EXPLORATION OF NOVEL COMBINATIONS OF LI-BASED COMPOUNDS
AND ADDITIVES: A NEW MEANS OF SOLID-STATE HYDROGEN STORAGE

A THESIS SUBMITTED TO THE GRADUATE DIVISION OF THE
UNIVERSITY OF HAWAI'I IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF SCIENCE

IN

CHEMISTRY

DECEMBER 2007

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We certify that we have read this thesis and that in our opinion it is satisfactory in scope and quality as a thesis for the degree of Master of Science in Chemistry.
DEDICATION

To my ever supportive parents June, David, Betty, and Terry—hang in there I’m almost finished. Also to my beautiful nieces Ashley and Morgan and their great parents Eric and Kelly.
ACKNOWLEDGEMENTS

Well, I am not sure if there is enough room to thank all those who have made this possible. Firstly, I would like to thank Dr. Craig Jensen my advisor and mentor. Also the other members of the Jensen research team, particularly Zhaohui Wang (a great mentor himself), Meredith Kuba, Dick Longley, Caleb Brown, and Lance Culnane for their friendship and advice.

I had many question that required many people to answer. The people that provided me with information and technical assistance included: Godwin Severa, Dr. Walter Niemczura, Dr. Kristin Kumashiro, Dr. Sonjong Hwang, Dr. Robert Bowman assisted me with performing and interpreting NMR. Dr. Karl Seff, Dr. John Vajo, Dr. Sky Skeith assisted me with powder XRD. Thank you all for your patience.

Lastly, I would like to thank my de facto spouse partner Jadyn Ikeda for emotional support.
Currently, energy is primarily derived from the burning of fossil fuels. Given the finite amount of fossil fuels, this work sought to overcome the problem of hydrogen storage, one of the obstacles preventing hydrogen from becoming a renewable energy source. This work was directed towards the development of high capacity, high-performance hydrogen storage materials. It consists of two parts: Novel combinations of Li-based metal hydrides and an exploration of the interaction between metal chloride additives and borohydrides.

The Li-based metal hydride combinations explored yielded many positive results. Most notably, the previously irreversible compound, LiAlH₄ was shown to be reversible in the presence of alpha and beta-phase quaternary hydrides. Other notable improvements were achieved via the method of combining metal hydrides in order to improve their properties for solid-state hydrogen storage.

The second part of this work focused on the interaction of metal additives (TiCl₃, NiCl₂, PtCl₂, etc.) and borohydrides, particularly LiBH₄. Currently, there is much research pertaining to the synthesis of novel borohydrides. Thus, it is essential to have a clear understanding of how these compounds interact with commonly used additives such as those listed above. This work shed light on the interaction by using B¹¹ NMR and PXD. A multi-step reaction was identified to describe the decomposition.
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Al  Aluminum
B   Boron
C   Celsius
CPMAS  Cross-polarization Magic Angle Spinning Nuclear Magnetic Resonance
cm  Centimeters
DOE  Department of Energy
Eq.  Equation
e⁻  Electron
FSU  Former Soviet Union States
H⁺  Proton
H₂  Hydrogen Gas, Molecular Hydrogen
kJ  KiloJoules
Li  Lithium
MAS  Magic Angle Spinning Nuclear Magnetic Resonance
mp  Melting Point
M   Molarity (mole/L)
m   Mass
meV  Millielectron-Volts
mg  Milligram
mol  Mole
ml  Milliliter
N   Nitrogen

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<tr>
<td>Na</td>
<td>Sodium</td>
</tr>
<tr>
<td>OPEC</td>
<td>Organization of the Oil Producing Countries</td>
</tr>
<tr>
<td>Pa</td>
<td>Pascal</td>
</tr>
<tr>
<td>ppm</td>
<td>Parts Per Million</td>
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<td>P</td>
<td>Pressure</td>
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<td>PXD</td>
<td>Powder X-ray Diffraction</td>
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<td>psi</td>
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<tr>
<td>T</td>
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<tr>
<td>V</td>
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CHAPTER 1

Introduction

1.1 Energy Crisis

Dependence on energy has characterized human development from its outset. Wood was one of the first sources of energy humans came to rely on, it was used as fuel for fire. Although rarely wood, people are more dependent on burning carbon for energy than ever before. This heavy dependence began during the industrial revolution when coal was the primary source of energy and proved quickly to be environmentally detrimental. Since then petroleum has become our primary source of energy. It is now estimated that fossil fuels (oil, coal, and natural gas, respectively) account for approximately 85% of energy consumption in the United States. The US uses about 140 million barrels of oil per week at a cost of about two billion dollars per week.

It is now becoming obvious that this dependence is coming at a heavy price to the planet. Since the beginning of the industrial revolution 150 years ago, the use of fossil fuels has caused the amount of carbon dioxide in the atmosphere to increase by 25%. While there is some debate over what effect this is having on global weather and climate, most agree that fossil fuel production globally has or will be peaking within the next 50 years. As figure 1.1 and 1.2 show, it has already peaked in most places outside of the Middle East. The Middle East currently holds approximately two-thirds of the world’s oil reserves. Making the situation more dire, is the fact that many of the governments in
this part of the world are

Non-OPEC, non-FSU Oil Production Has Peaked and is Declining

![Graph showing oil production for Non-OPEC and non-FSU worldwide since 1900 to 2001 and predicted to 2010.]

**Figure 1.1** Oil production for Non-OPEC and non-FSU worldwide since year 1900 to 2001 and predicted to 2010.

**Figure 1.2** Predicted peak oil production for the current leading oil producers worldwide. Countries with a negative value have already reached their peak oil production. As can be seen, only countries in the Middle East are significantly far from their peak.
highly unstable. As a result the flow of oil from the Middle East is capricious, at best. Putting aside environmental issues it is obvious that fossil fuels, particularly oil, are a finite resource that will be exhausted relatively soon. What resources and technology are available to meet the impending energy crisis?

As long as the oil has been flowing, corporations and governments have been reluctant to invest in alternative energy sources. However, as it becomes more obvious that oil resources are finite, interest in alternative energy has risen. In 2003 President Bush, in his State of the Union Address, declared that America was ‘addicted to oil’ and pledged 1.2 billion dollars for hydrogen infrastructure research and development. Alternative energy sources such as wind, solar power, electric, hydroelectric, biomass and hydrogen are needed to fill the void left by petroleum.

