- 11 -
FIGURE 2 HYDROGEN DESORPTION KINETICS OF UNMILLED, MILLED AND CATALYZED MgH_2 AT $250^{\circ}C$, 0.1 BAR H_2	- 12 -
FIGURE 3 STAINLESS STEEL BOWL WITH STAINLESS STEEL BALLS (LEFT), HOLDER (MIDDLE), HEBM (RIGHT).....	- 14 -
FIGURE 4 PROCESSING CONDITION FLOW CHART FOR THE PREPARATION OF NOVEL COMPLEX HYDRIDES	- 15 -
FIGURE 5 NITROGEN FILLED GLOVE BOX	- 15 -
FIGURE 6 FT-IR INSTRUMENT (LEFT), KBR DIE SET AND KBR WINDOW (RIGHT).....	- 16 -
FIGURE 7 PCTPRO-E&E HYDROGEN SORPTION UNIT (LEFT) AND HYDRIDE CANISTER WITH FRITTED CAP (RIGHT).....	- 17 -
FIGURE 8 X-RAY DIFFRACTION WITH VERTICAL GONIOMETRY (θ - 2θ).....	- 17 -
FIGURE 9 AUTOSORB IQ RESIDUAL GAS ANALYZER/MASS SPECTROMETER	- 18 -
FIGURE 10 GENERAL PROCEDURE FLOW CHART OF SYNTHESIS AND CHARACTERIZATION EXPERIMENTAL APPROACH	- 19 -
FIGURE 11 MS OF $LiNH_2$ (LEFT) AND MS OF $LiAlNH$ (RIGHT).....	- 20 -
FIGURE 12 MS OF MgH_2 (LEFT) AND MS OF BNH_6 (RIGHT).....	- 21 -
FIGURE 13 MASS SPEC OF $LiBH_4$	- 21 -
FIGURE 14 MS AND KINETICS OF $LiMgNH$	- 22 -
FIGURE 15 THERMOGRAVIMETRIC ANALYSIS (TGA) OF UNDOPED AND CATALYST DOPED $Li-nMg-N-H$	- 23 -
FIGURE 16 MS OF $Li-nMg-N-H$ DOPED WITH 2WT % Ni NANOCATALYST	- 23 -
FIGURE 17 HYDROGEN ABSORPTION KINETICS OF $Li-nMg-N-H$ IN ALTERNATIVE CYCLES AT DIFFERENT TEMPERATURES	- 24 -
FIGURE 18 HYDROGEN DESORPTION KINETICS OF $Li-nMg-N-H$ IN ALTERNATIVE CYCLES AT DIFFERENT TEMPERATURES	- 24 -
FIGURE 19 FT-IR OF $LiMgNH$ BEFORE AND AFTER HYDROGEN PCT EXPERIMENTS	- 25 -
FIGURE 20 MS (LEFT) AND KINETICS (RIGHT) OF $Li-nMg-AL-N-H$	- 26 -
FIGURE 21 RGA/MS OF $LiMgALNH$ AFTER PCT SORPTION CYCLES.....	- 27 -
FIGURE 22 RAMPING DEHYDROGENATION KINETICS OF $LiMgALNH$ IN CONSECUTIVE CYCLES.....	- 27 -
FIGURE 23 XRD OF $LiMgBNH$	- 29 -
FIGURE 24 FT-IR OF PLAIN HYDRIDES AND AS-PREPARED $LiBNH$ AND $LiMgBNH$	- 30 -
FIGURE 25 MS OF $LiMgBNH$ BEFORE PCT (LEFT) AFTER PCT (RIGHT)	- 30 -
FIGURE 26 CYCLE LIFE KINETICS OF $LiMgBNH$ AT 200 AND $250^{\circ}C$	- 31 -
FIGURE 27 HYDROGEN RELEASE IN $BNH_6.MgH_2$ COMPLEX HYDRIDES	- 32 -
FIGURE 28 DIBORANE RELEASE IN $BNH_6.MgH_2$ COMPLEX HYDRIDES.....	- 33 -
FIGURE 29 AMMONIA RELEASE IN $BNH_6.MgH_2$ COMPLEX HYDRIDES	- 33 -
FIGURE 30 DEHYDROGENATION KINETICS OF $BNH_6.2MgH_2$ IN CONSECUTIVE ABS/DES CYCLES.	- 34 -
FIGURE 31 FT-IR $BNH_6.MgH_2$ RELATED SAMPLES.....	- 35 -

INTRODUCTION

Complex hydrides are light weight solid state materials that have proven to be the most convenient materials to store hydrogen in a clean, safe and convenient manner. These materials have proven to have the ability to store great quantities of hydrogen at moderate operating conditions, thus giving them the possibility to be used as fuel for mobile and stationary applications. Our work will focus on finding the suitable complex hydrides for hydrogen storage.

Human population has increased exponentially in the last century as well as its energy consumption. Close to 80.9% of the world's petroleum use is covered by fossil fuels. In absence of viable alternatives, the exhaustion of the petroleum reserves expected in no more than 40 years causes a progressive increment in price. More to that, the combustion of these fossil fuels during their consumption release toxic gases such as Carbon dioxide (CO_2) which causes global warming and pollution. The increase in threats from global warming due to the consumption of fossil fuels requires our planet to adopt new strategies to harness the inexhaustible sources of energy.

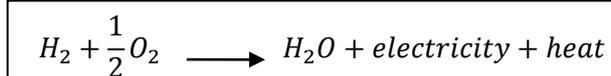
The use of hydrogen as a fuel is a solution to the problems created by fossil fuels and this research will focus on finding materials which can store hydrogen conveniently. After severe bibliographical research, three main steps were used to determine which complex hydrides will suit best for high hydrogen storage at moderate operating conditions for mobile applications. Firstly, we synthesize the complex metal hydride materials for hydrogen storage. Secondly, we characterize the metal hydrides using state of the art techniques such as: Pressure-Composition Isotherms (PCT), Residual Gas and/or Mass Spectrometric analysis (RGA/MS), the Fourier Transform Infrared Spectroscopy (FT-IR) and the X-Ray Diffraction (XRD) in order to study the thermal, chemical and structural properties of these hydrides. Lastly, we improve the physical, chemical, surface, hydrogen sorption (kinetics, reversibility, cycle life, PCT etc.) properties which currently limit the usefulness of complex hydrides for hydrogen storage applications.

In this thesis chapter 1 gives us the vital research information done on hydrogen storage. Chapter 2 discusses the details of the experimental part of this dissertation, more specifically, the details of the synthesis equipment, as well as the characterization techniques employed for the manufacture of novel complex hydrides. We have successfully synthesized and characterized light weight, high capacity hydrogen storage systems which are prepared from various starting hydride compounds such as Lithium Borohydride (LiBH_4), Lithium Amide (LiNH_2), Ammonia Borane (BNH_6), Lithium Aluminum Hydride (LiAlH_4) and Magnesium Hydride (MgH_2). Chapter 3 gives the detail results of the synthesis and characterization procedures carried out in chapter 2 and Chapter 4 finally concludes the work completed as part of this dissertation and offers some suggestions for future work.

CHAPTER 1: STATE OF THE ART AND BACKGROUND

1. HYDROGEN- A CLEAN AND RENEWABLE FUEL

Hydrogen is an energy carrier which holds tremendous promise as a new renewable and clean energy option. It is the most abundant element in the universe (not in its pure state due to its light weight), convenient, safe and a versatile fuel source that can be easily converted to a desired form of energy without releasing harmful emissions from its combustion. It has a heating value three times higher than petroleum because the energy per mass of hydrogen ($33.3 \text{ kWh}\cdot\text{kg}^{-1}$) is almost three times larger than that of other chemical fuels, e.g. liquid hydrocarbons ($12.4 \text{ kWh}\cdot\text{kg}^{-1}$). Annexure 1 compares the various basic properties between hydrogen fuel and other hydrocarbon fuels. Hydrogen can be used in a fuel cell (FC) to produce electricity as well as burned in a Hydrogen Internal Combustion Engine (HICE), provided it is adjusted for use of hydrogen as the main fuel. Hydrogen, used in the fuel cell directly converts the chemical energy of hydrogen into water, electricity, and heat as shown in the equation below.



It is the ideal fuel for the future since it significantly reduces the greenhouse gas emissions, reduces the global dependence on fossil fuels, and increases the efficiency of the energy conversion process for both Internal Combustion Engines (ICE) and Proton Exchange Membrane (PEM) fuel cells.

Due to its abundance on earth, hydrogen can be produced from several methods. It can be produced from fossil resources such as natural gas and coal, as well as renewable resources, such as biomass and water with input from renewable energy sources (e.g. sunlight, wind, wave or hydro-power). A variety of process technologies can also be used, namely, chemical, biological, electrolytic, photolytic, photo catalytic and thermo-chemical etc. Each of these technologies is in a different stage of development, and each offers unique opportunities, benefits and challenges. Local availability of resources, the maturity of the technology, market applications and demand, policy issues, and costs will all influence the choice and timing of the various options for hydrogen production in various areas.

2. OBSTACLES FACING THE STORAGE OF HYDROGEN

Despite its wonderful qualities, hydrogen has its limits. For hydrogen to be used as a general source of energy, its storage and transport should be economical and efficient. This supposes a considerable change compared to the transport and storage of conventional fossil fuels, due to its

DESIGN AND DEVELOPMENT OF HIGH STORAGE CAPACITY COMPLEX HYDRIDES FOR REVERSIBLE HYDROGEN STORAGE IN VEHICLES

low density. At the present time, hydrogen can be stored in the gaseous, liquid or solid form, for both the stationary applications and the transportation sector. Table 1 below shows the various hydrogen storage methods and their various characteristics.

Table 1 Comparison of some hydrogen storage methods [36]

Storage method	Gravimetric density (wt. %)	Volumetric density (kg H ₂ /m ³)	Temperature (°C)	Pressure (bar)	Phenomena and remarks
Compressed	13	<40	Room Temperature	300-1000	Compressed gas in light weight composite cylinders demand high pressures due to low hydrogen density. Risky method. Spacious and safety issues.
Liquid	Size dependent	70.8	-252	1	Boils off and energy demanding for state conservation. Expensive cryogenics
Adsorbed hydrogen	~2	20	-80	100	Physisorption - large specific surface area, irreversible, low hydrogen capacity.
Absorbed in interstitial (Metal Hydrides)	~2	150	Room Temperature	1	Atomic H ₂ intercalation in host sites in metal, reversible low hydrogen capacity
Complex Hydrides	<18	150	>100	1	High Temperature, high Pressure, toxic gases release with hydrogen.

The type of storage method adequate for us depends on our chosen application of hydrogen. Given that we want to use it for mobile applications, using complex hydrides is the ideal storage method. They are light weight compounds, have high reversible gravimetric capacities, low temperatures and pressures of operation. These materials will therefore occupy less space in the vehicle, move for long distances and will function efficiently.

One of the main problems to be solved when using hydrogen energy as fuel for transportation is the lack of an adequate storage system, which can fulfill the safety requirements, costs, and the required provision characteristics set by the United States Department of Energy (US DOE). US DOE has set basic needs which a material must have for hydrogen economy and technical targets for 2017 for a material to be eligible for mobile applications. The basic needs are (i) Light weight (ii) Long term cycling stability (iii) Favorable thermodynamics (iv) Fast kinetics (v) High degree of reversibility (vi) Low temperatures of decomposition or dissociation (<100°C) and . The 2017 technical targets are found in Table 2 below with more details listed in annexure 2.

DESIGN AND DEVELOPMENT OF HIGH STORAGE CAPACITY COMPLEX HYDRIDES FOR REVERSIBLE HYDROGEN STORAGE IN VEHICLES

Table 2 US DOE and Freedom CAR Hydrogen Storage Team Technical Targets [31]

Technical Targets	Units	Year 2017
Gravimetric capacity (GrC) (net useful energy/max system mass)	kg H ₂ /kg	0.055
	kWh/kg	1.8
Volumetric Capacity (VC) (net useful energy/max system volume)	kg H ₂ /L	0.040
	kWh/kg	1.3
Fuel cost	\$/gauge at pump	2-4
Min/Max delivery temperature	°C	-40/85
Cycle life	Cycles	1500
Refueling rate	kg H ₂ /min	1.5

Therefore, our research will focus on the design and development of hydrogen storage materials with characteristics as close as possible to those set by the US DOE.

3. COMPLEX METAL HYDRIDES

3.1. General Overview

Complex metal hydrides are synthesized from the mixture of two or more metal hydrides. A metal hydride is a compound of hydrogen bonded (by ionic or metallic bonds) with another more electropositive element (metal). An example is Calcium Hydride (CaH₂). The chemical bonding characteristics of complex hydrides have intermediate bond strength with a heat of reaction in the range of 30-55 kJ/molH₂ and therefore operate at conditions of 0-100°C. Their range of heat of reaction lies between the highly stable covalent compounds (70-80 kJ/molH₂) which need high temperatures (>400°C) for hydrogen release and weakly bonded (4-20 kJ/molH₂) physisorbed carbons which need high pressures for rehydrogenation.

3.2. Properties of chosen metal hydrides

This research focuses on developing new complex hydrides having the most promising hydrogen storage capacities at moderate temperature and pressure conditions. The most interesting metal hydride so far has been Magnesium hydride (MgH₂) with a hydrogen storage capacity of 7.6 wt. %. From previous studies, the only metal or complex hydrides which are capable of achieving a gravimetric capacity >5 wt. % are limited to Lithium (Li), Boron (B), Magnesium (Mg) and Aluminum (Al) based compounds. Despite their acceptable gravimetric capacity, they possess slow kinetics, high activation energies and thermodynamic stability thus releasing hydrogen at very high temperatures. To solve these problems, we have proposed destabilizing the hydrides with either nano MgH₂ or a 3d transition metal catalyst. Destabilization using nano MgH₂ enables thermal

**DESIGN AND DEVELOPMENT OF HIGH STORAGE CAPACITY COMPLEX
HYDRIDES FOR REVERSIBLE HYDROGEN STORAGE IN VEHICLES**

decomposition of hydrogen at much lower temperatures than their pristine counterparts. Table 3 below shows the sorption properties of some of the complex hydrides previously studied.

Table 3 Theoretical hydrogen storage capacities of some complex hydrides [26]

Complex hydrides	Gravimetric Capacity (wt. %)	Reversible capacity (wt. %)	Operating temperature (°C)	Remarks
Undoped and Ti-doped LiAlH_4	10.5	6.3	120-170	Problems with reversibility and reduced thermodynamic stability
Undoped and doped LiBH_4	18.2	9.0	200-400	High operating temperature, rehydrogenation problem, possible borane gas evolution
$\text{Mg}(\text{AlH}_4)_2$	9.3	6.6	200-250	High operating temperature, thermodynamic stability
Li_3N (LiNH_2/LiH)	11.3	6.5-7	255-285	High operating temperature, ammonia evolution
B-H-Li-N	10	-	80-150	Rehydrogenation problem
BNH_6	18.3	No reversibility	180°C	Ammonia and di-borane evolution, irreversible

Based on the information obtained from Table 3 and other references, we have prepared new solid state complex hydrides and studied their various sorption properties employing state-of-the-art techniques. Table 4 below shows the theoretical hydrogen sorption properties of all the starting materials we used to synthesize the proposed novel complex hydrides. In addition to the synthesis of various combinations of complex hydride materials, various methods to improve the kinetics, thermodynamics and reversible hydrogen storage behavior of the starting hydride mixtures at moderate temperature and pressure conditions have been proposed.