1.2 A Potential Solution

Hydrogen is the most abundant element in the universe. Coal, natural gas, biomass, and water are all domestically available resources that can be used to produce hydrogen. Water is of particular interest. When combined with existing renewable energy sources such as photovoltaic, wind, geothermal, biomass, and hydroelectric power, water can be used to produce hydrogen via electrolysis. Figure 1.3 shows how utilizing these technologies would allow hydrogen to become part of a sustainable energy loop.
Hydrogen has for some time been seen as a potential alternative to fossil fuels. Hydrogen combined with oxygen has been used as rocket fuel since the mid-1950s. This highly exothermic combination produces water as a by-product. A simple reaction, yet, currently the use of hydrogen and oxygen is still up against substantial obstacles. There are two main problems with hydrogen at this stage: safe storage and production of molecular hydrogen (H\textsubscript{2}). Despite these challenges hydrogen remains a promising carrier and storage medium. Renewable energy sources that could be used to produce hydrogen domestically are abundant. Currently, renewable energy sources account for approximately 10 percent of the United States’ energy production.\textsuperscript{6} With an even
distribution of renewable energy sources nationally, the cost of hydrogen storage and transport would be greatly reduced.

1.3 The Fuel Cell

Hydrogen, in its molecular form, is a highly volatile compound. As such, storing compressed hydrogen onboard a vehicle is inherently dangerous. To avoid this potential safety hazard, researchers have turned to fuel cells as the preferred method of onboard hydrogen storage.

There are many types of fuel cells currently being investigated for use in automobiles. Most of these fuel cells function like batteries. Like a battery the fuel cell consists of a cathode (positive) and an anode (negative) wrapped around an electrolyte medium. In this case the battery is recharged with hydrogen. Hydrogen is directed to the anode while oxygen goes to the cathode. Unlike a typical rechargeable battery the fuel cell will be designed to last for many years.

There are many types of fuel cells. Phosphoric acid (PAFC), solid oxide fuel cells (SOFC), and proton-exchange membrane fuel cells (PEM) are the most common types to employ hydrogen. PAFC are already being used to power hotels, hospitals, and other large buildings. SOFC would most likely be used for high powered applications such as a central electrical plant. The PAFC and SOFC are too bulky for use in a vehicle. PEM fuel cells hold the most promise for light-duty vehicles and buildings. As a result, the PEMFC will likely be the most commonly used fuel cells.

Proton-exchange membrane fuel cells employ an ion exchange membrane with a polymeric membrane as the electrolyte. These fuel cells operate at relatively low temperatures and can vary their output depending on energy demand thus making them
ideal for use in automobiles. A platinum coating on the anode helps split the molecular hydrogen into protons and electrons according to the following equation:

$$H_2 \rightarrow 2H^+ + 2e^- \text{ (eq 1.1)}$$

The electrons and protons both end up at the cathode. The protons pass through a thin membrane and the electrons pass through an external circuit before arriving at the cathode. Passage of an $e^-$ through the external circuit produces electricity. At the cathode a platinum catalyst helps combine the protons, electrons, and oxygen to produce heat and water according to the following equation:

$$\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O \text{ (eq 1.2)}$$

Each individual fuel cell provides only a small amount of energy. To provide enough energy for automotive applications it is necessary to stack the fuel cells (figure 1.5). Increasing the number of cells in a stack increases the voltage, while increasing the area of the cells increases the current.
Figure 1.4 Depiction of a proton-exchange membrane fuel cell. Protons flow through a thin membrane as electrons flow through an external circuit thus producing energy.

Figure 1.5 Expanded view of a fuel cell showing how proton-exchange membranes would be stacked in order to generate enough power for an automobile.
1.4 Obstacles

As mentioned previously, there are two main obstacles preventing the widespread use of hydrogen fuel cells: finding a suitable hydrogen storage material that meets standards established by the Department of Energy and establishing a system for producing molecular hydrogen without creating more greenhouse gases in the process.

Although hydrogen is the most abundant element in the universe, it is typically not in the form of molecular hydrogen, H₂. Hydrogen is most commonly encountered in the form of water, methanol, and hydrocarbons. The need to isolate hydrogen makes it four times more costly than gasoline for the equivalent amount of energy. The Department of Energy estimates that by 2040 cars and light trucks powered by fuel cells in the United States will consume 150 megatons of hydrogen per year. Currently the US produces 9 megatons of hydrogen per year. The vast majority of this hydrogen is produced by reforming natural gas, a process that produces greenhouse gases. The most promising method for producing molecular hydrogen is the electrolysis of water mentioned previously. Although this method requires a great deal of energy, researchers are hoping to overcome that with innovative renewable energy sources such as solar, wind, biomass, geothermal, or photovoltaic (figure 1.3). Researchers have already made great progress in overcoming this obstacle.

The second major obstacle is finding a way to safely store hydrogen. Molecular hydrogen is one of the lightest and most volatile compounds. As such, it is difficult to contain without leakage and possesses a low energy to volume ratio. To use hydrogen in its molecular state requires that it be stored at extremely high pressure and reduced temperatures. This only exacerbates the dangers associated with its volatility.
and potential for leakage. The hydrogen tank must be small enough to fit onboard an automobile, it must be relatively safe, and it must be relatively cheap to manufacture. Compressed hydrogen cannot meet these requirements and as a result it is not a viable option for onboard hydrogen storage. Currently, hydrogen stored in the solid-state is the most promising alternative to compressed hydrogen. As with the first obstacle, great advances have been made in this field.

1.5 Solid-State Hydrogen Storage

Since establishing that compressed or liquefied hydrogen is not a viable option for onboard storage researchers have been exploring the possibility of solid-state hydrogen storage. Many different types of storage materials are being explored.

Metal hydrides and physi-sorbents are the main types of materials being investigated as practical solid-state hydrogen storage materials. Metal hydrides are referred to as chemi-sorbants as they chemically bond to atomic hydrogen. Physi-sorbents, on the other hand, have only weak interaction with molecular hydrogen. Carbon nanotubes and fibers as well as metal-organic frameworks (MOFS) have been investigated as sorbents for this type of hydrogen storage. However, the weight percents demonstrated with these materials at ambient temperature are extremely low; typically about one-tenth of what is required. Chemi-sorption by reversible metal hydrides has been explored for a huge spectrum of elements. Metal hydrides can be broken into two basic classes, simple and complex metal hydrides. These compounds consist of one or more metals, ideally light weight, combined with hydrogen. When heated these compounds release hydrogen gas that is in turn used to produce energy.
1.6 Metal Hydrides

Metal hydrides are already commonly employed in batteries for electronics such as cell phones, cameras, and DVD players. These batteries are typically discarded after a relatively short period of time. In contrast, metal hydrides employed in fuel cells would be expected to last the life of the vehicle. As mentioned previously, the metal hydride releases hydrogen gas when heated. Hydrogen can also be reabsorbed under the appropriate temperature and pressure conditions. In this way, metal hydrides provide a reusable source of hydrogen, unlike some batteries that are discarded after discharging their energy. Although not intuitively obvious, metal hydrides, with few exceptions, store hydrogen at higher volumetric densities than pure liquid or compressed gas hydrogen. All the compounds in figure 1.6 store hydrogen at higher densities than liquid or compressed gas at 10,000psi (700 bar).

![Figure 1.6](image_url)

Figure 1.6 The storage density of hydrogen in compressed gas, liquid, graphite monolayer, and selected chemical compounds plotted as function of hydrogen mass density and hydrogen volume density. As can be seen, all chemical compounds listed exceed the storage density of both gas and liquid hydrogen. **11**
The US Department of Energy has set forth targets for the development of metal hydrides as hydrogen carriers that are considered to be necessary in order to provide a means of safe, economical, and practical onboard storage. In addition to being safe, readily available, and relatively inexpensive, the targeted metal hydrides should also be able to store at least 6.4 weight % or 65g/litre of hydrogen. Lastly, in order to be utilized with a PEM fuel cell, the cycling kinetics must be achieved between 0-100°C and 1-10 bars. Although the DOE requirements set forth are quite stringent, it is believed that metal hydrides can meet or exceed these standards.

1.7 Lithium-Based Metal Hydrides

Lithium-based compounds show great promise as hydrogen storage materials due to the light weight of the lithium atom. Compounds such as LiAlH₄, LiNH₂, and LiBH₄, have theoretical hydrogen storage capacities well above the targets set forth by the Department of Energy. (10.5, 8.6, and 18.3wt%, respectively) Unfortunately, many of these compounds release hydrogen only at temperatures well above the range that would allow their utilization as an onboard hydrogen carrier for a vehicle powered by a PEM fuel cell. However, it was found that when these compounds are mechanically ball-milled with catalytic amounts of Ti-based additives the kinetic barrier is lowered and thus, hydrogen is given off at much lower temperatures. The real problem with many lithium compounds is that upon dehydrogenation they form highly stable species such as LiH. LiH, with bond energy of 238kJ/mol, requires extremely high pressures to reabsorb hydrogen. If the formation of this compound can be avoided, or if a method can
be found to destabilize the bond, many Li-based compounds will be compatible with DOE standards.

With this goal in mind researchers have explored creative ways to manipulate Li-based compounds to avoid the formation of LiH. The compounds explored thus far have sought to avoid the formation of the Li-H bond upon dehydrogenation. The following combinations, among others, have been explored:

\[
\text{LiNH}_2 + 2\text{LiH} \leftrightarrow \text{Li}_2\text{NH} + \text{H}_2 \quad \text{(eq 1.3)}
\]
\[
2\text{LiNH}_2 + \text{LiBH}_4 \rightarrow \text{Li}_3\text{BN}_2 + 4\text{H}_2 \quad \text{(eq 1.4)}
\]
\[
2\text{LiNH}_2 + 2\text{MgH}_2 \leftrightarrow \text{Li}_2\text{Mg(NH)}_2 + 2\text{H}_2 \quad \text{(eq 1.5)}
\]

It should be noted that all of the above reactions benefit from the use of catalytic amounts of metal chloride (TiCl\(_3\), NiCl\(_2\), TiCl\(_3\), respectively\(^{16,17,18}\)). The combination of various simple and complex lithium compounds with other metal hydrides show great promise for either destabilizing the Li-H bond or preventing its formation altogether and thus making fuel cells a reality.
1.8 Scope of Thesis

This thesis presents some novel approaches to the problem of solid-state hydrogen storage. More specifically, Li-based compounds are investigated due to their relative light weight. These novel approaches seek to overcome the previously discussed issues associated with the formation of a stable dehydrogenation products while destabilizing the reactants in order to release $H_2$.

Also, there are many questions left unanswered in regards to the role metal chloride additives play in the accelerated release of hydrogen from lithium borohydride. As a result, the second objective of this thesis is to explore the possibility that initially, metal chlorides can react in a stoichiometric fashion with borohydride compounds to give a one-time increase in weight percent hydrogen desorbed. A greater level of clarity on this issue is paramount to understanding why some compounds are incapable of rehydrogenation and also, insuring dopants employed are in fact acting as catalysts.
CHAPTER 2

The Exploration of Novel Combinations of Li-based Compounds as Hydrogen Storage Materials

2.1 Introduction

Lithium based compounds are appealing candidates for hydrogen storage because of their light weight and resulting high weight percent hydrogen capacity. However, the use of Li-based compounds is challenging from a thermodynamic and kinetic standpoint. Due to kinetic limitations, the reversible storage of hydrogen often does not occur at moderate temperatures with Li-based compounds even with the appropriate dopant.\(^8\) From the standpoint of thermodynamics, the stability of the compound must lie within a specified range to achieve practical dehydrogenation and rehydrogenation (known as cycling). A compound that readily gives off H\(_2\) tends not to reabsorb it. Conversely, a compound that reabsorbs H\(_2\) but requires an extremely high temperature to release H\(_2\) is impractical. In this work we have sought to address these issues by combining lithium compounds with other complex metal hydrides. Ideally, these combinations will have improved thermodynamic and kinetic properties while preserving H\(_2\) storage capacity. By using multiple compounds, it is hoped that the kinetics can be improved and the thermodynamic properties of these systems can be fine tuned to allow for rehydrogenation under practical conditions.

As early as 1910\(^{20}\), the results of reactions involving multiple lithium based compounds were being reported. However, Chen et al.\(^{21}\) were the first to apply these compound mixtures to the problem of hydrogen storage. Their system initially involved
hydrogenating Li₃N according to the following equation:

\[
\text{Li}_3\text{N} + 2\text{H}_2 \leftrightarrow \text{Li}_2\text{NH} + \text{LiH} + \text{H}_2 \leftrightarrow \text{LiNH}_2 + 2\text{LiH} \quad \text{(eq 2.1)}
\]

Although Chen et al. started with a single compound, they found that upon hydrogenation two compounds formed. Ichikawa et al. explored the other side of the reaction listed above. They found that by ball-milling a 1:1 mixture of LiH and LiNH₂ the mixture desorbed ~5.5 weight % H₂ in the range 150-200°C.²² In this case LiH is destabilized by reacting with NH₃ gas as shown below:

\[
2\text{LiNH}_2 \rightarrow \text{Li}_2\text{NH} + \text{NH}_3 \quad \text{(eq 2.2)}
\]

\[
\text{LiH} + \text{NH}_3 \rightarrow \text{LiNH}_2 + \text{H}_2 \quad \text{(eq 2.3)}
\]

Ichikawa et al. were able to show this conclusively by ball-milling LiH in the presence of NH₃ gas. It was found that about 70% of the NH₃ reacted with LiH to produce H₂. Thus in this system, NH₃ creates a destabilized system that allows the Li-H bond to be broken.