Table 4 Hydrogen sorption properties of starting materials

	cMgH_2	LiNH_2	LiBH_4	BNH_6	LiAlH_4
Gravimetric capacity (wt. %)	7.6	8	18.5	18.5	10.5
Volumetric capacity (kgH_2/m^3)	108	-	121	-	99
Temperature of first significant loss due to hydrogen release (°C)	400	350-400	330-380	120-130	120-170
Remarks	High thermodynamic stability and slow kinetics			Irreversible but very fast kinetics	Irreversible dehydrogenation and slow kinetics

3.3. Methods to improve kinetics and thermodynamic stability of starting hydrides

Various methods can be adopted to improve the sorption properties of the starting hydrides. The kinetic behavior of a material is controlled by mechanisms which are determined by specific material properties; therefore, it should be possible to improve kinetics by altering these properties.

➤ Mechano-chemical synthesis [8]

A critical factor for hydrogen absorption by metals is the metal surface, which activates dissociation of hydrogen molecules and allows easy diffusion of hydrogen into the bulk. Intimate contact between two different phases may improve kinetics by enhanced diffusion through inter-phase grain boundaries. This can be produced by mechanically milling a mixture of phases together. This mixture can make a new compound with different and better chemical properties.

The ball-milling is an economic process by which there is constant collision between the stainless steel balls and the sample powder at room temperature thus produces fresh surface and achieve greater surface properties. The vital effects of ball-milling process are (i) increased surface area, (ii) formation of micro/nanostructures, (iii) particle size reduction by homogeneous pulverization and (iv) creation of defects on the surface and in the interior of the material. The induced lattice defects may aid the diffusion of hydrogen in materials by providing many reactive sites with low activation energy of diffusion. Besides, the induced micro-strain in the material assists the diffusion of atomic hydrogen by reducing the sorption hysteresis.

.Significant progress has recently been reported in the mechano-chemical synthesis of magnesium hydride (MgH_2) at 300rpm for 15hours. Apparently careful ball milling of MgH_2 helps to enhance the kinetics of the material and decrease its hydrogen decomposition temperature by nearly 150°C. At 300°C, ball milled MgH_2 absorbs about 4.8 wt. % of hydrogen in 3 minutes. In comparison, unmilled MgH_2 absorbs about 2.8 wt. % of hydrogen in 30 minutes (see Figure 1 left below). The absorption kinetics of milled MgH_2 is about 10 times faster than in the case of unmilled MgH_2 . With regarding to the desorption process, at 300°C, the unmilled powder is not completely desorbed after 30 minutes. While milled MgH_2 is approximately completely desorbed after about 12 minutes. On the other hand, both the milled and unmilled curves have a sigmoidal shape which means that a nucleation and growth processes take place during desorption (see Figure 1 right below).

DESIGN AND DEVELOPMENT OF HIGH STORAGE CAPACITY COMPLEX HYDRIDES FOR REVERSIBLE HYDROGEN STORAGE IN VEHICLES

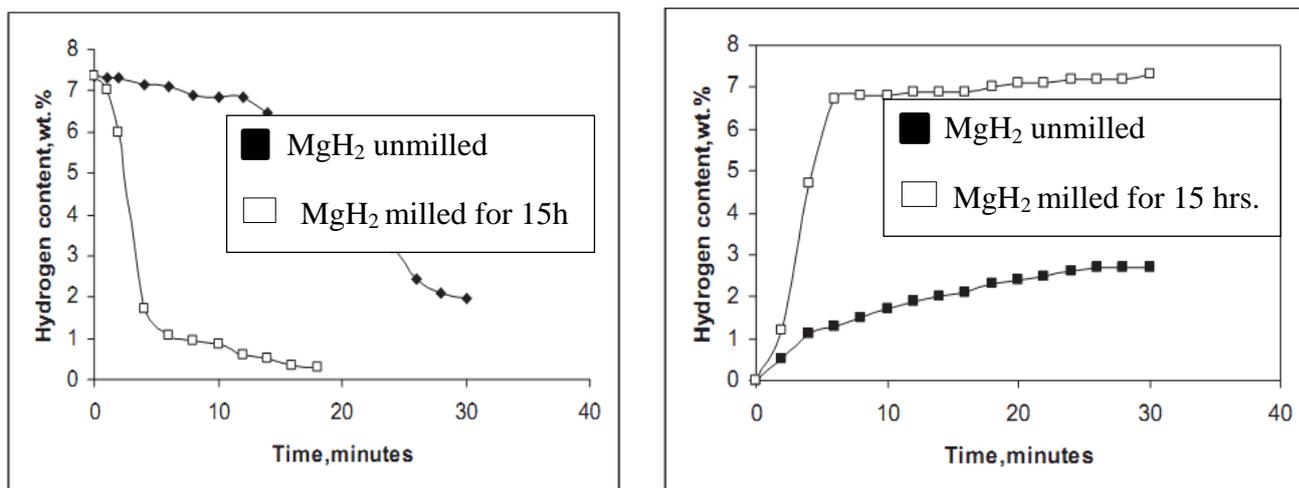


Figure 1 Hydrogen absorption (left) and desorption (right) of MgH₂ at 300°C and 10bars

➤ Presence of other elements (catalytic effect) [8]

Catalysis is one of the critical factors in the improvement of hydrogen sorption kinetics in metal hydride systems that enable fast and effective dissociation of hydrogen molecules. Effective catalysts, even added in small amounts enhance the formation of a hydride in reasonable extent. It was reported that the rate of absorption is controlled by the following factors: (i) the rate of hydrogen dissociation at the surface, (ii) the capability of hydrogen to penetrate from the surface which is typically covered by an oxide layer into metal, (iii) the rate of hydrogen diffusion into the bulk metal and through the hydride already formed bulk. Many diverse elements have been investigated as possible catalysts to accelerate the sorption properties of hydrogen. These include predominantly titanium (Ti), zirconium (Zr), nickel (Ni), Cobalt (Co) and iron (Fe). One should keep in mind that the method of doping deeply influences the performance of the resulting materials.

It has been shown above that the hydrogen sorption kinetics of MgH₂ can be greatly improved if the material is prepared with a nanocrystalline microstructure through high velocity ball milling. An enhancement in the absorption/desorption kinetics of MgH₂ is also observed through reaction with small amounts of Ni ultrafine particles. The reaction kinetics has been accelerated significantly, even at ambient temperature. The hydrogen desorption kinetics of MgH₂ with 0.5 wt.% Ni addition after six hydrogen desorption and reabsorption cycles are shown in Figure 2 below, compared to MgH₂ milled for 15 hrs. It is apparent that MgH₂ with 0.5 wt. % Ni addition desorbed hydrogen significantly faster than both the unmilled and milled MgH₂. The combination of MgH₂ with the smaller crystallites, the nano Ni catalyst and the high H₂ pressure gives rise to the excellent absorption /desorption kinetics. An improvement in the contact between

DESIGN AND DEVELOPMENT OF HIGH STORAGE CAPACITY COMPLEX HYDRIDES FOR REVERSIBLE HYDROGEN STORAGE IN VEHICLES

catalyst and metal hydride in the solid phase proves to be among the most decisive factors for achieving fast kinetics of hydrogen transformations.

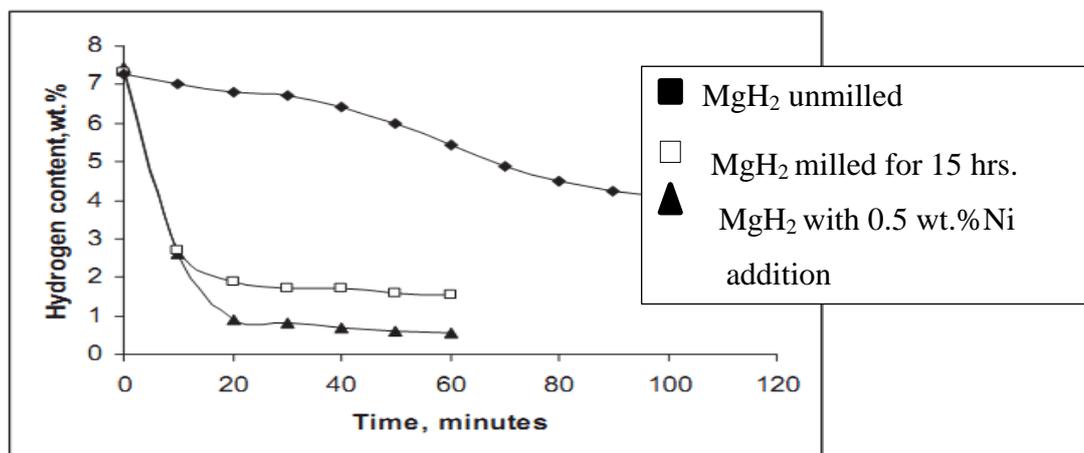


Figure 2 Hydrogen desorption kinetics of unmilled, milled and catalyzed MgH₂ at 250°C, 0.1 bar H₂

4. THESIS AIM AND SIGNIFICANCE

One of the most important targets among those set by the US DOE is the gravimetric capacity of the hydrogen storage material. Much research has been done on this field, but none of the materials have met all the targets set by the US DOE. Keeping this fact in view, we explore novel combination of complex hydride materials and obtain new information that leads for the improvement of the sorption properties of complex hydrides or other related materials.

The main objective of this research is to develop a novel solid state complex hydride from existing and already studied materials with properties close or similar to the targets set by the US DOE to store hydrogen reversibly and efficiently.

The hydrogen sorption properties at different working hydrogen pressures and temperatures will enable us to explore *holy-grail* hydrogen storage systems for mobile and stationary applications. The results of our experimental approach will either meet the targets set for hydrogen storage materials or will be another contribution to the advancement on the research in this field.

CHAPTER 2: EXPERIMENTAL APPROACH

Based on the theoretical knowledge acquired and the results obtained from various researches, we have successfully prepared various possible complex hydrides from 5 different parent hydrides (LiNH_2 , LiAlH_4 , MgH_2 , BNH_6 and LiBH_4) which have greater gravimetric capacities. All these parent materials have been obtained commercially and used without further purification. The synthesis and characterization of the novel new complex hydride systems have directed to further optimize the experimental conditions for high hydrogen storage characteristics.

1. MATERIALS AND EQUIPEMENT

Starting materials, and chemical compounds without further purification are used for the synthesis of novel complex hydrides which are listed in Table 5.

Table 5 Starting materials, chemical compounds and gases

Materials	Purity (%)	Description	Manufacturer
LiBH_4	H_2 storage grade	White fine powder	Sigma Aldrich
LiNH_2	98	White fine powder	Sigma Aldrich
cMgH ₂	95 and 98	Grey fine powder	Sigma Aldrich/Alfa Aesar
nMgH ₂	95	Dark brown fine powder	Prepared in the lab by ball milling cMgH ₂
LiAlH_4	H_2 storage grade	Grey pellets	Sigma Aldrich
BNH_6	90	White fine powder	Sigma Aldrich
Nanocatalysts, e.g. Ni, Co, Fe, etc.	95	Fine Nanoparticles	Quantum Sphere Inc. Sigma Aldrich
UHP Hydrogen	99.9999	Gas cylinder	Dennis Welding Supply
UHP Nitrogen	99.9999	Gas cylinder	Dennis Welding Supply
UHP Helium	99.9999	Gas cylinder	Dennis Welding Supply
Ar/H ₂	95/5	Gas cylinder	Dennis Welding Supply

2. SYNTHESISING METHODS AND EQUIPMENT

2.1 Planetary high energy ball mill (HEBM)

Ball milling is a mechano-chemical synthesis process that involves the interaction of stainless steel balls in a stainless steel bowl and any sample at very high speeds (up to 600rpm). This process is necessary for a successful solid state preparation of hydrogen storage materials because it

DESIGN AND DEVELOPMENT OF HIGH STORAGE CAPACITY COMPLEX HYDRIDES FOR REVERSIBLE HYDROGEN STORAGE IN VEHICLES

determines the chemical and physical structure of the sample. This process stands out among the most important factors for achieving fast kinetics of hydrogen transformations.

The HEBM shown in Figure 3 contains a holder for a stainless steel bowl. The sample to be milled is then placed in the bowl containing 100 balls, sealed and milled at a speed of 400rpm. When the ball mill runs, the bowl rotates in a clockwise direction, while the base of the bowl rotates in the opposite direction. This generates a centrifugal force in planetary motion. This rotation, combined with the translation of the balls, provides for a high impact of the grinding balls with the material that is being milled. It is made by Across International Inc.



Figure 3 Stainless steel bowl with stainless steel balls (left), holder (middle), HEBM (right).

In addition to the vital effects of ball milling listed in the introduction, ball milling changes also include: (i) physical, mechanical and chemical combination of materials (ii) strengthening of particles through grain size reduction (iii) forming new chemical compounds by destabilization of a parent compounds structure. The conventional metal hydrides usually have higher activation energy and thus difficult in obtaining reversible hydrogen storage behavior. Mechano chemical milling helps to form a new compound with lower activation energy thus ensures better reversibility. The stainless steel container used during synthesis also has an inlet and outlet vent. This allows purging of the sample with a gas cylinder containing Ar (95%)/H₂ (5%) which is essential for the synthesis of these reactive and moisture sensitive materials. Ar/H₂ purging is done before and after every two hours of the milling process not only to suppress the release of hydrogen during milling but also to avoid the solid state agglomeration of milled nanoparticles.

Nano MgH₂ (nMgH₂) was used to destabilize the new complex hydrides. Nano MgH₂ was prepared by milling the commercial MgH₂ (cMgH₂) for 15 hours under inert ambient at a speed of 400rpm. The crystallite sizes of nano MgH₂ were estimated via XRD analysis and found to be 27nm, whereas the commercial MgH₂ has a particle size of 212nm.

DESIGN AND DEVELOPMENT OF HIGH STORAGE CAPACITY COMPLEX HYDRIDES FOR REVERSIBLE HYDROGEN STORAGE IN VEHICLES

Figure 4 below shows a flow chart showing the five different processing schemes proposed in this work to synthesize novel complex hydride systems. The as-prepared samples are referred to in this thesis according to the naming convention shown in the bold boxes of the figure.