Significant results, utilizing a destabilized system, were also achieved by Vajo et al.²³ In this case, the hydrogen storage system consists of two stable metal hydrides (one complex; one simple metal hydride) mixed with a metal chloride dopant (TiCl₃). In the presence of each other these two metals hydrides combine to make a system that releases energy at a new, lower energy level. In the case of Vajo et al., their system used LiBH₄ and MgH₂ to create this destabilized system. The mixture reacts according to:

\[
2\text{LiBH}_4 + \text{MgH}_2 \leftrightarrow 2\text{LiH} + \text{MgB}_2 + 4\text{H}_2 \quad \text{(eq. 2.4)}
\]

In doing so, Vajo et al. were able to reversibly store up to 8 weight % hydrogen. They found the enthalpy of dehydrogenation and rehydrogenation were both lowered by 25 kJ compared with pure LiBH₄. Here, formation of MgB₂ stabilizes takes the system to a lower energy state and as a result, shifts the equilibrium of equation 2.4 to the right.
Most recently, Pinkerton et al. have explored the use of lightweight compounds that produce hydrogen-free end products to ensure full release of hydrogen. They have synthesized a novel quaternary compound with composition $\text{Li}_4\text{BN}_3\text{H}_{10}$ by ball-milling $\text{LiNH}_2$ and $\text{LiBH}_4$ in a 2:1 molar ratio. This composition was termed the $\alpha$-phase. Subsequently, three other phases, $\beta$, $\gamma$, and $\delta$ were synthesized by altering the molar ratios of $\text{LiNH}_2$ and $\text{LiBH}_4$. These compounds share the characteristic of having a relatively low melting point (45-190°C). However, reversibility has not been achieved with these compounds.

The results discussed above suggest that there is a potentially favorable interaction to be explored at the interface of $\text{LiNH}_2$, $\text{LiBH}_4$, and $\text{MgH}_2$ systems. Also, the benefits of combining these compounds with other hydrogen storage compounds, such as $\text{LiAlH}_4$, will be explored. Further, it was thought that by combining the methods discussed above in novel ways one might further elucidate the mechanisms by which the reactions take place, encounter new reactions and compounds, and improve the performance of the systems from a thermodynamic and/or kinetic standpoint. As mentioned previously, the various phases, $\alpha$, $\beta$, $\gamma$, and $\delta$ originally synthesized by Pinkerton et al., share the property of having a molten phase. In the hopes of taking advantage of this, the Pinkerton compounds ($\alpha$ and $\beta$-phases) were mixed with several hydrogen storage systems in the hope that the molten phase would disrupt the Li-H bond by keeping the Li and H in a molten ionic solution.

LiAlH$_4$ was initially a promising hydrogen storage candidate due to its high hydrogen capacity (7.9wt %) and its favorable dehydrogenation kinetics. The dehydrogenation reaction of LiAlH$_4$ is a three-step process. The first two steps occur in
the range 160-210°C, a perfect overlap with the melting range of the β and α-phases. As a result, we have studied mixtures of these materials.

As discussed previously, Vajo et al. were able to achieve reversibility in LiBH₄. Their reaction also drastically improved dehydrogenation kinetics and thermodynamics, which, unlike LiAlH₄, were poor during both dehydrogenation and rehydrogenation. However, cycling temperatures required for the Vajo system are far beyond those required for practical applications. Thus, the activity of LiBH₄, like LiAlH₄, in combination with α and β-phases was explored in an attempt to improve the performance of this system. The α and β-phases were chosen because they could be isolated from other phases and they have the greatest H₂ capacity. Lastly, it was thought that the Vajo system, that is Ti-doped LiBH₄ and MgH₂, might be further improved by combination with the α- or β-phases.

2.2 Experimental

The mixtures of LiH, LiBH₄, MgH₂, and LiNH₂ were prepared from commercially available powders. (All were purchased from Aldrich at 95% purity) LiAlH₄ was initially purchased as a powder. (95% purity from Aldrich) To increase purity this compound was dissolved in diethyl ether and stirred for several hours until complete solvation occurred. The compound was then filtered through a soxlet apparatus containing celite to capture impurities. A liquid nitrogen trap was then used to vacuum off the diethyl ether. The compound was then vacuum-dried overnight while stirring. The resultant purity is near 99% with the main removed impurity being aluminum.

Li₃AlH₆ used in this experiment was mechano-chemically synthesized. LiH and LiAlH₄ were ball-milled in 2:1 ratio in order to synthesize Li₃AlH₆.
Samples were doped with various catalysts. All catalysts, NiCl₂ (Alfa Aesar, 99% purity), PtCl₂ (Pressure Chemical Co., 99% purity), and TiCl₃ (Aldrich, 99.999% purity) were purchased commercially. All compounds in this study are moisture-sensitive and as a result, all samples were prepared in an inert (Ar) atmosphere glove-box.

All samples were ball-milled using a Fritsch Pulverisette P-5 Planetary Mill. The powders were milled in hardened steel milling containers. The milling jars contained 77-mm steel balls that perform the milling action. The containers were sealed with a Teflon O-ring and wrapped with Parafilm to prevent oxidation.

<table>
<thead>
<tr>
<th>Composition of Mixture</th>
<th>Milling Time (minutes)</th>
<th>Milling Speed (rpm)</th>
<th>Additive Type and Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>(LiNH₂)ₓ(LiBH₄)₁₋ₓ</td>
<td>180</td>
<td>400</td>
<td>2 mol % PtCl₂, NiCl₂, or no additive</td>
</tr>
<tr>
<td>LiBH₄</td>
<td>60</td>
<td>400</td>
<td>2 mol % TiCl₃</td>
</tr>
<tr>
<td>LiAlH₄</td>
<td>20</td>
<td>350</td>
<td>2 mol % TiCl₃</td>
</tr>
<tr>
<td>2LiBH₄, MgH₂</td>
<td>60</td>
<td>400</td>
<td>2 mol % TiCl₃</td>
</tr>
<tr>
<td>2LiH, LiAlH₄</td>
<td>270</td>
<td>350</td>
<td>2 mol % TiCl₃</td>
</tr>
</tbody>
</table>

Table 2.1 Summary of milling time, speed, additive type and amount for various compound compositions.