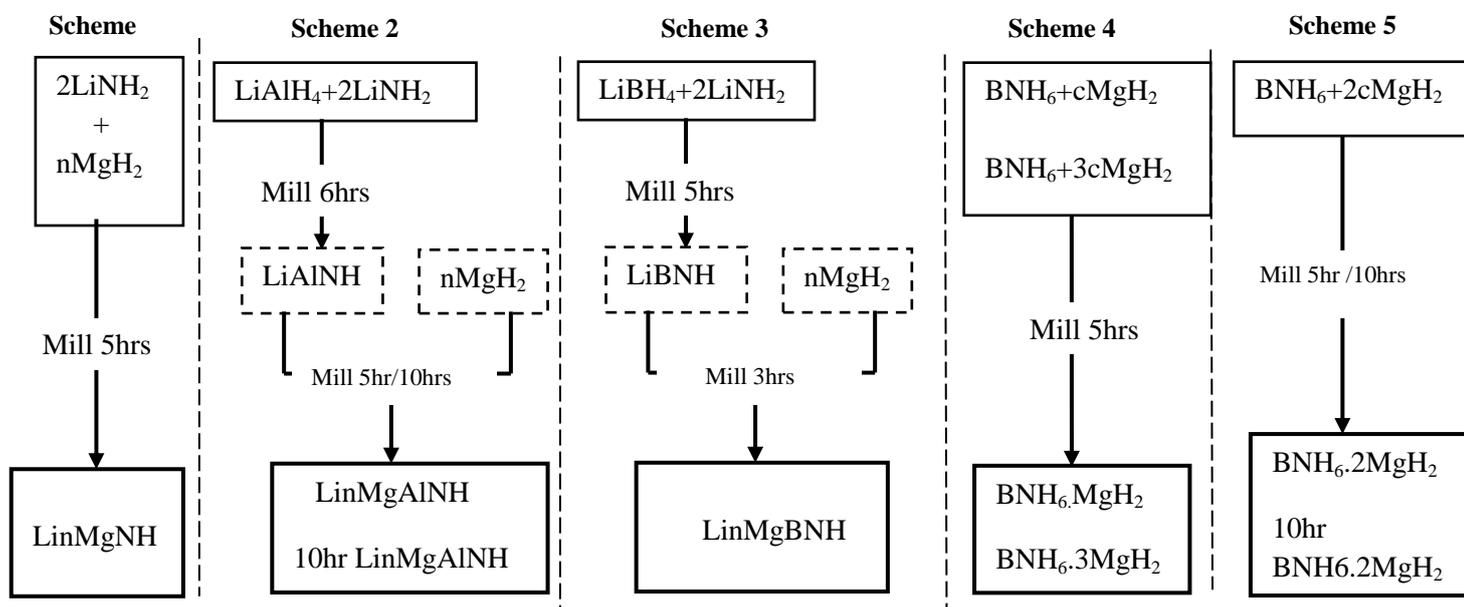


Figure 4 Processing condition flow chart for the preparation of novel complex hydrides

2.2 Nitrogen Filled Glove Box (<1 ppm O_2 / moisture)

The materials used for the complex hydrides were all stored and manipulated in a nitrogen filled glove box. The glove box shown in Figure 5 is filled with a 99.999% ultrahigh pure nitrogen atmosphere to protect all starting materials from reacting with moisture or oxygen. The continuous flow of nitrogen in the glove box controls and maintains the oxygen and moisture levels below 1ppm. All sample preparations and manipulations were performed inside the glove box. The principal components of the glove box are shown in the figure below and the details are found in annex 3:



Figure 5 Nitrogen filled Glove box

3. CHARACTERIZATION METHODS AND EQUIPMENT

3.1 Fourier Transform Infrared Spectroscopy (FT-IR)

Figure 6 shows the FTIR instrument and it measures the infrared intensity (percentage of IR transmittance or absorbance) versus wavenumber in cm^{-1} . Infrared spectroscopy detects the vibration characteristics of chemical functional groups in the as-prepared and starting compounds. When an infrared light interacts with the matter, chemical bonds will stretch, contract and bend. As a result, a chemical functional group tends to absorb infrared radiation in a specific wavenumber (frequency) range regardless of the structure of the rest of the molecule. This helps us to know the chemical functional groups and bond strength of a material.

During the FT-IR measurements, a systematic sample preparation protocol was developed so that to avoid any contact of moisture/ O_2 with the sample. Each sample studied, was mixed with KBr (due to its IR transparency behavior) in the ratio 1:5 respectively. With the use of a hand press, the KBr powder and the sample mixtures were pelletized using the die set and then carefully inserted in to the KBr cell with window as shown in the right hand side of Figure 6. Intensity and frequency of sample absorption are depicted in a two-dimensional plot called a FT-IR spectrum. Intensity is generally reported in terms of percent transmittance, the fraction of the light that passes through it. The FT-IR is made by Shimadzu Inc. and the KBr die set and window by ICL Inc.



Figure 6 FT-IR instrument (left), KBr die set and KBR window (right).

3.2 Pressure-Composition Isotherms (PCT)

Figure 8 below is an automated Sieverts type pressure composition isotherm instrument (PCTPro hydrogen storage and metal hydride applications. With this instrument, PCT, gas sorption kinetics, heat-of-formation, cycle-life kinetics, cycle-life PCT, volume calibration and packing density can be accurately measured. A Lab View HyEnergy software program is used for PCT system operation, data monitoring and recording.

DESIGN AND DEVELOPMENT OF HIGH STORAGE CAPACITY COMPLEX HYDRIDES FOR REVERSIBLE HYDROGEN STORAGE IN VEHICLES

In the Sieverts technique, the sample is loaded in a canister sealed with a hydrogen filtered lid shown in Figure 7 and then connected to the instrument via a copper enclosure reactor. The calibrated reference volume at a constant temperature is filled with gas to a measured pressure and then opened to the sample chamber, the gas uptake or release by the sample is calculated from the change in the gas pressure in the system at the isothermal conditions. A helium gas bottle (UHP 99.9999%) is used for calibrating the volume, leak test and for purging air from the manifolds.

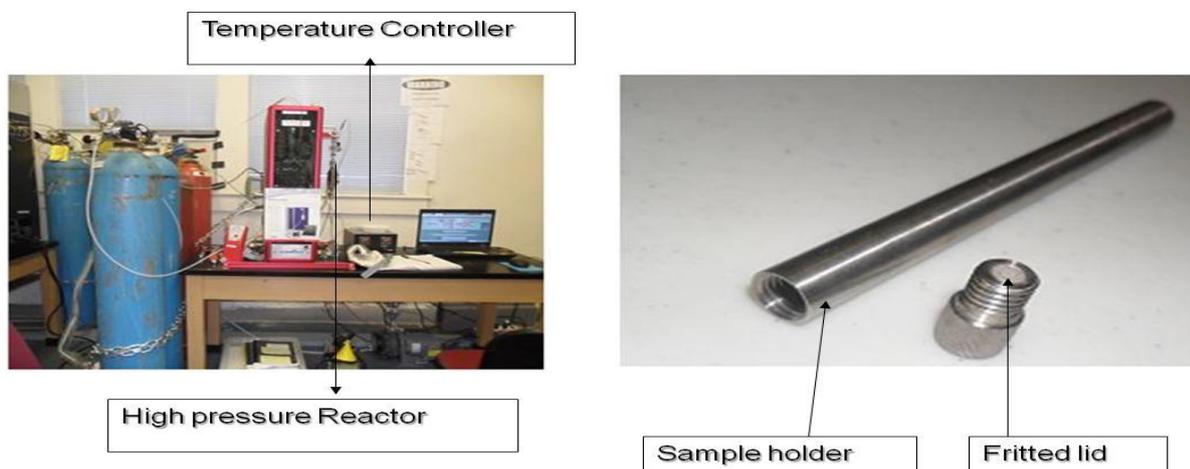


Figure 7 PCTPro-E&E hydrogen sorption unit (left) and hydride canister with fritted cap (right).

As it is mentioned above the PCTPro-E&E is a Sieverts' type instrument that uses the difference in pressure to calculate the amount of hydrogen absorbed or desorbed, the basic indicator diagram developed by Hy-Energy is shown in annex 4.

3.3 X-ray Diffraction (XRD)

The structural characteristics such as phase formation, crystal structure and crystallite sizes of the starting compounds and new complex hydrides were examined and analyzed using a Philips X'Pert XRD system, as shown in Figure 8.



Figure 8 X-ray Diffraction with vertical goniometry (θ - 2θ)

DESIGN AND DEVELOPMENT OF HIGH STORAGE CAPACITY COMPLEX HYDRIDES FOR REVERSIBLE HYDROGEN STORAGE IN VEHICLES

The principle of XRD is rather simple and ingenious. One takes a crystalline material and uses an x-ray source to provide a concentrated beam of x-rays, which then hit the surface at a certain incident angle, θ . This angle is then increased at a fixed rate while a receptor plate with an x-ray sensor is moved around to record the intensity of the emitted x-rays. When the x-rays do not hit atoms of several planes at the same time, the x-rays are out phase, causing a base line of the spectrum. If, however, the x-rays hit atoms of several planes at the same time, the resulting x-rays are in phase and cause a spike in the x-ray signal. Therefore, it is easy to see why only crystalline materials, with a periodic arrangement of atoms, can be successfully investigated using XRD. Amorphous materials, with randomly arranged atoms, will always cause an annihilation of the x-ray signal, causing this technique to be useless. This instrument helps determine the crystallite sizes of materials and the structure of the new material made.

3.4 Autosorb iQ Gas Sorption and Residual Gas Analyzer

We have used Autosorb iQ from Quantachrome Instruments to determine the gas sorption properties from the complex hydrides. Figure 9 shows the Autosorb tool which has a capability for analysis of residual gases evolving from the hydride materials using quadruple mass spectrometer. This involves the determination and quantification of the gaseous components evolved in the thermal decomposition of the sample. As input in the software is the molecular weight of the gases we expect to be released from the sample. A sophisticated ASiQ version 2.0 and Quadera version 4.5 software are simultaneously used to monitor and analyze the gas sorption characteristics with the help two individual computers.

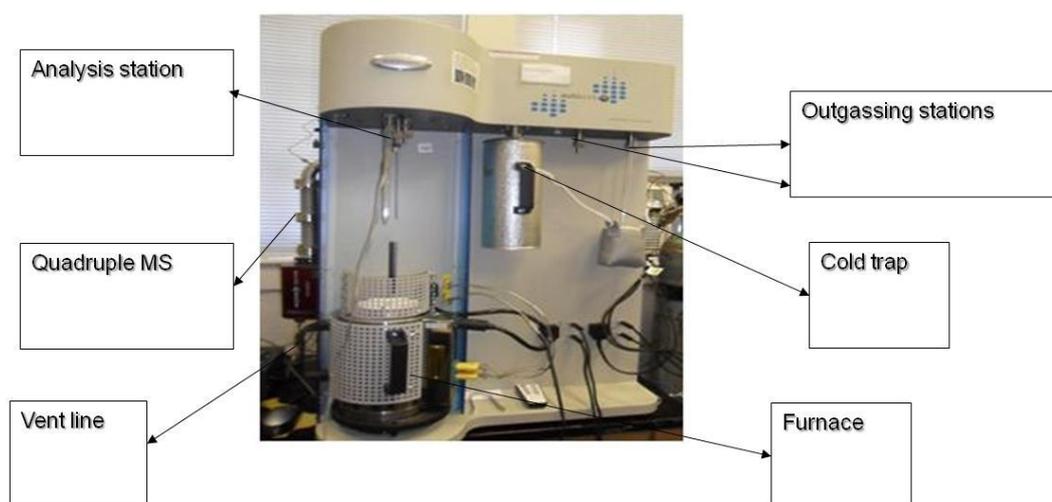


Figure 9 Autosorb iQ residual gas analyzer/Mass spectrometer

Other characterization equipment such as Thermo Gravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC), Temperature Programmed Desorption (TPD) and Scanning electron

DESIGN AND DEVELOPMENT OF HIGH STORAGE CAPACITY COMPLEX HYDRIDES FOR REVERSIBLE HYDROGEN STORAGE IN VEHICLES

microscopy (SEM) can be employed to determine the thermal gravimetric, heat flow and microstructural (morphological) characterization of the novel complex hydride materials.

4. GENERAL PROCEDURE

For the synthesis and characterization of each material, the same basic procedures were followed. The ratio of the starting materials used to synthesize the new complex material was calculated using an excel sheet which is given in annexure 5. Figure 10 below shows the flow chart of the general procedure to synthesize and characterize the new complex hydrides.

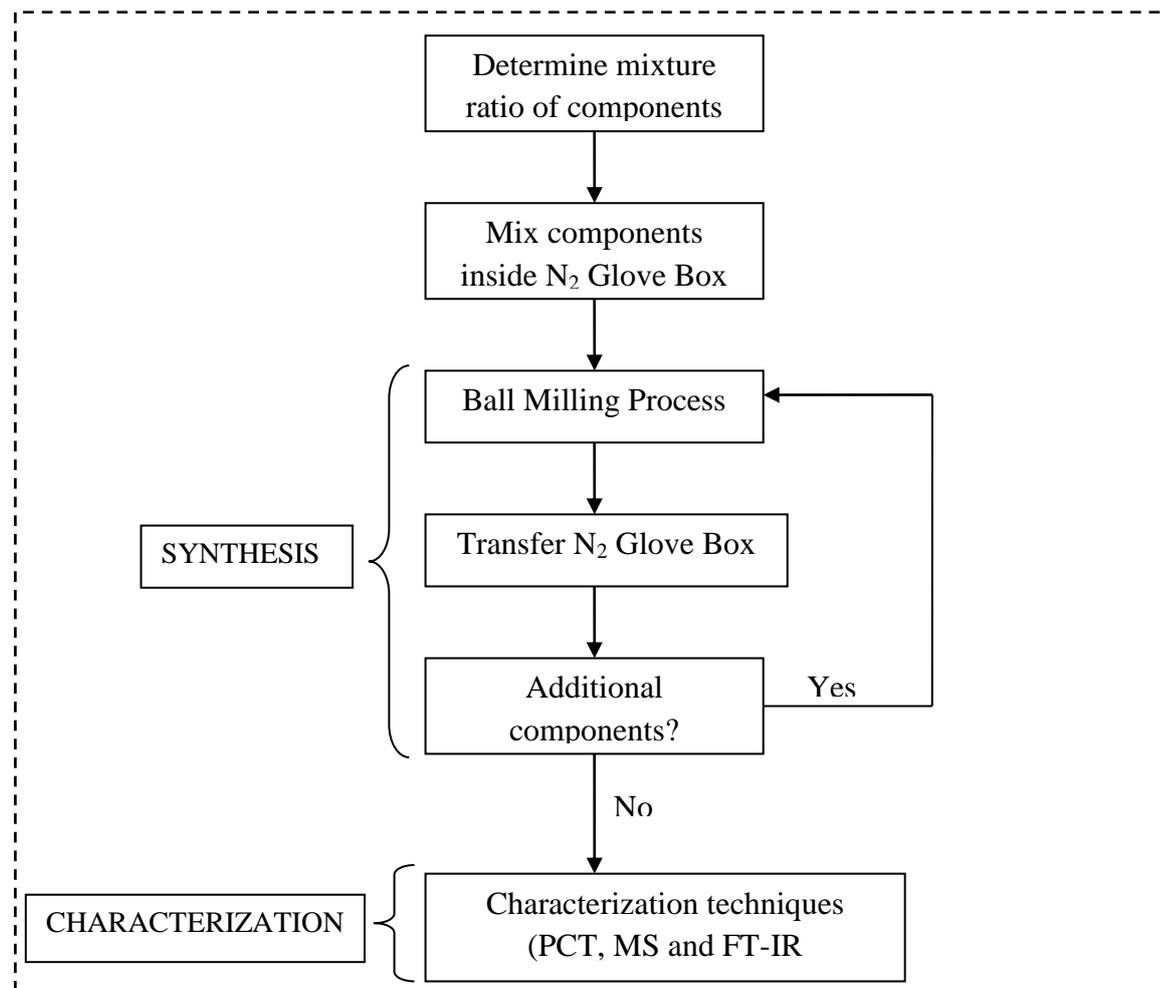


Figure 10 General procedure flow chart of synthesis and characterization experimental approach

CHAPTER 3: RESULTS AND DISCUSSION

RGA/MS Analysis of Starting Materials

Starting materials as listed in Table 5 are subjected to thermal decomposition to analyze the evolving gaseous species using Autosorb iQ quadruple mass spectrometer. Figure 11 represents the MS analysis of the as-purchased and/or as-prepared materials such as LiNH_2 and $\text{LiAlH}_4/2\text{LiNH}_2$ respectively. For the case of LiNH_2 , ammonia is the major gas species which is released from the material in at least three different temperature regions. A small fraction of hydrogen evolved at a high temperature greater than 350°C . For the case of $\text{LiAlH}_4/2\text{LiNH}_2$, both ammonia and hydrogen gases released for a wide range of temperatures from 100 to 250°C . Figure 12 demonstrates the MS spectral analysis from the starting materials MgH_2 and BNH_6 . Magnesium hydride evolves hydrogen at high temperatures $>400^\circ\text{C}$. In addition to hydrogen release, an additional peak corresponds to hydroxyl (OH) ion (molecular weight = 17) is visible due to reaction of magnesium with air/moisture and water vapor while transferring the sample from the glove box to the Autosorb instrument. On the other hand, the ammonia borane complex BNH_6 shows the co-existence of the H_2 , B_2H_6 and NH_3 gases in decreasing concentrations (or ionic current) per the chemical reactions with ratios of $\text{H}_2:\text{NH}_3:\text{B}_2\text{H}_6$ is 6:2:1. For the case of plain LiBH_4 , three step release of hydrogen at temperatures, 120 , 350 and 450°C respectively are shown in Figure 13. The release of hydrogen at 120°C is due to α to β phase change of LiBH_4 as similar to the reported results. However, the hydrogen release $>350^\circ\text{C}$ is from the β phase of LiBH_4 finally decomposes to LiH and elemental boron.

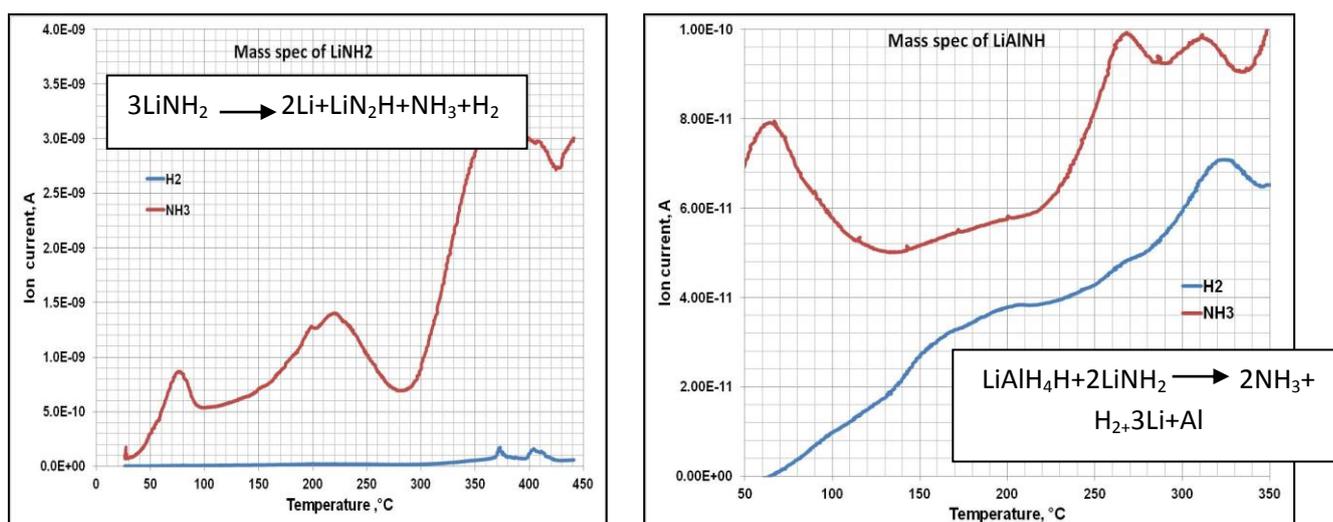


Figure 11 MS of LiNH_2 (left) and MS of LiAlNH (right)

DESIGN AND DEVELOPMENT OF HIGH STORAGE CAPACITY COMPLEX HYDRIDES FOR REVERSIBLE HYDROGEN STORAGE IN VEHICLES

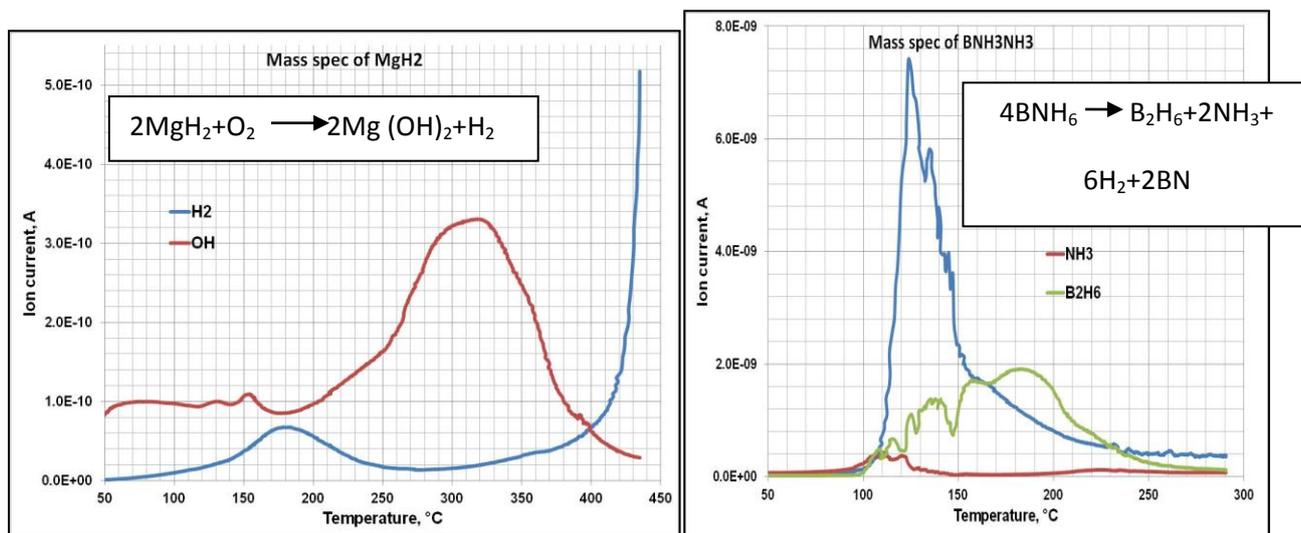


Figure 12 MS of MgH_2 (left) and MS of BNH_6 (right)

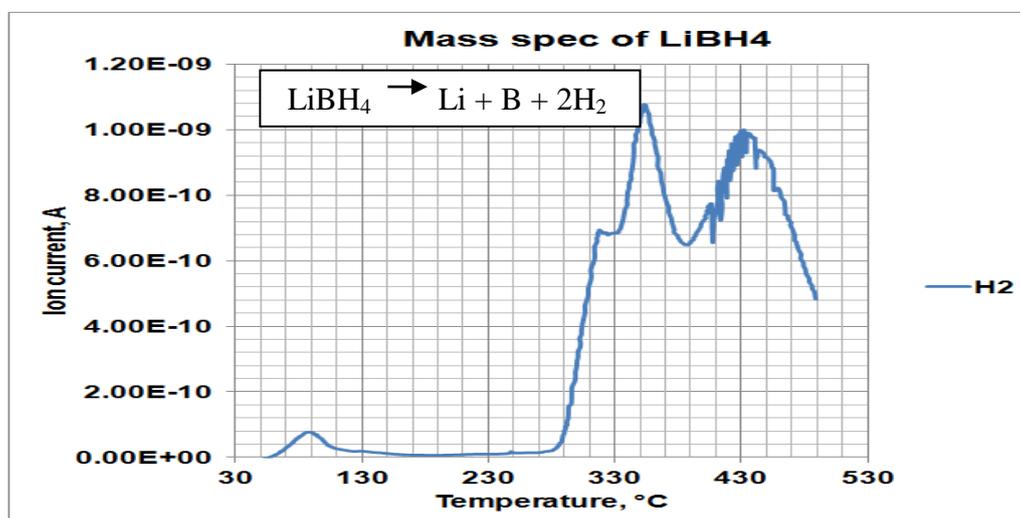


Figure 13 Mass Spec of LiBH_4

SCHEME 1

1. Li-nMg-NH Complex Hydrides

Li-nMg-NH is formed from the mechano-chemical milling of LiNH_2 and nano MgH_2 in the ratio 2:1 under Ar/H_2 purging for 5 hours. The purpose of mixing LiNH_2 and MgH_2 is to form a compound exhibiting faster sorption kinetics, less thermodynamically stable and possessing a higher gravimetric capacity. As an individual entities, both LiNH_2 and MgH_2 releases hydrogen at higher temperatures ($>350^\circ\text{C}$), and are thermodynamically stable with slow sorption kinetics. Milling of 2LiNH_2 with $n\text{MgH}_2$ destabilizes both the lithium amide and magnesium hydride and forms a new and less stable compound (Li-nMg-N-H) with faster kinetics and lower activation energy.

DESIGN AND DEVELOPMENT OF HIGH STORAGE CAPACITY COMPLEX HYDRIDES FOR REVERSIBLE HYDROGEN STORAGE IN VEHICLES

1.1. Mass Spectrometry, Ramping kinetics and TGA Analysis

The RGA/MS analysis of the $2\text{LiNH}_2/n\text{MgH}_2$ shows ion current of gas species such as hydrogen and minor component of ammonia at a wide temperature increase with ramping rate of $10^\circ\text{C}/\text{minute}$. The onset hydrogen decomposition from the material starts early at around 150°C and the peak hydrogen concentration was attained at higher temperature around 325°C . If one can compare the MS result of this novel $2\text{LiNH}_2/n\text{MgH}_2$ compound with either pristine LiNH_2 or MgH_2 as demonstrated in Figures 11 and 12, it is easily discernible that a reduction in the ammonia formation for a wide range of operating temperatures. The first ramping kinetic curve (see the overlay secondary axis of Figure 14) for the desorption of Li-nMg-N-H and the hydrogen release weight percentage is plotted on the MS profile and undoubtedly one can notice a hydrogen release of $\sim 6\text{wt.}\%$ with same onset temperature of 150°C .

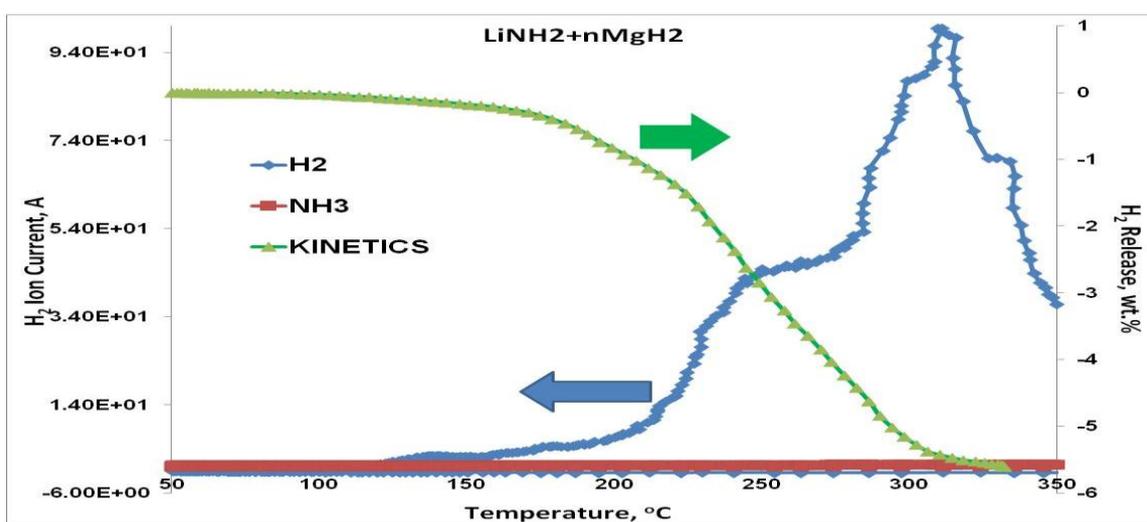


Figure 14 MS and kinetics of LinMgNH

For further destabilization, undoped Li-nMg-N-H was doped with various nanocatalysts such as Ni, Co, Fe, Ti and TiF_3 . Figure 15 represents the thermogravimetric (TGA) analysis of the various doped materials. When compared to the undoped Li-nMg-N-H sample, all the catalyst doped materials exhibit early onset hydrogen decomposition temperatures with increase in desorption kinetics and storage capacity as well (i.e. $\sim 6\text{wt.}\%$ H_2 release below 250°C). Looking at the decomposition reaction kinetics of the catalysts, the best performances are categorized as $n\text{Co} > n\text{Ni} > \text{TiF}_3$, and looking at the total effective hydrogen capacity, the best performances are categorized as $n\text{Ni} > \text{TiF}_3 > n\text{Co}$. So the Nickel was chosen as the most effective catalyst for this material. Nevertheless, the total effective hydrogen storage capacity obtained from all of the catalyzed Li-nMg-N-H materials corresponds to 7-9 wt. %.

DESIGN AND DEVELOPMENT OF HIGH STORAGE CAPACITY COMPLEX HYDRIDES FOR REVERSIBLE HYDROGEN STORAGE IN VEHICLES

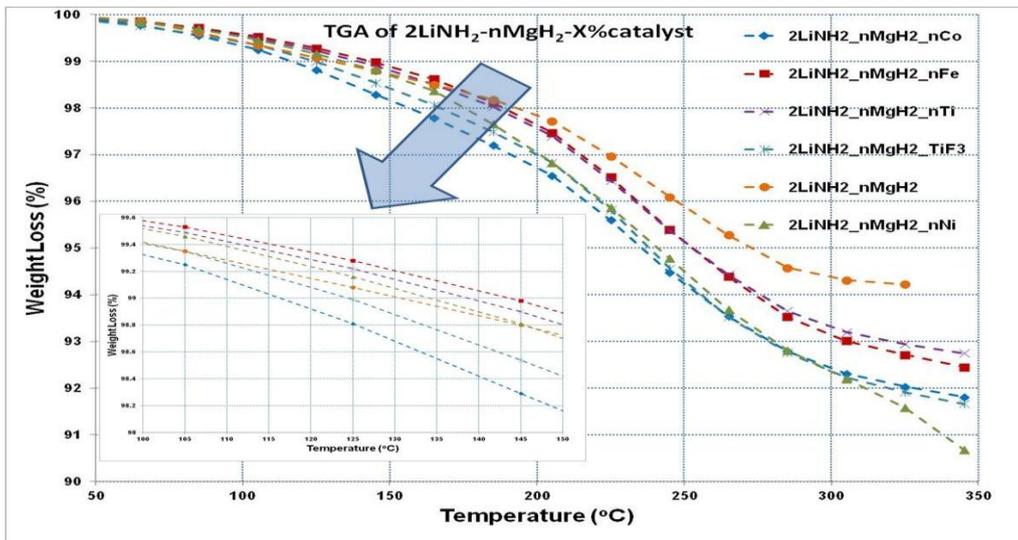


Figure 15 Thermogravimetric analysis (TGA) of undoped and catalyst doped Li-nMg-N-H

We then milled 2wt. % nanoNi catalyst with the host hydride $2\text{LiNH}_2/\text{nMgH}_2$. Figure 16 below represents the MS analysis of Ni doped Li-nMg-B-N-H with primary Y-axis showing the ion current of various gases (He carrier gas, H_2 , N_2 , H_2O , O_2 and NH_3) and the secondary Y-axis showing the temperature at which these gases evolve and disappear. It is very clearly seen that the on-set for hydrogen release early at room temperature; the peak hydrogen decomposition was observed at 160°C which is at least 150°C less than the undoped Li-nMg-N-H counterpart. Another interesting fact is that for the Ni doped Li-nMg-N-H, no significant NH_3 gas is detected for wide operating temperature ranges.