Mixtures of the form (LiNH₂)ₓ(LiBH₄)₁₋ₓ were synthesized for compositions x = 0.50 and 0.67 corresponding to β (mp 75-90°C) and α (mp 150-190°C) phases, respectively.

Pressure-Composition Isotherms (PCI) were performed on an Isuzu SS-K-300 PCT Measurement system. This instrument is capable of measuring the amount of gas absorbed or desorbed as a function of time. During absorption and desorption the temperature in all experiments remained constant. Measurements are typically carried
out until hydrogen evolution ceases which can vary greatly depending on the compound being analyzed. The data was recorded and plotted as megaPascals versus time. The data is then converted to weight % H₂ versus time in Microsoft Excel using the following modified ideal gas law equation:

\[
\text{Number of Moles} = \frac{P (V_1 + V_2 + V_3)}{RT_1} \quad \text{(eq 2.5)}
\]

Here, \( T_1 \) = PCT temperature (held at 303K)
\( T_2 \) = Reactor temperature (controlled by heating mantle)
\( V_1, V_2 \) = PCT volume and line in volume, respectively
\( V_3 \) = Reactor volume

This molar value is then multiplied by the molecular weight of hydrogen (2g/mol) in order to derive the weight. The weight is then divided by the total weight of the sample to derive weight % H₂. All hydrogen capacities are reported with respect to full hydrogenation, but do not include the weight of the catalyst. Samples are heated using a Glas-Col Mantle Minder II with a custom heating mantle. Powder X-ray diffraction analyses were conducted on a Phillips PX3040/60 X’Pert Pro diffractometer²⁵ (CuKα₁ radiation with \( \lambda = 1.5418\text{Å} \)). Samples shipped for outside analysis were sealed in glass ampules under vacuum using an O₂-natural gas torch.²⁶

²⁷Al NMR was also performed on a Varian Inova 400MHz Wide Bore NMR Spectrometer System²⁷ in order to characterize some species. Solid-state NMR is typically performed by taking advantage of the Magic angle spinning (MAS) technique developed by E.R. Andrew.²⁸ The MAS technique allows for an increase in resolution of several orders of magnitude. In typical NMR experiments the nuclear spins interact with an external magnetic field or electric field. In classical solution-state NMR, the random movement of particles allows for anisotropic interactions on the time-scale of an NMR
experiment to be averaged out and therefore, in this case, neglected. In contrast, in solids, with little or no mobility, anisotropic interactions become a significant influence on the nuclear spins orientations. As a result, anisotropic interactions affect the resonance frequency of all sites in a molecule which contributes to peak broadening in the spectrum. However, by spinning at the magic angle (54.7° with respect to the magnetic field, thus $3 \cos^2 \theta_m - 1 = 0$ leading to a sequestering of the dipolar coupling) peaks narrow and resolution is increased. Samples are packed under the inert atmosphere of an argon glove-box and deposited into ceramic rotors. Since the samples analyzed in this experiment are highly air-sensitive to prevent contamination during analysis each rotor is sealed at both ends with plastic caps that have rubber gaskets. Samples are then spun in a stream of N₂ as fast as possible, typically 8-15 kHz. Spinning samples at high speeds, in addition to utilizing the MAS technique, allows for partial suppression of anisotropic interactions and dipolar coupling and as a result, greater resolution.

The following table summarizes the various compound mixtures studied in an attempt to improve both the kinetics of dehydrogenation and rehydrogenation of these Li-based compounds.
Table 2.2 A summary of reaction mixtures run to derive Pressure-Composition isotherms. Samples were prepared as described in Table 2.1. α, β-Phases consist of $(\text{LiNH}_2)_x(\text{LiBH}_4)_{1-x}$ with $x=0.667, 0.5$, respectively.

The two samples, from columns 1 and 2 in the table above, were mixed by employing mortar and pestle. The two powder mixtures were ground together for 2-3 minutes to insure thorough mixing and small particle size.

2.3 Results and Discussion

Samples of the Pinkerton material were prepared as described previously. First it was necessary to establish that the quaternary hydrides (substances of the type, $(\text{LiNH}_2)_x(\text{LiBH}_4)_{1-x}$) were in fact being synthesized. This was accomplished by employing XRD analysis. The powder diffraction pattern in figure 2.1 shows the peaks that are associated with the β-phase or $(\text{LiNH}_2)_{0.5}(\text{LiBH}_4)_{0.5}$ mixture thus confirming that the correct phase was indeed synthesized.
Figure 2.1 Powder X-ray diffraction spectrum for 1:1 molar ratio mixture of LiNH$_2$ and LiBH$_4$.

The peaks highlighted with grey arrows at $\theta = 11.80^\circ$ and $27.39^\circ$ in Figure 2.1 are associated with the $\beta$-phase of the quaternary hydride exclusively. Although peaks associated with LiBH$_4$ (starting material) are present (highlighted by red dashed-line arrows) at $\theta = 17.93^\circ$, $23.91^\circ$, $24.79^\circ$, and $26.18^\circ$, they are much less intense than the peaks associated with the $\beta$-phase. Looking at the most intense peaks for these compounds it is possible to make a qualitative judgement that the $\beta$-phase is most abundant.

Figure 2.2 shows diffraction pattern of a (LiNH$_2$)$_{0.67}$(LiBH$_4$)$_{0.33}$ mixture which indicates the presence of the intended $\alpha$-phase.
Figure 2.2 Powder X-ray diffraction spectrum for a 2:1 molar ratio (α-phase) mixture of LiNH₂ and LiBH₄, respectively.