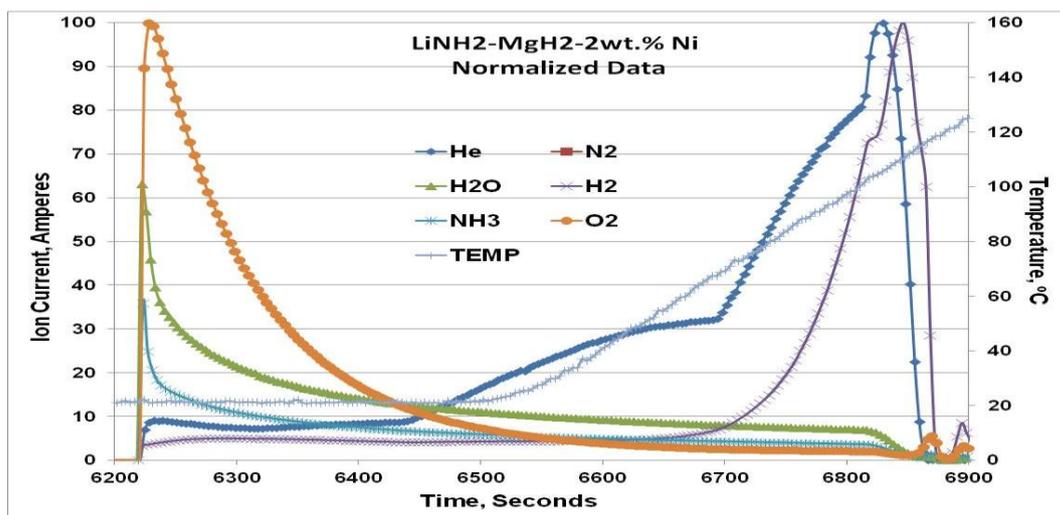


Figure 16 MS of Li-nMg-N-H doped with 2wt % Ni nanocatalyst

- **Optimization of Absorption Temperature:** The initial desorption ramping kinetics (see Figure 14) after ball milling of $2\text{LiNH}_2/\text{nMgH}_2$ shows a hydrogen storage capacity of $\sim 6\text{wt.}\%$. However, in the consecutive hydrogen absorption and desorption runs, the reversible hydrogen

DESIGN AND DEVELOPMENT OF HIGH STORAGE CAPACITY COMPLEX HYDRIDES FOR REVERSIBLE HYDROGEN STORAGE IN VEHICLES

storage capacity of ~2.5wt.% was observed. An attempt has been made to optimize the hydrogen absorption temperature and pressure and is demonstrated in Figures 17 and 18 respectively. After the initial desorption, the material has been subjected to various hydrogen pressures (>85bars) and absorption at temperatures varies from 100-300°C in 3, 5, 7, 9 and 11 cycles. From Figure 17, it is clearly seen that absorption temperature of 200°C, the uptake of hydrogen is much pronounced (>2wt.%) with a reversible fast kinetics as supported by the 8th desorption ramping kinetics of Figure 18. Overall analysis of Figures 17 and 18, the optimized hydrogen absorption temperature and pressure conditions were 200°C and 85bars respectively and reversibility of hydrogen storage capacity was maintained in this novel material at about 2.5wt.%

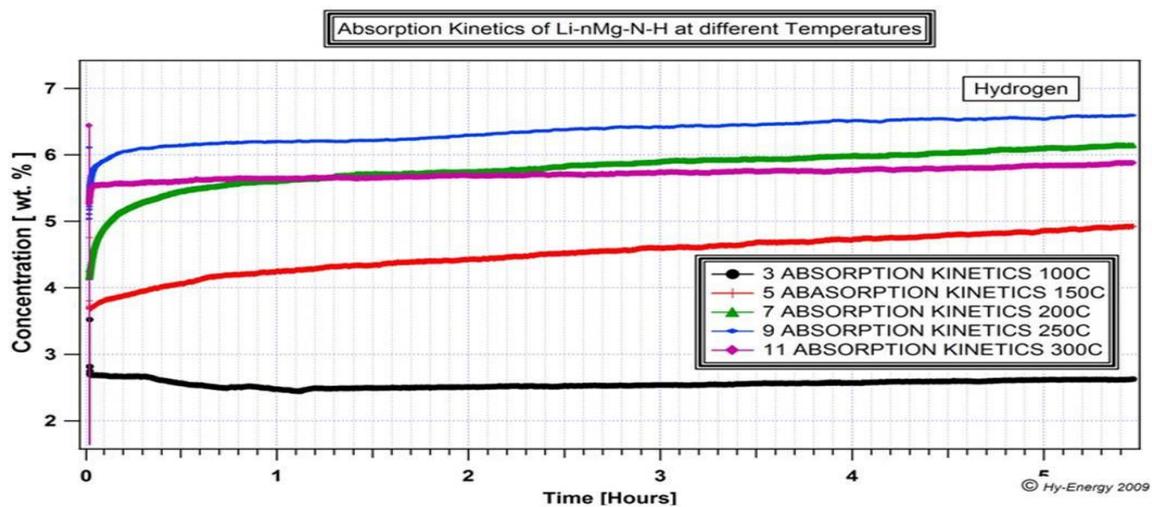


Figure 17 Hydrogen absorption kinetics of Li-nMg-N-H in alternative cycles at different temperatures

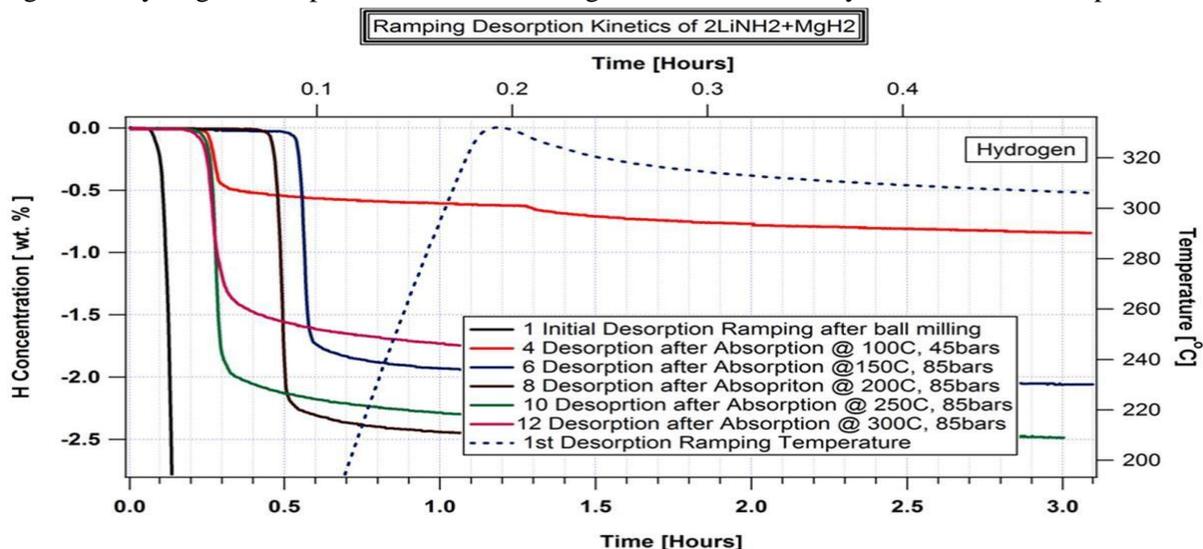


Figure 18 Hydrogen desorption kinetics of Li-nMg-N-H in alternative cycles at different temperatures

DESIGN AND DEVELOPMENT OF HIGH STORAGE CAPACITY COMPLEX HYDRIDES FOR REVERSIBLE HYDROGEN STORAGE IN VEHICLES

1.2. FT-IR Spectroscopy

The chemical bonding of N-H stretches for the Li-nMg-N-H material before and after hydrogen sorption (PCT) were observed by FT-IR spectroscopic measurements with wavenumber ranges from 400-4000 cm^{-1} . Figure 19 shows the FT-IR profiles for notable regions from wavenumber 3000 to 3500 cm^{-1} . For the case of as-synthesized Li-nMg-N-H, obtained from ball milling of 2LiNH_2 and nano MgH_2 , asymmetric and symmetric N-H stretches due to LiNH_2 is observed at the wavenumbers 3300 and 3250 respectively. However, for the case of Li-nMg-N-H after hydrogenation and dehydrogenation experiments, a new much deeper and wider bonding band arises from N-H due to the intermediated hydride compound $\text{Li}_2\text{Mg}(\text{NH})_2$ in between wavenumbers 3150 and 3200 cm^{-1} . No parent N-H stretches from LiNH_2 were seen, this reflects not only the complete consumption of parental compounds during mechano-chemical process.

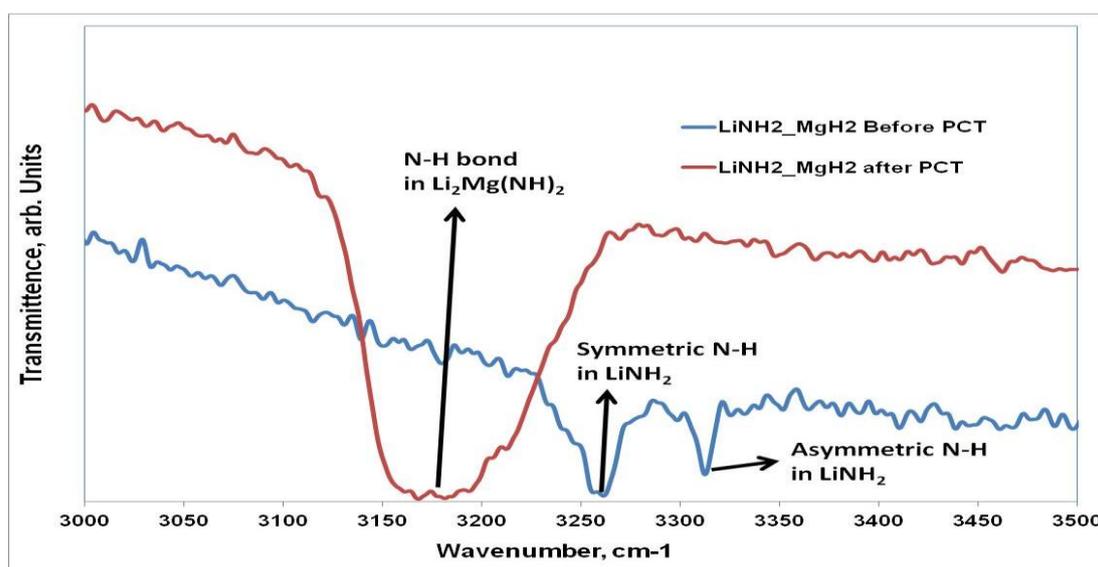


Figure 19 FT-IR of $\text{Li}_n\text{Mg}_n\text{NH}$ before and after hydrogen PCT experiments

1.3. Analysis of scheme 1

Table 6 Summary of scheme 1 results compared to US DOE targets

Sample (Li-nMg-N-H)	Without catalyst	With 2% Ni	Jun Yang in 2007
Kinetics (maximum time for hydrogen release)	~20minutes	<20minutes	~4.5hours
Hydrogen capacity (wt. %)	6	6-9	4.3-6
Temperature of hydrogen release ($^{\circ}\text{C}$)	325	160	220
Reversibility of hydrogen storage capacity (wt. %)	2.5	-	-

DESIGN AND DEVELOPMENT OF HIGH STORAGE CAPACITY COMPLEX HYDRIDES FOR REVERSIBLE HYDROGEN STORAGE IN VEHICLES

Comparing our resulting complex hydrides and similar complex hydrides found in literature aimed for hydrogen storage, we notice that there is an increase in kinetics as well as a reduction in the thermodynamic stability of the novel material. The gravimetric capacity of 6-9wt.% is below that of LiNH_2 and $\text{MgH}_2 > 7.6\text{wt.}\%$ and the temperature of hydrogen release is less than 400°C but still high due to the visible presence of LiNH_2 as shown in the FT-IR. The presence of Ni as a catalyst enhances the kinetics, the gravimetric capacity, reduces NH_3 gas release and reduces the thermodynamic stability thus reducing the temperature of hydrogen release to about half its original temperature. During the PCT analysis, we notice that the optimal temperature of reversible hydrogen release reduces to 200°C due to the complete disappearance of LiNH_2 in the structure of the material. This material does not meet the US DOE targets but may be further studied and improved.

SCHEME 2:

2. Li-nMgAlNH Complex Hydrides

Li-nMg-Al-N-H compound is synthesized from the mechano-chemical milling of pre-milled LiAlNH hydride ($\text{LiAlH}_4 + 2\text{LiNH}_2$) and nano MgH_2 under Ar/H_2 atmosphere for two different time durations such as 5h (Li-nMgAlNH) and 10h (10hrLi-nMgAlNH) respectively. For the case of 10hr Li-nMgAlNH material, due to the prolonged milling, the total hydrogen storage capacity obtained was even much less than $1.0\text{wt.}\%$. The results obtained were not interesting so only results from the 5 hour milling will be presented.

2.1. Mass Spectrometry, Ramping kinetics

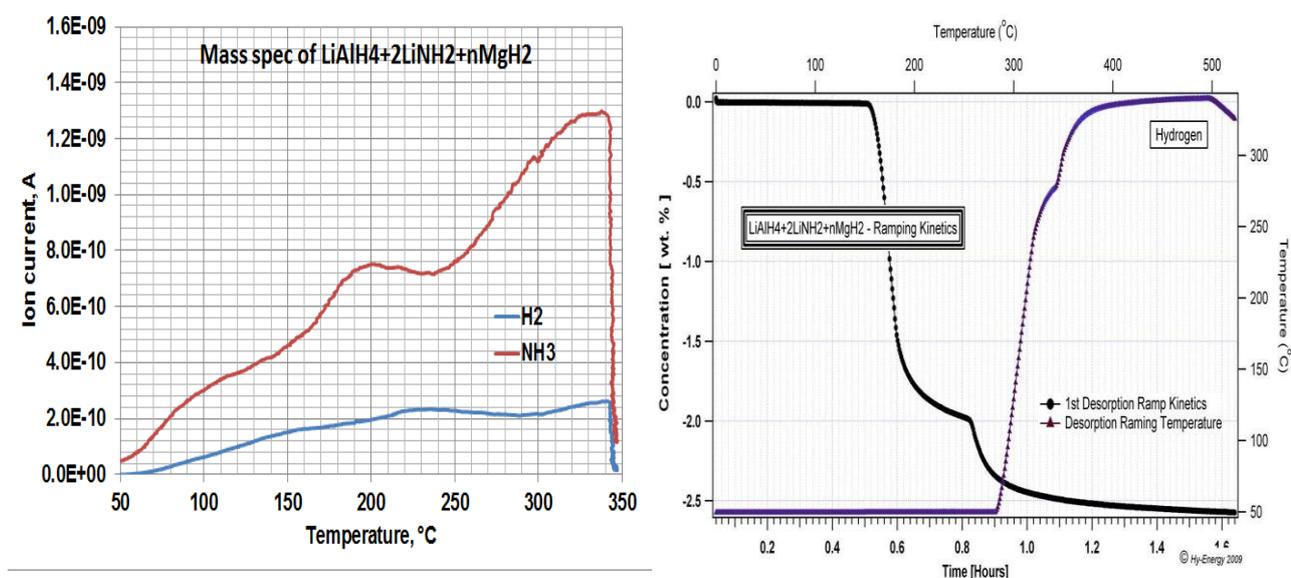


Figure 20 MS (left) and kinetics (right) of Li-nMg-Al-N-H

DESIGN AND DEVELOPMENT OF HIGH STORAGE CAPACITY COMPLEX HYDRIDES FOR REVERSIBLE HYDROGEN STORAGE IN VEHICLES

Figure 20 (left) above shows the RGA/MS of Li-nMg-Al-N-H from 50-350°C. Hydrogen is released in less proportion when compared to the ammonia. Figure 20 (right) also represents the dehydrogenation kinetics of LinMgAlNH which is plotted against the ramping temperatures up to 350°C. This graph shows a gravimetric capacity of 2.5wt% and faster kinetics than the Scheme 1 material LinMgNH; however, the majority of hydrogen release was obtained within 150°C. Anyway for this sample no catalyst was used for further destabilization because the RGA/MS analysis of cycled LinMgAlNH shows the evolution of only hydrogen gas species as demonstrated in Figure 21 below.