The peaks highlighted with solid grey arrows at 2θ = 11.5°, 29.0° and 20.5° are associated exclusively with the α-phase of this mixture. Unlike the β-phase discussed above, no residual LiBH₄ is present in the sample. However, some un-reacted LiNH₂ can be seen in the XRD indicated by the red dashed-arrow. It is likely that this residual LiNH₂ reacts to form additional α-phase during the initial heating process (20-100°C) as this has been shown to be an alternative synthesis method.¹⁷ The presence of LiCl and Li₂O is the result of some dehydrogenation occurring during the ball-milling process and contamination during preparation, respectively.¹⁷ LiCl peaks are marked with brown arrows at 2θ = 30.0, 34.7 while the Li₂O peak is marked with a blue dashed-arrow at 2θ = 33.5. However, the strongest peaks are associated with the α-phase. Also, the isothermal dehydrogenation data, shown in figure 2.5, is consistent with previous experiments.¹⁷

Having established that (LiNH₂)ₓ(LiBH₄)₁₋ₓ with x = 0.67 and 0.50 was successfully synthesized, we then explored combining these phases (α and β respectively) with other Li-based complex hydrides in order to determine whether improved kinetics and/or thermodynamics of dehydrogenation of the hydrides could be achieved. The first
experiments performed involved combining LiAlH₄ in a 1:1 and 1:4 molar ratio with α and β-phases respectively.

![LiAlH₄ doped with 2 mol% TiCl₃ desorbed with and without Beta-Pinkerton at 400C](image)

**Figure 2.3** Pressure-Composition Isotherm displaying weight % H₂ desorbed as a function of time for a mixture of LiAlH₄ doped with TiCl₃ and β-phase (LiNH₂)₀.₅(LiBH₄)₀.₅ doped with NiCl₂.

As can be seen, the addition of the β-phase resulted in a decreased H₂ capacity. This is to be expected as the hydrogen capacity of pure LiAlH₄ is greater than that of the pure β-phase. However, the kinetics were also affected in a negative way. It is likely that the molten β-phase slows the release of hydrogen from LiAlH₄.

However, the primary objective in this study was to find a means of rehydrogenating Li-based systems, particularly LiAlH₄. This was achieved by combining LiAlH₄ in a 1:4 ratio with the β-phase. Complete rehydrogenation was not achieved. However, with addition of the β-phase, 25.6% of the total hydrogen capacity of LiAlH₄ was reabsorbed. **Figure 2.4** does not include the weight of the β-phase since it is only
acting as a catalyst for rehydrogenation and as a result, does not itself reabsorb any hydrogen.

![Graph showing rehydrogenation of LiAlH4 with and without Beta-phase at 400C](image)

**Figure 2.4** PCI showing the rehydrogenation of LiAlH4 by combination with the beta-phase. The attempted rehydrogenation of pure LiAlH4 is also shown. The inability of LiAlH4 to reabsorb hydrogen is well-documented.

The combination of doped LiAlH4 with the α-phase was next explored, with favorable results. It was found that, as with the β-phase, the LiAlH4 without the additional phase showed better kinetics. However, the weight % H2 desorbed with addition of the α-phase was comparable to that of the pure doped LiAlH4. As can be seen in figure 2.5, the LiAlH4-α phase system gave off slightly more than the TiCl3 doped LiAlH4 alone. Thus even with addition of the α-phase the hydrogen capacity of the LiAlH4 is preserved.
Figure 2.5 PCI showing weight % H2 desorbed versus time for a 2 mol% TiCl3 doped LiAlH4 with and without the addition of the NiCl2 doped alpha-phase (LiNH2)0.67(LiBH4)0.33 in a 1:1 molar ratio.

As with the β-phase, the α-phase allowed for partial rehydrogenation of LiAlH4. With the α-phase, LiAlH4 absorbed approximately 1 weight % H2 constituting 14.2 % of the original weight percent associated with LiAlH4. This is approximately ½ of what was absorbed with the β-phase.
Figure 2.6 PCI showing rehydrogenation of LiAlH₄ by combination with (LiNH₂)₀.₆₇(LiBH₄)₀.₃₃ (α-phase) under ~9.5MPa at 400°C.

The mechanism explaining how LiAlH₄ and the β and α-phases interact has not been identified with certainty. However, a plausible explanation follows. The dehydrogenation of LiAlH₄ occurs in three-steps according to the following reactions:

\[ \text{LiAlH}_4 \rightarrow \frac{1}{3}\text{Li}_3\text{AlH}_6 + \frac{2}{3}\text{Al} + \text{H}_2 \quad (\text{eq} \ 2.6) \]
\[ \frac{1}{3}\text{Li}_3\text{AlH}_6 \rightarrow \text{LiH} + \frac{1}{3}\text{Al} + \frac{1}{2}\text{H}_2 \quad (\text{eq} \ 2.7) \]
\[ \text{LiH} \rightarrow \text{Li} + \frac{1}{2}\text{H}_2 \quad (\text{eq} \ 2.8) \]

The theoretical weight % for the reactions listed above is 5.3, 2.6, and 2.6, respectively. However, equation 2.8 does not typically occur until extremely high temperatures (around 720°C²⁹). Given this, it is unlikely that equation 2.8 is contributing to the overall weight % H₂ desorbed. Still, this leaves two reactions that could potentially be reversible in the solid-state. The first dehydrogenation (eq. 2.6) was determined to be
exothermic with $\Delta H = -10\text{kJ/(mol of H}_2\text{)}$. However, the second dehydrogenation (eq. 2.7) was determined to be endothermic with $\Delta H = 25\text{kJ/(mol of H}_2\text{)}$. The enthalpy of the first dehydrogenation indicates it could not be reversible under moderate conditions. However, given the enthalpy of second dehydrogenation (eqn 2.7) it is possible that this reaction is reversible. This notion is further supported by Ritter et al. who were able to achieve reversibility in a THF solution. These investigators found that formation of the THF adduct of Li$_3$AlH$_6$ from dehydrogenated material occurred in solution and was further improved by addition of titanium additives. The $\beta$-phase allows one of the species in equations 2.6-2.8 to reabsorb more hydrogen than the $\alpha$-phase. The partial rehydrogenation by combination with the $\beta$ or $\alpha$-phases seen in figures 2.4 and 2.6 represents approximately 2.0 and 1.0 weight % reabsorption, respectively. It has been shown that the pure $\alpha$ and $\beta$-phases give off 1.6 and 2.0 weight % NH$_3$, respectively. Given this correlation it is likely that NH$_3$ is acting to destabilize this system. Recently, Lu and Fang showed that LiAlH$_4$ could be rehydrogenated under 13.8 MPa H$_2$ at 300°C by addition of LiNH$_2$. While it is possible that the presence of residual LiNH$_2$, seen in XRD figure 2.2, is causing a similar reaction in this system, it is unlikely, due to the nature of the (LiNH$_2$)$_x$(LiBH$_4$)$_{1-x}$ quaternary hydrides. More specifically, the quaternary systems ($\alpha$, $\beta$) form at or below 100°C, thus it is unlikely that LiNH$_2$ would be available to react with LiAlH$_4$ in the way explored by Lu and Fang. At this point, the most probable explanation is that a small amount of NH$_3$ is given off during dehydrogenation of the quaternary hydrides($\alpha$, $\beta$). This NH$_3$ gas in turn reacts with LiH formed during LiAlH$_4$ dehydrogenation. Destabilization of the Li-H bond by NH$_3$ has been seen before. Since the amount of NH$_3$ given off by both $\alpha$ and $\beta$-phases in these studies is
small (0.7 and 1.5 wt% NH₃ respectively), the system is only partially reversible. To further support the notion that LiAlH₄ is the reversible specie, solid-state $^{27}$Al NMR was performed on a mixture of LiAlH₄ and the β-phase before and after rehydrogenation. As can be seen in figures 2.7B and C below, Li$_3$AlH$_6$ goes from constituting 41.3% of the aluminum containing species in the sample to 59.8%. Elemental aluminum is concentrated around 1639ppm while Li$_3$AlH$_6$ is concentrated between 160 and 10ppm.