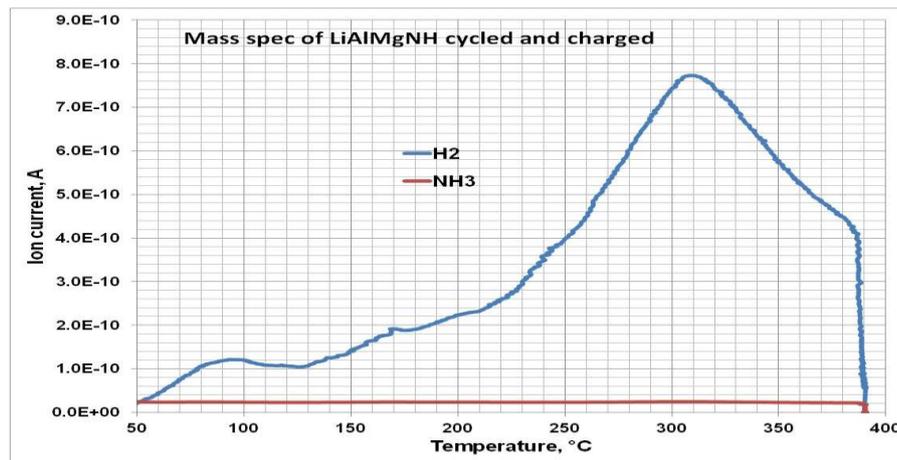


Figure 21 RGA/MS of LinMgAlNH after PCT sorption cycles

The desorbed LinMgAlNH as discussed above was then rehydrogenated at different temperatures and pressure conditions. We have also executed consecutive dehydrogenation ramping kinetics to optimize to set experimental parameters. From Figure 22, it is understood that the optimized hydrogen absorption temperature and pressure conditions were 300°C and 90bars respectively and reversibility of hydrogen storage capacity was maintained in this novel material at about 0.6wt.%

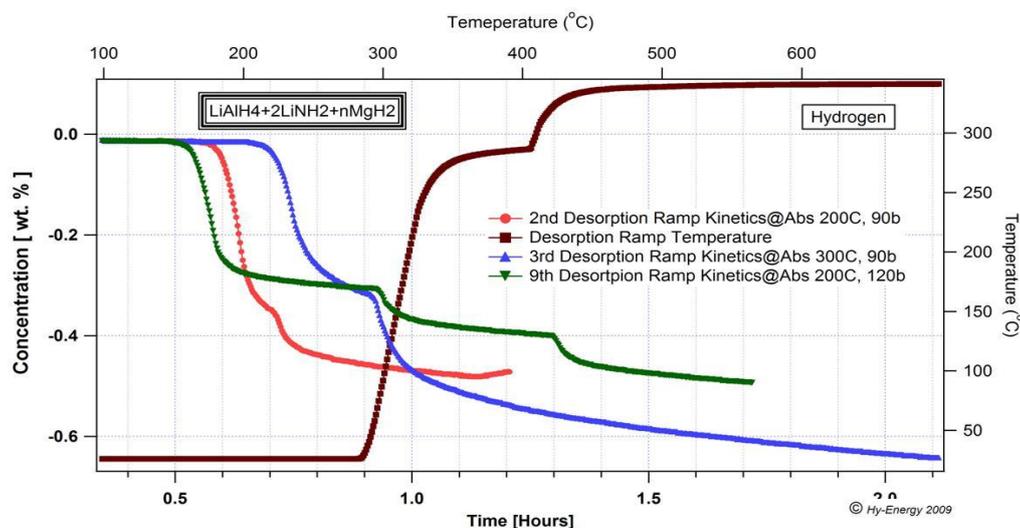


Figure 22 Ramping dehydrogenation kinetics of LinMgAlNH in consecutive cycles

DESIGN AND DEVELOPMENT OF HIGH STORAGE CAPACITY COMPLEX HYDRIDES FOR REVERSIBLE HYDROGEN STORAGE IN VEHICLES

2.2. Analysis of scheme 2

A summary of the results of both 5hrs and 10hrs ball milled LinMgAlNH samples are represented in Table 7 below.

Table 7 Summary of scheme 2 results compared to US DOE targets

Scheme 2 samples	LinMgAlNH	10hr LinMgAlNH	Andrew Vittetoe; 2009
Kinetics (maximum time for hydrogen release)	~1hour	~2hours	20minutes
Temperature of release (°C)	350	350	300
Gravimetric capacity (wt. %)	2.5 (1 st Ramp Kinetics)	0.5 (1 st Ramp Kinetics)	5.2

Comparing our resulting complex hydrides and similar complex hydrides found in literature aimed for hydrogen storage, we notice that there is a decrease in kinetics as well as no improvement in the thermodynamic stability of the novel material. The gravimetric capacity of 2.5wt.% is far below that of LiAlH₄+nMgH₂ (5.2wt.%) and the temperature of hydrogen release is more than 300°C. LiAlH₄+MgH₂ was made from 2h ball milling. We can say that the high temperatures of hydrogen release is due to the presence of lithium in scheme 1 and 2 and its addition to LiAlH₄ and MgH₂ as LiNH₂ does not improve the sorption properties of this material. In this NH₃ gas reduces with further hydrogenation and dehydrogenation cycling. We can therefore say that additional milling hours on this material reduces its sorption properties.

SCHEME 3:

3. LinMgBNH Complex Hydrides

The multinary complex hydride, LinMgBNH has been synthesized by stoichiometric milling of quaternary hydride Li-B-N-H (LiBH₄+2LiNH₂) with nano MgH₂ under Ar/H₂ ambient for 5 hours. The formation of Li-nMg-B-N-H compound was confirmed from structural and chemical characterizations using X-ray diffraction and Fourier Transform Infrared spectroscopic analysis which are elaborated in the following sections.

3.1. X-Ray Diffraction

Figure 23 shows the XRD pattern of the parent hydrides such as LiBH₄, LiNH₂ and MgH₂, nano MgH₂, the as-synthesized quaternary (LiBNH) and multinary (LinMgBNH) systems. The peak around 21° is from the Parafilm[®] used to protect the samples during XRD measurements.

DESIGN AND DEVELOPMENT OF HIGH STORAGE CAPACITY COMPLEX HYDRIDES FOR REVERSIBLE HYDROGEN STORAGE IN VEHICLES

Neither LiBH_4 nor LiNH_2 peaks are observed in the as-prepared LiBNH and LiMgBNH complex hydrides. This confirms that these two materials are fully consumed during the milling process and actually form a new quaternary structure, referred to as LiBNH . The quaternary structure has been reported to be $\text{Li}_4\text{BN}_3\text{H}_{10}$. When the nano sized MgH_2 is added to the quaternary LiBNH , the MgH_2 peaks are barely picked up by the XRD. This indicates that the small size of the MgH_2 causes the material to intermix and fill voids of the quaternary structure, which results in a nanocrystalline particle distribution, while still preserving the quaternary structure formed by the LiNH_2 and LiBH_4 . The as-synthesized multinary complex hydride is a physical, rather than a chemical, mixture of the quaternary structure LiBNH with nano MgH_2 .

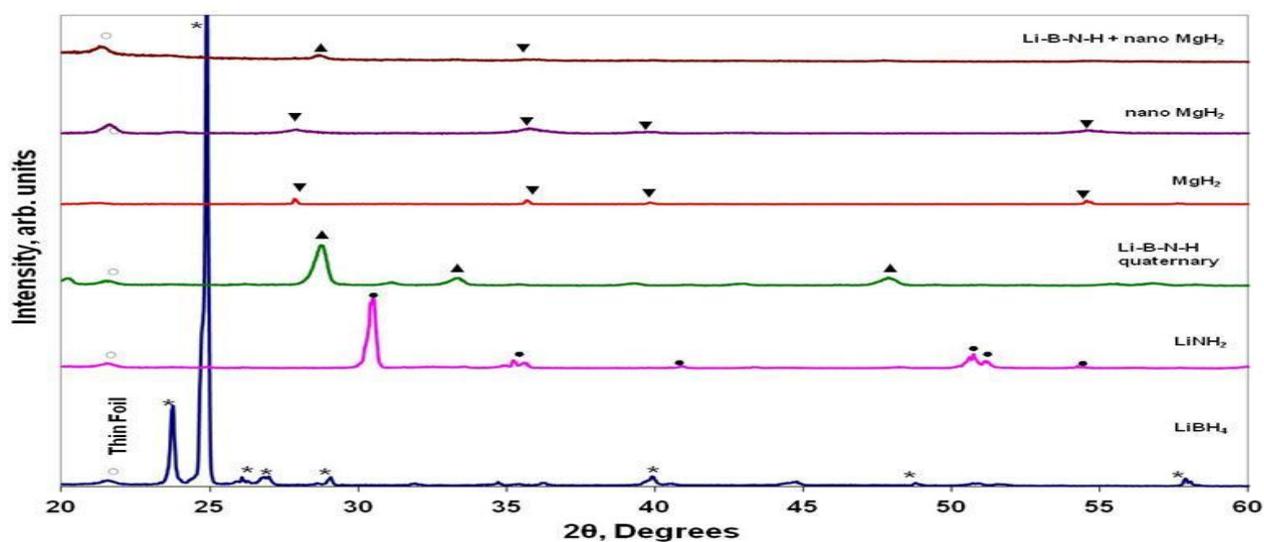


Figure 23 XRD of LiMgBNH

3.2. FT-IR Spectroscopy

The as-prepared quaternary (LiBNH) and multinary (LiMgBNH) complex hydrides were characterized using FT-IR to obtain information about the B-H and NH_2 stretches and BH_2 deformation, as seen in Figure 24. The peaks of the symmetric and asymmetric amide anions are shifted from the expected 3312 and 3259 cm^{-1} to 3302 and 3244 cm^{-1} , respectively. Furthermore, the peak around 1560 cm^{-1} is characteristic of the amide ion. The B-H stretches, usually found at 2225 , 2237 , 2293 , and 2387 cm^{-1} , overlap in the samples to form one large B-H stretch with a peak around 2320 cm^{-1} . Finally, the BH_2 deformation peaks found at 1120 and 1092 cm^{-1} in LiBH_4 are observed at 1120 and 1082 cm^{-1} , respectively, though the peak around 1120 cm^{-1} is extremely weak.

DESIGN AND DEVELOPMENT OF HIGH STORAGE CAPACITY COMPLEX HYDRIDES FOR REVERSIBLE HYDROGEN STORAGE IN VEHICLES

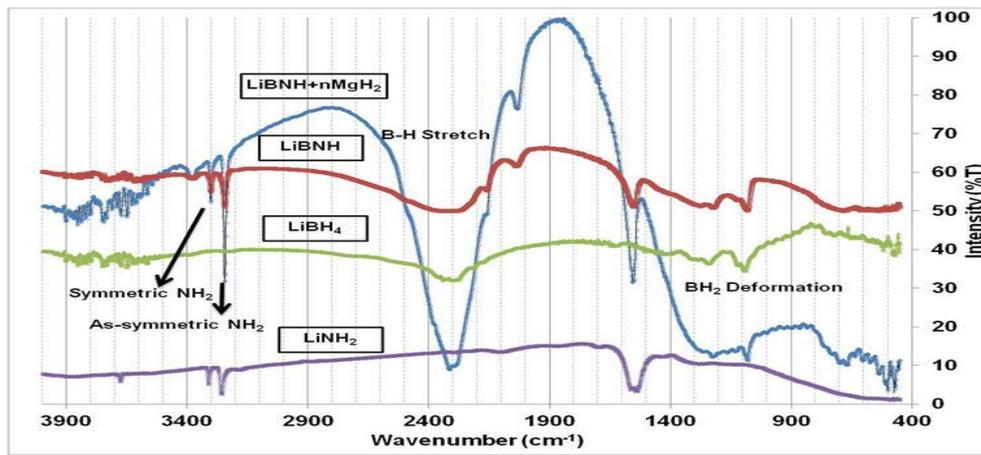


Figure 24 FT-IR of plain hydrides and as-prepared LiBNH and LinMgBNH

However, there is no observable shift in any of the main stretches indicating that the chemical composition of the quaternary hydride is kept intact, and there is in fact no formation of a new compound other than the previously reported structure. There is no evidence in the FTIR data indicating the reaction of MgH_2 with either the amide or borohydride, further confirming the XRD data shown in figure 23.

3.3. Mass Spectrometry and Kinetics of LinMgBNH

Figure 25 below shows the RGA/MS of LinMgBNH before and after PCT. The main peak of hydrogen is noticed at 250°C which has been the lowest temperature so far among all the new materials previously studied in this thesis. The graph on the left shows two peaks of ammonia release at 100°C and 240°C but the release of ammonia decreases after the PCT to one peak released at 85°C. After 100°C, only hydrogen is the species transport inside the host matrix during sorption phases.

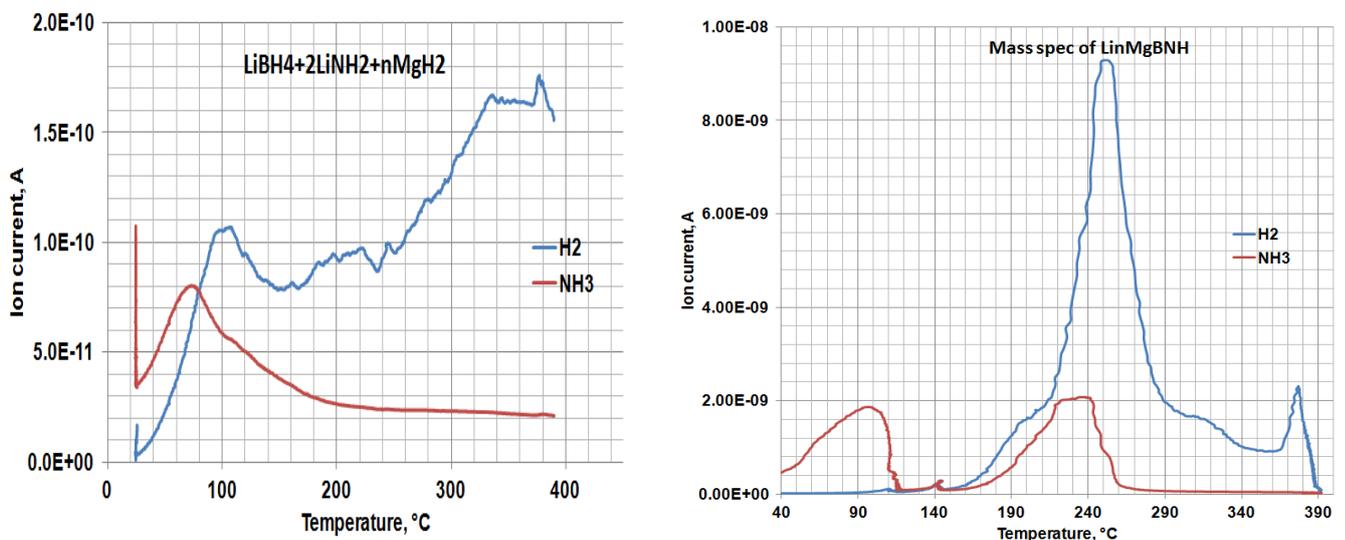


Figure 25 MS of LinMgBNH before PCT (left) after PCT (right)

DESIGN AND DEVELOPMENT OF HIGH STORAGE CAPACITY COMPLEX HYDRIDES FOR REVERSIBLE HYDROGEN STORAGE IN VEHICLES

The as-synthesized LinMgBNH multinary complex hydride after XRD and FTIR characterizations are analyzed in the PCT under high hydrogen pressure of 90 bars in charging phase and 1bar in discharging phase. Figure 26 represents the cycle kinetics showing fast kinetics rate for the reversible hydrogen capacity of 6-8 wt.% . The optimal conditions of temperature and pressure are 200°C and pressure of 90bars.

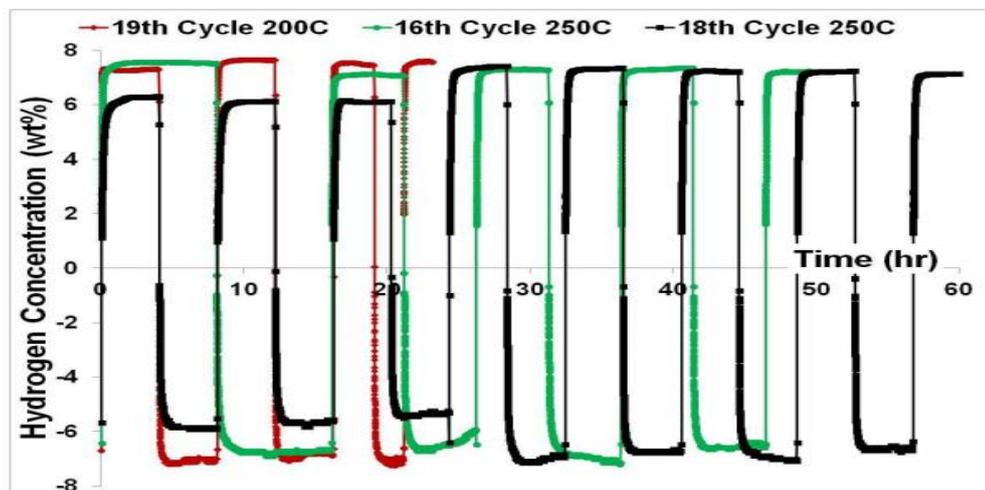


Figure 26 Cycle life kinetics of LinMgBNH at 200 and 250°C.

3.4. Analysis of scheme 3

Despite the high temperatures of its metal hydrides, LinMgBNH multinary hydride is an exceptional hydride good reversible hydrogen capacity (>6wt.%), as well as favorable thermodynamics release of hydrogen at temperatures between 200 and 250°C because the FT-IR shows the absence of any lithium compound confirming that lithium compounds have high temperatures of hydrogen release compared to boron containing. Even though its gravimetric capacity is far below that of LiNH₂, LiBH₄ and MgH₂, its weight capacity meets the US DOE targets of >5.5wt.% compounds. This compound releases hydrogen in 10minutes compared to LiBH₄+MgH₂ from literature review which releases hydrogen in 2.5hours. NH₃ release reduces with further hydrogenation and dehydrogenation cycling. The XRD and FT-IR show that a new compound was actually synthesized which have significantly different properties than the parental counterparts. This material is efficient but does not meet the technical targets of the US DOE due to its temperature of hydrogen release which is greater than 100°C. This material then needs more destabilization to further reduce its temperature of hydrogen release.

SCHEME 4

4. BNH₆.MgH₂ Complex Hydrides

Four different complex hydrides were made from milling BNH₆ and MgH₂. The various samples were made to see the ratio and milling effects on the different complex hydrides. BNH₆ has shown very high hydrogen capacity, fast kinetics and low temperatures of hydrogen release but it is irreversible. The RGA/MS analysis of all four samples was first carried out to examine the gases released and the temperature of hydrogen release of hydrogen before studying the kinetics and sorption properties of the most interesting sample.

4.1. Mass Spectrometry and Kinetics of all BNH₆ Complex hydrides

4.1.1. Hydrogen release in complexes

Figure 27 below shows the hydrogen release in all 4 samples including the plain BNH₆. The primary Y-axis show the hydrogen release by all the complex hydrides but the secondary Y-axis shows the hydrogen release of the plain BNH₆. This release varies for temperatures between 50 and 350°C represented on the X- axis of the graph.

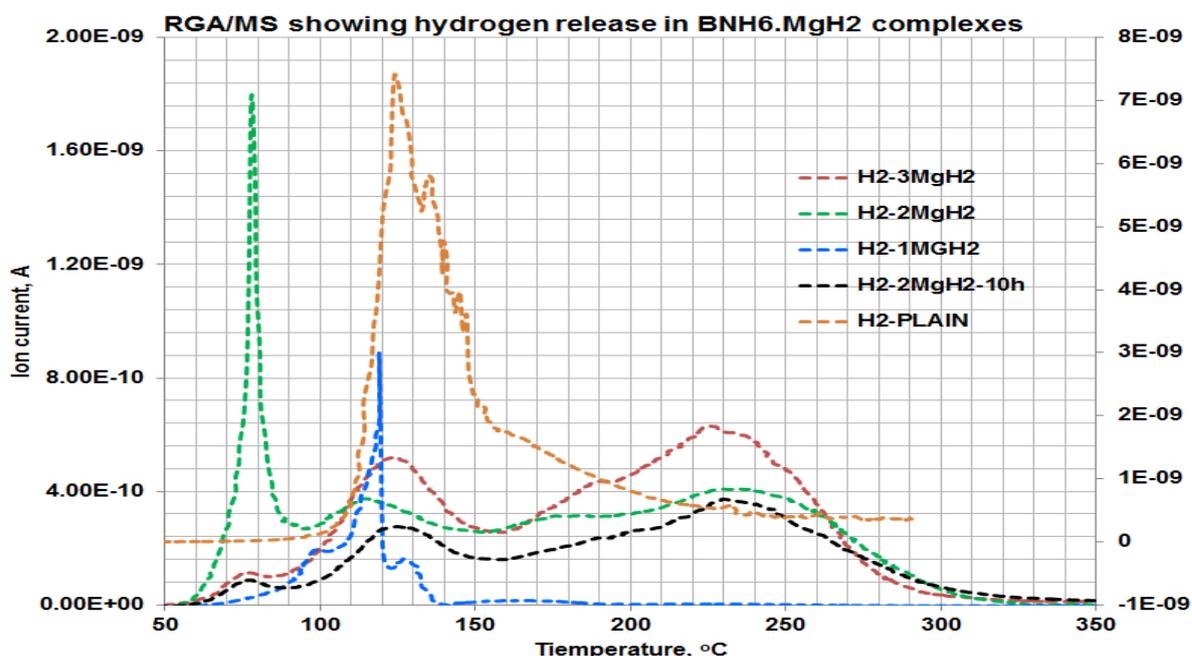


Figure 27 Hydrogen release in BNH₆.MgH₂ Complex hydrides

Figure 27 shows that destabilizing BNH₆ with nMgH₂ reduces its hydrogen capacity tremendously. Plain BNH₆ has an ion current of about 4 times those of the other complex hydrides. Focusing on the hydrogen release the hydrides can be categorized as BNH₆ > BNH₆.2MgH₂ > BNH₆.MgH₂ > BNH₆.3MgH₂ > BNH₆.2MgH₂-10hr. So hydrogen release neither varies proportionally with the ratio of MgH₂ nor with the milling hours but for optimal results milling

DESIGN AND DEVELOPMENT OF HIGH STORAGE CAPACITY COMPLEX HYDRIDES FOR REVERSIBLE HYDROGEN STORAGE IN VEHICLES

should be done for less than five hours and the ratio of MgH_2 should be between 1 and 2. Among the destabilized complex hydrides $BNH_6 \cdot 2MgH_2$ has the highest peak of hydrogen release and at a temperature below $100^\circ C$.

4.1.2. Toxic gas release in complexes

Figure 28 and 29 show the NH_3 and B_2H_6 release in various complex hydrides. This also shows the MgH_2 ratio effects as well as the milling effects on the toxic gas release of the various complex hydrides.

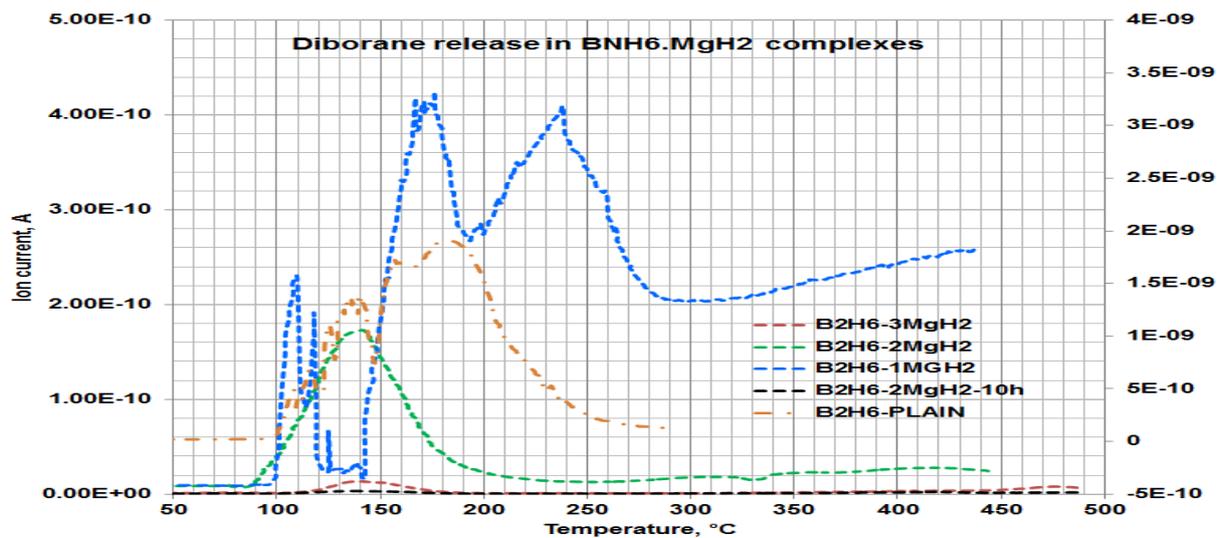


Figure 28 Diborane release in $BNH_6 \cdot MgH_2$ Complex hydrides

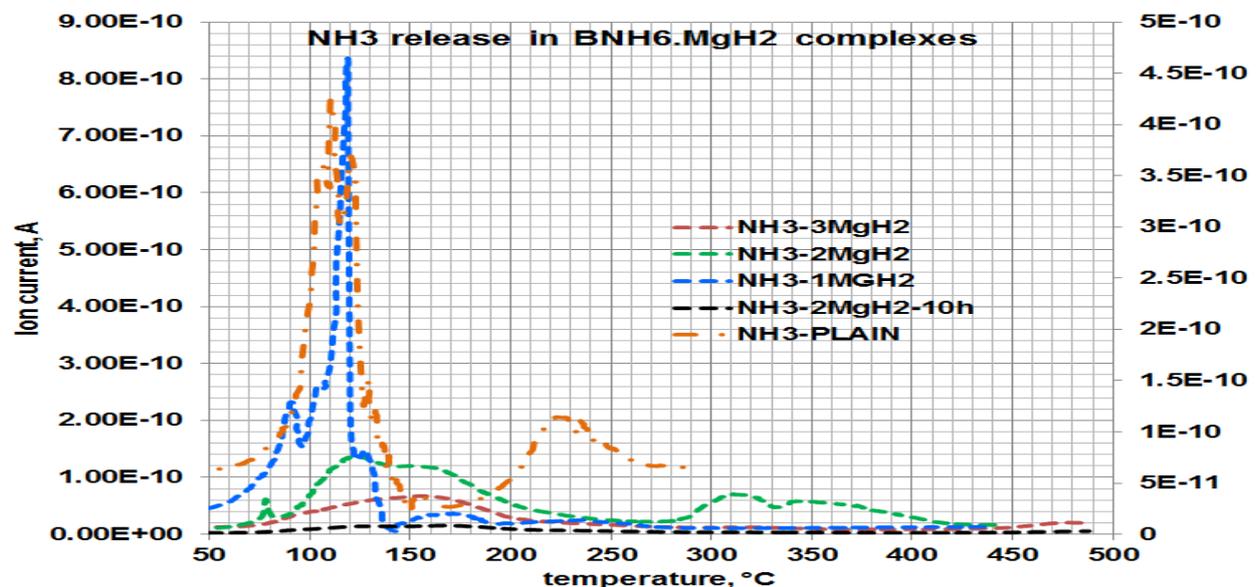


Figure 29 Ammonia release in $BNH_6 \cdot MgH_2$ Complex hydrides

DESIGN AND DEVELOPMENT OF HIGH STORAGE CAPACITY COMPLEX HYDRIDES FOR REVERSIBLE HYDROGEN STORAGE IN VEHICLES

The diborane release from figure 28 can be categorized as $\text{BNH}_6.\text{MgH}_2 > \text{BNH}_6 > \text{BNH}_6.2\text{MgH}_2 > \text{BNH}_6.3\text{MgH}_2 > \text{BNH}_6.2\text{MgH}_2\text{-10hr}$. After 250°C , all samples reduce their release of diborane to approximately zero except $\text{BNH}_6.\text{MgH}_2$.

The ammonia release from figure 29 has a similar pattern to the diborane release but from 150°C the release of ammonia reduces to approximately zero in all samples. be categorized as $\text{BNH}_6.\text{MgH}_2 > \text{BNH}_6 > \text{BNH}_6.2\text{MgH}_2 > \text{BNH}_6.3\text{MgH}_2 > \text{BNH}_6.2\text{MgH}_2\text{-10hr}$.

So from these graphs we notice that extended milling reduces both the toxic gas and hydrogen release. Considering all the figures $\text{BNH}_6.2\text{MgH}_2$ will be the most appropriate complex hydride amongst our novel hydrides. It has the closest hydrogen release to plain BNH_6 and its toxic gas release reduces to approximately zero after 200°C . We then studied the kinetics of this sample to see its actual hydrogen capacity, its kinetics and its reversibility.

4.1.3. Kinetics of $\text{BNH}_6.2\text{MgH}_2$

Figure 30 below shows the kinetics of $\text{BNH}_6.2\text{MgH}_2$. This graph shows very fast kinetics for this sample, very low temperatures of hydrogen release and a reversible hydrogen capacity of 3.7wt.%.

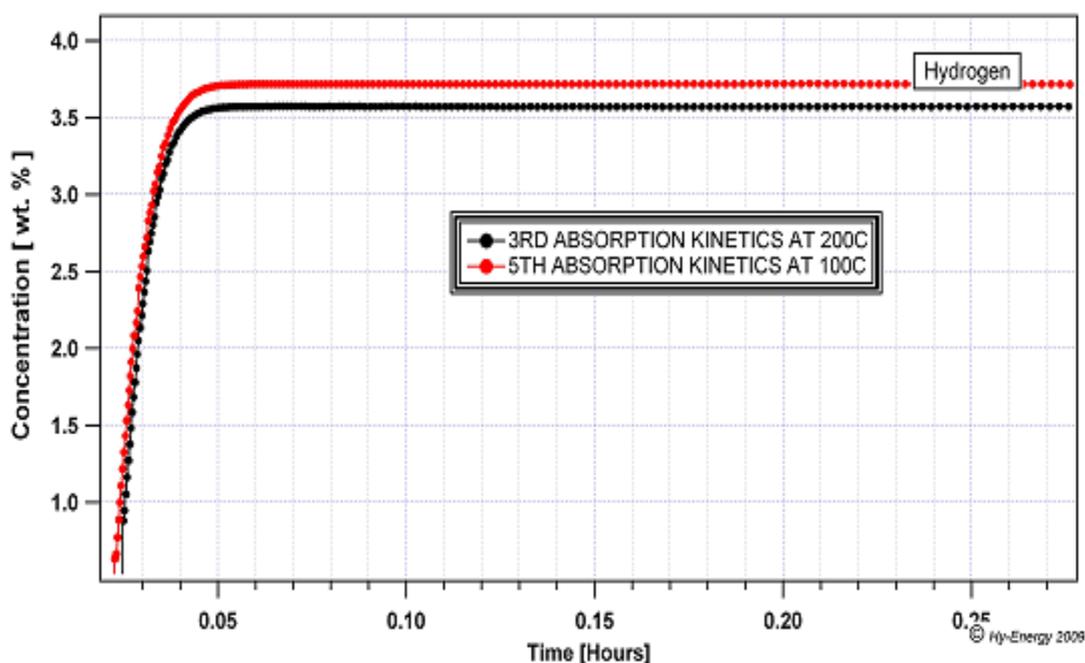


Figure 30 Dehydrogenation Kinetics of $\text{BNH}_6.2\text{MgH}_2$ in consecutive abs/des cycles.