![Figure 2.7a $^{27}$Al NMR spectrum of mechano-chemically synthesized Li$_3$AlH$_6$ from LiAlH₄ and 2LiH used here as a standard for comparison with figures 2.7b and c. This spectrum shows a Li$_3$AlH$_6$ peak around 120ppm, a LiAlH$_4$ peak (leftover from synthesis) at 10ppm, and an aluminum oxide peak at 0ppm peak due to sample contamination.](image-url)
After dehydrogenation

Figure 2.7b $^{27}$Al NMR spectrum of a dehydrogenated sample originally consisting of LiAlH$_4$ and the β-phase.

After rehydrogenation

Figure 2.7c $^{27}$Al NMR spectrum of a rehydrogenated sample originally consisting of LiAlH$_4$ and the β-phase.

There are in all the NMR spectra two shoulder peaks near the Li$_3$AlH$_6$ peak. The peak closest to the Li$_3$AlH$_6$ at ~10ppm is LiAlH$_4$. Lastly, the peak centered at 0ppm indicates the presence of an aluminum oxide due to oxygen contamination. These NMR results strongly support the notion that Li$_3$AlH$_6$ is formed upon rehydrogenation.
The next system explored was LiBH$_4$ mixed with the $\beta$-phase. The weight $\%$ H$_2$ given off by this combination at 400°C was a great improvement over TiCl$_3$ doped LiBH$_4$ by itself. The addition of LiBH$_4$ to the $\beta$-phase resulted in an overall composition of (LiNH$_2$)$_{0.33}$(LiBH$_4$)$_{0.67}$. Two pieces of evidence were obtained that thwart the notion that this is simply a new quaternary phase. Firstly, formation of the $\alpha$ or $\beta$-phase is prevented when LiBH$_4$ and LiNH$_2$ are ball-milled in the presence of TiCl$_3$. Secondly, XRD studies by Pinkerton et al.$^{17}$ show that the composition (LiNH$_2$)$_{0.33}$(LiBH$_4$)$_{0.67}$ corresponds to $\beta$-phase and LiBH$_4$ even when ball-milled together in the absence of TiCl$_3$. Thus, it is believed that much like equation 2.4, addition of the $\beta$-phase leads to stabilization of the dehydrogenated state and destabilization of the system. It is believed that destabilization occurs through the action of NH$_3$ gas generated by the $\beta$-phase during dehydrogenation.

![TiCl$_3$ doped LiBH$_4$ desorption at 400°C with and without Beta-Phase](image)

**Figure 2.8** PCI showing the dehydrogenation of 2 mol$\%$ TiCl$_3$ doped LiBH$_4$ with and without the addition of the doped $\beta$-phase. Also, the 2 mol$\%$ NiCl$_3$ doped beta-phase is shown in black.
Although the addition of the β-phase to LiBH₄ gave a great improvement in the dehydrogenation, the rehydrogenation was unsuccessful.

The α-phase was then combined with doped LiBH₄ in the same fashion as the β-phase. Like the β-phase, the α-phase did increase the overall weight % H₂ given off by the doped LiBH₄, but only moderately. The α-phase gives off much more H₂ alone then when combined with the Ti-doped LiBH₄. The presence of the LiBH₄ decreased the amount of hydrogen given off by the α-phase by several weight %. There are two reasons why this is to be expected. Firstly, the α-phase gives off more hydrogen than the β-phase. Thus to provide an overall improvement in weight % the amount of H₂ given off by the doped LiBH₄ would have to be very large. Secondly, the β-phase gives off more NH₃ than the α-phase. Thus, there is less NH₃ to react with the doped LiBH₄ to free

![Graph](image)

**Figure 2.9** PCI showing dehydrogenation of LiBH₄ doped with TiCl₃ with and without the alpha-phase. Also, the pure alpha-phase is shown for comparison.
H₂. As a result of these two characteristics, addition of LiBH₄ resulted in an insignificant H₂ capacity improvement. Additionally, the rehydrogenation was unsuccessful. Overall, no benefits were seen with this combination.

Based on the work of previous researchers, a high-throughput, combinatorial study by Lewis et al. has explored the dehydrogenation of mixtures of LiBH₄, LiNH₂, and MgH₂. Desorption was performed at 220°C while absorption was performed at 200°C.

Figure 2.10 Graphic depiction of the work of other researchers that constituted the basis for Lewis et al.'s high-throughput study. The orange dots show the molar ratio used by that researcher. Also shown is the theoretical weight % of the three compounds, MgH₂, LiBH₄, and LiNH₂.

This study found that the maximum performance of ternary mixtures of LiNH₂, MgH₂, and LiBH₄ came at a molar ratio of 0.6 : 0.3 : 0.1, respectively. At this concentration, the ternary mixture was found to desorb 3.8 weight % H₂ and reabsorb 3.4 weight % H₂. This is a great improvement over all previous research using these compounds. This high-
throughput study did have shortcomings that arose from the pursuit of efficiency. This study did not account for variations in preparation methods: ball-milling variations (time of ball-milling, chemical combinations, etc.) and

![Diagram of MgH\(_2\), LiBH\(_4\), and LiNH\(_2\)](image)

**Figure 2.11** Results of the high-throughput experiment performed by Dr. Greg Lewis. Cycling was performed at 200°C by varying the molar ratios of MgH\(_2\), LiBH\(_4\), and LiNH\(_2\).