4.2. FT-IR Spectroscopy

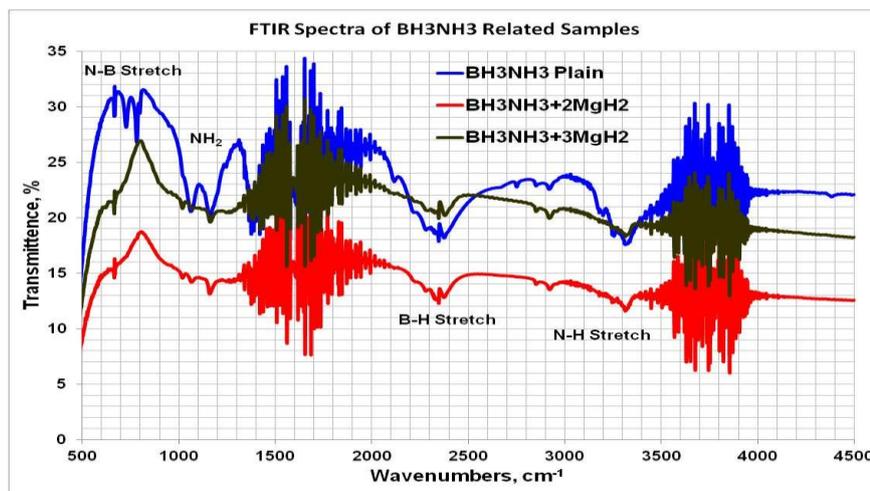


Figure 31 FT-IR BNH₆.MgH₂ related samples

The FT-IR measurements are taken at room temperature in the range of 4500-500cm⁻¹ to characterize the BNH₆ complex compounds. Figure 31 shows that BNH₆.2MgH₂ and BNH₆.3MgH₂ have the same chemical structure and are parent compounds to BNH₆ so both compounds are entirely different from BNH₆ but are similar to each other.

4.3. Analysis of scheme 4

All BNH₆.MgH₂ compounds have low temperatures of hydrogen emission (80-125°C), excellent kinetics and reversibility but their greatest problem is the quantity and type of gases they emit simultaneously with hydrogen. Among the four BNH₆.MgH₂ compounds studied only BNH₆.2MgH₂ showed the most interesting properties in terms of gas emission and other sorption properties due to its milling hours and MgH₂ ratio. Despite the wonderful properties (excellent kinetics and temperatures of hydrogen release below 100°C) of BNH₆.2MgH₂, its main problem was its gravimetric capacity. Which does not meet the US DOE targets.

CONCLUSION

Our results show that, $\text{LiBH}_4+2\text{LiNH}_2+n\text{MgH}_2$ and $\text{BNH}_6.2\text{MgH}_2$ are the the most efficient hydrogen storage system in this thesis. Their properties are very close to US DOE targets but for the temperature of hydrogen release ($>100^\circ\text{C}$) and the hydrogen capacity ($<5.5\text{wt.}\%$) respectively. Even though the gravimetric capacity is less than $5.5\text{wt.}\%$, it can still be used for mobile applications considering the other properties.

Comparing all the schemes in this thesis, it is noticed that the materials with the lowest temperatures of hydrogen release, very good kinetics and highest gravimetric capacities are boron containing compounds especially in the absence of lithium. Therefore Boron containing compounds are promising for hydrogen storage systems, lithium compounds will need further destabilization to reduce their temperature of hydrogen release or reduce their barrier of activation energy and catalyst generally reduce the emission of toxic gases during cycling in the materials. Ball milling contributes to the greatest destabilization method for all complex hydrides. Till date, no research has found any material meeting the US DOE targets but the closest complex hydrides so far has been Boron containing compounds especially BNH.

New materials were studied to see the effect of adding or subtracting another metal hydride from already studied or existing material. The effect of ball milling, doping and material ratio was seen on different compounds and the limiting element in various compounds was noticed to orient the formation of another complex hydride.

These complex multinary hydrides therefore have potential applicability in H_2 fuel cell devices. They can be manufactured at large scale due to inexpensive single step ball milling approach. The development of novel light weight, high capacity hydrogen storage systems have a great impact on the economy of implementing clean and alternative (hydrogen) fuel for automotive.

RECOMMENDATIONS

Given that complex hydrides seem promising hydrogen storage systems but have various problems such as toxic gas release, kinetics and temperature of hydrogen release, additional research should be done on these complex hydrides so that they can be more efficient hydrogen.

- Firstly more research should be done to further destabilize complex hydrides and make them less thermodynamically stable. This will further improve their kinetics and further reduce their temperature of hydrogen release.
- Further research on various catalytic doping methods should be done on various complex nanoscale hydrides. This will not only improve their sorption properties but it will also reduce their toxic gas release as much as possible.
- Optimum milling conditions, ratio of additional materials should be found because these factors have a great impact on hydrogen storage systems.

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HYDRIDES FOR REVERSIBLE HYDROGEN STORAGE IN VEHICLES**

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ANNEXURES

ANNEX 1: Comparism of hydrogen fuel to other hydrocarbon fuels

Basic Properties of Hydrogen, Methane, and Propane

Gas Properties:	Hydrogen	Methane	Propane
Chemical Formula	H ₂	CH ₄	C ₃ H ₈
Molecular Weight	2.016	16.04	44.097
Gas Density (kg/m ³) @ STP	0.0808	0.643	1.767
Diffusivity (m ² /sec) x 10 ⁵	6.11	1.60	1.00
Combustion Properties:			
Stoichiometric Fuel Volume Fraction %	29.5%	9.48%	4.03%
Lower Heating Value (MJ/m ³)	9.9	32.6	81.2
Lower Heating Value (MJ/kg)	118.8	50.0	46.35
Adiabatic Flame Temperature (K)	2380	2226	2267
Flammability Limits (Volume %)			
Lean Limit:	4%	5.3%	2.2%
Rich Limit:	75%	15%	9.5%
Max. Flame Velocity (m/sec)	3.06	0.39	0.45
Min. Ignition Temperature (K) ¹	845	905	766
Min. Ignition Energy (10 ⁻⁶ J) ¹	2.0	33	30.5
Storage Conditions:			
Tank Type	Cylinder	Cylinder	Barbecue
Volume (liters)	49	49	21
Pressure (psi) ²	34 MPa	17 MPa	1.6 MPa
Phase	Gas	Gas	Liquid
Mass (kg)	1.35	5.36	0.61

¹ At stoichiometric conditions

² Pressure conversions: 5000 psi = 34 MPa; 2500 psi = 17.0 MPa; 240 psi = 1.6 MPa

Source: Robert Schefer, Sandia National Laboratory

**DESIGN AND DEVELOPMENT OF HIGH STORAGE CAPACITY COMPLEX
HYDRIDES FOR REVERSIBLE HYDROGEN STORAGE IN VEHICLES**

ANNEX 2: US DOE detail targets for onboard hydrogen systems

DOE Targets for Onboard Hydrogen Storage Systems for Light-Duty Vehicles

Table 2 Technical Targets: Onboard Hydrogen Storage Systems				
Storage Parameter	Units	2010	2017	Ultimate
System Gravimetric Capacity: Usable, specific-energy from H ₂ (net useful energy/max system mass) ^a	kWh/kg (kg H ₂ /kg system)	1.5 (0.045)	1.8 (0.055)	2.5 (0.075)
System Volumetric Capacity: Usable energy density from H ₂ (net useful energy/max system volume)	kWh/L (kg H ₂ /L system)	0.9 (0.028)	1.3 (0.040)	2.3 (0.070)
Storage System Cost ^b :	\$/kWh net (\$/kg H ₂)	TBD (TBD)	TBD (TBD)	TBD (TBD)
• Fuel cost ^c	\$/gge at pump	3-7	2-4	2-4
Durability/Operability:				
• Operating ambient temperature ^d	°C	-30/50 (sun)	-40/60 (sun)	-40/60 (sun)
• Min/max delivery temperature	°C	-40/85	-40/85	-40/85
• Operational cycle life (1/4 tank to full) ^e	Cycles	1000	1500	1500
• Min delivery pressure from storage system; FC= fuel cell, ICE= Internal combustion engine	bar (abs)	5 FC/35 ICE	5 FC/35 ICE	3 FC/35 ICE
• Max delivery pressure from storage system ^f	bar (abs)	12 FC/100 ICE	12 FC/100 ICE	12 FC/100 ICE
• Onboard Efficiency	%	90	90	90
• "Well" to Powerplant Efficiency	%	60	60	60
Charging / Discharging Rates:				
• System fill time (5 kg)	min (kg H ₂ /min)	4.2 (1.2)	3.3 (1.5)	2.5 (2.0)
• Minimum full flow rate	(g/s)/kW	0.02	0.02	0.02
• Start time to full flow (20°C) ^g	s	5	5	5
• Start time to full flow (-20°C) ^g	s	15	15	15
• Transient response 10%-90% and 90% - 0% ^h	s	0.75	0.75	0.75
Fuel Purity (H ₂ from storage) ⁱ :	% H ₂	SAE J2719 and ISO/PDTS 14687-2 (99.97% dry basis)		
Environmental Health & Safety:				
• Permeation & leakage ^j	Sec/h	Meets or exceeds applicable standards		
• Toxicity	-	Meets or exceeds applicable standards		
• Safety	-	Meets or exceeds applicable standards		
• Loss of useable H ₂ ^k	(g/h)/kg H ₂ stored	0.1	0.05	0.05

Useful constants: 0.2778 kWh/MJ; 33.3 kWh/kg H₂; 1 kg H₂ = 1 gal gasoline equivalent.

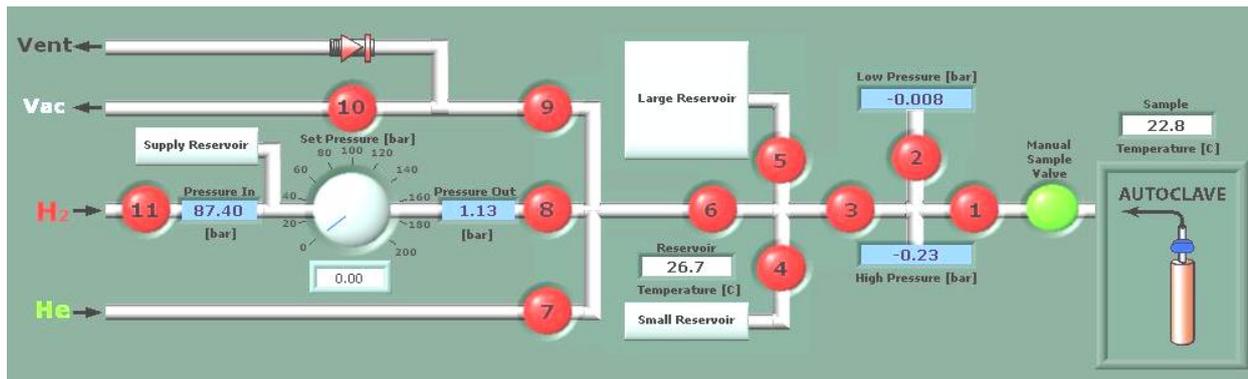
DESIGN AND DEVELOPMENT OF HIGH STORAGE CAPACITY COMPLEX HYDRIDES FOR REVERSIBLE HYDROGEN STORAGE IN VEHICLES

ANNEX 3: The principal components of the glove box and its functions

- ✓ Gloves which gives access to our hands to the glove box for manipulation.
- ✓ Edwards' high vacuum pump to evacuate the ante chambers.
- ✓ Electronic sensors to monitor oxygen and moisture content.
- ✓ Two antechambers or ports used to transfer materials in and out of the glove box; both ports can be opened from the inside and outside the box.
- ✓ The automatic gauge controls maintains the pressure inside the glove box, the system will increase or reduce pressure by injecting nitrogen or evacuating with vacuum pump, respectively according to the pressure range set for operation.
- ✓ The foot pedal, it allows the operator to manually adjust the pressure inside the glove box.
- ✓ The purification system removes and maintains low levels (less than 1ppm) of O₂ and moisture.
- ✓ Two blower controls which circulate the nitrogen gas inside the glove box with a speed of 50rpm. However higher speeds such as 80-100rpm can be set by the user if the O₂/moisture level is increased due to no flow of nitrogen or electrical power shortage etc.

DESIGN AND DEVELOPMENT OF HIGH STORAGE CAPACITY COMPLEX HYDRIDES FOR REVERSIBLE HYDROGEN STORAGE IN VEHICLES

ANNEX 4: Description of valve operations of the PCTPro E&E instrument



Valves 1 through 11 are air/nitrogen operated automatic solenoid valves and they are normally closed (red color indication), except valve 1 which is a normally open valve (green color indication). The description of the valve operations are given below.

Valve 1 - Main valve that delivers aliquots of gas to and from the sample. It is a normally open valve because it maintains its open position for the majority of the measurement time. It is closed only when reservoir volumes are being charged with gas and during some preparation processes.

Valve 2 - Protects the low-pressure transducer from manifold pressures that are greater than the maximum allowable pressure of the low-pressure sensor.

Valve 3 - Admits gas into the upper manifold. The smallest calibrated reservoir volume consist of the upper manifold between valves 1, 2 and 3; it has a total volume on the order of 5 cubic centimeters.

Valve 4 - Provides access to the medium sized calibration volume that has a volume of approximately 145 cubic centimeters.

Valve 5 - Provides access to the largest of the calibration volumes which is approximately one liter.

Valve 6 - Separates the lower manifold from the gas supply and vacuum manifold.

Valve 7 - Supplies helium gas to the gas supply manifold.

Valve 8 - Provides hydrogen to the gas supply manifold.

Valve 9 - Connects the gas supply manifold to the vent and vacuum system.

Valve 10 - Connects the vent system to the vacuum line.

Valve 11 - Test gas supply valve that connects to the test gas supply line.

**DESIGN AND DEVELOPMENT OF HIGH STORAGE CAPACITY COMPLEX
HYDRIDES FOR REVERSIBLE HYDROGEN STORAGE IN VEHICLES**

**ANNEX 5: Example of excel page used for ratio calculation for complex
compounds**

		aA + bB + x mol% of catalyst	
		Purity from bottles	
A =	BNH6	90. %	
B =	MgH2	95. %	
a =	1		
b =	2		
x =	.mol%		
(mw) of BNH6 =	30.86534 g/gmol		
(mw) of MgH2 =	26.32088 g/gmol		
Desired mixture of A + B =		2.g	
Ratio of a/b in reaction =		0.5	
Moles of pure MgH2 needed =		0.04790	moles
Moles of pure BNH6 needed =		0.02395	moles
Real mass of MgH2 from bottle =		1.3271	g
Real mass of BNH6 from bottle =		0.8214	g

DESIGN AND DEVELOPMENT OF HIGH STORAGE CAPACITY COMPLEX
HYDRIDES FOR REVERSIBLE HYDROGEN STORAGE IN VEHICLES

ANNEX 6: Summary of the characteristic absorption lines for the FT-IR

Bond type	Characteristic absorption lines (cm ⁻¹)
Symmetric N-H ion in LiNH ₂	3312
Asymmetric N-H ion in LiNH ₂	3302
B-H stretch	2320
Li ₂ Mg(NH) ₂	3150-3200
BH ₂ deformation in LiBH ₄	1120
N-B stretch	800
NH ₂ stretch	1560

**DESIGN AND DEVELOPMENT OF HIGH STORAGE CAPACITY COMPLEX
HYDRIDES FOR REVERSIBLE HYDROGEN STORAGE IN VEHICLES**

ANNEX 7: Summary of results obtained from the various materials

Sample	Max. H₂ storage Cap. (wt.%)	Reversible storage Cap. (wt. %)	Optimal temp (°C)/pressure (bars)	Kinetics rate
LinMgNH	6	2.5	200/85	Good
LinMgNH with 2% Ni	9	-	-	Fast
LinMgAlNH (5hrs Mill)	2.5	0.6	300/90	Fast
LinMgAlNH (10hrs Mill)	1.2	0.2	350/90	Slow
LinMgBNH	6-8	6-8	250/90	Very fast
BNH₆.2MgH₂ (5hrs Mill)	3.7	3.7	100/90	Excellent