As a result the data of Lewis et al. was used as a guide to further explore the LiBH\(_4\), MgH\(_2\), and LiNH\(_2\) interface by varying sample preparation and dopant addition. The proportions of the compounds were guided by both the Lewis et al. high-throughput method as well as our earlier studies, discussed above. Table 2.3 below details how the various compounds were combined and prepared.
Table 2.3 Table showing samples prepared in order to explore the interface of MgH₂, LiNH₂, and LiBH₄ based on the high-throughput experiment performed by Lewis et al. Positive results were seen with these compositions. Improvements in weight % H₂ desorbed were seen with all additive compositions attempted. Addition of NiCl₂ and PtCl₂ resulted in a slightly improved weight % H₂ over what was found by Lewis et al. However, the reversibility of these systems was extremely limited, thus negating the benefits achieved during dehydrogenation. The effect of NiCl₂ and PtCl₂ additives on these systems (i.e., rendering them irreversible), suggests these additives are acting as reactants and not catalysts as has been proposed. On the other hand, doping with 2 mol% TiCl₃ (sample D) resulted in a ~33% improvement in weight % H₂ desorbed while maintaining a comparable level of reversibility to that seen by Lewis et al. (sample 0.6LiNH₂:0.3MgH₂:0.1LiBH₄).
<table>
<thead>
<tr>
<th>Composition</th>
<th>Reference</th>
<th>Cycle 1 (wt% H₂@200°C)</th>
<th>Reversibility (% reabsorbed@220°C)</th>
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</thead>
<tbody>
<tr>
<td>2LiNH₂ : MgH₂</td>
<td>Chen et al.</td>
<td>0.5%</td>
<td>100%</td>
</tr>
<tr>
<td>2LiBH₄ : MgH₂</td>
<td>Vajo et al.</td>
<td>0.0%</td>
<td>0%</td>
</tr>
<tr>
<td>2LiNH₂ : LiBH₄</td>
<td>Pinkerton et al.</td>
<td>0.2%</td>
<td>0%</td>
</tr>
<tr>
<td>0.6LiNH₂:0.3MgH₂:0.1LiBH₄</td>
<td>Lewis et al.</td>
<td>3.8%</td>
<td>89%</td>
</tr>
<tr>
<td>Samples 7A : 3B</td>
<td>This work</td>
<td>5.2%</td>
<td>52%</td>
</tr>
<tr>
<td>7(2 LiNH₂:1 LiBH₄):3( 2 LiNH₂ : 1 MgH₂)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Samples C</td>
<td>This work</td>
<td>5.5%</td>
<td>0%</td>
</tr>
<tr>
<td>6 LiNH₂ : 3 MgH₂ : LiBH₄</td>
<td>This work</td>
<td>5.6%</td>
<td>84%</td>
</tr>
<tr>
<td>Sample D</td>
<td>This work</td>
<td>4.5%</td>
<td>5%</td>
</tr>
<tr>
<td>6 LiNH₂ : 3 MgH₂ : LiBH₄</td>
<td>This work</td>
<td>4.0</td>
<td>0%</td>
</tr>
</tbody>
</table>

Table 2.4 Comparisons of the dehydrogenation (200°C) and rehydrogenation (220°C) behavior of various Li-based compound mixtures. Results that were particularly interesting are highlighted in bold font.

2.4 Conclusion

Some of the combinations explored in this study resulted in no enhancement in the thermodynamic and/or kinetics of the dehydrogenation reaction. However, even the combinations that did not show improvements did shed light on how these compounds interact. It was hypothesized that the molten phase of the quaternary hydrides might allow for improved performance in these systems. However, the results show that the molten phase may have actually impaired the kinetics of the systems studied. Although the molten phase provided no benefit for these systems, the potential benefits of the presence of molten phases cannot be eliminated.
Although the envisioned utilization of the molten phases was not realized, great improvements in Li-based solid-state hydrogen were found in this study. The combination of both α and β-phases with LiAlH₄ showed that reversibility can be achieved with this compound. A possible mechanism for this reverse reaction is proposed below. Pinkerton has shown that the α-phase has an equilibrium composition of Li₄BN₃H₁₀. Combining the decomposition of the α-phase with that of LiAlH₄ (eqs. 2.6 and 2.7) gives the following equation:

\[
\text{LiAlH}_4 + 2\text{Li}_4\text{BN}_3\text{H}_{10} \leftrightarrow 2\text{Li}_3\text{BN}_2 + 15/2\text{H}_2 + 2\text{NH}_3 + 3\text{LiH} + \text{Al} \quad \text{(eq. 2.9)}
\]

As demonstrated by other experiments²¹,²²,³¹, interaction of NH₃ with LiH can yield favorable results. It also has the benefit of eliminating NH₃ from the system, which can destroy the PEM. Based on the work of Chen et al., discussed previously, it is believed that the following reaction then takes place allowing for reversibility in this system:

\[
2\text{LiH} + \text{NH}_3 \leftrightarrow \text{Li}_2\text{NH} + 2\text{H}_2 \quad \text{(eq. 2.10)}
\]

Thus, it is believed that the breakdown of the Li-H bond by NH₃ allows for reversibility. Using the weight % NH₃ ammonia given off by the α-phase (0.7 weight %) it is possible to calculate the amount of H₂ by weight that should be reabsorbed. The theoretical amount of H₂ that should be reabsorbed is 1.4 weight % H₂. However, it was shown by Ichikawa et al. that LiH in the presence of NH₃ absorbs 70% of the gas. Thus, this gives 0.98 weight % H₂ reabsorbed which is very close to the value seen in figure 2.6. Doing the same calculation for the β-phase gives a theoretical weight % H₂ reabsorbed as 2.1 weight %. As with the α-phase, this value matches well with what is seen experimentally. (figure 2.4)
The combination of LiBH₄ with the β-phase showed great improvement in H₂ weight capacity. It is believed that, much like equation 2.10, the decomposition of LiBH₄ takes place via interaction with NH₃:

\[
\text{LiBH}_4 + \text{NH}_3 \rightarrow \text{Li}_3\text{BN}_2 + 9\text{H}_2 \quad \text{(eq 2.11)}
\]

To increase the performance of these two systems would require using a (LiNH₂)ₓ(LiBH₄)₁₋ₓ that produced more NH₃.

Although the temperatures for this system are too high for practical on-board storage, it might be possible to utilize this system via off-board recharging where temperatures and pressures can be increased. Additionally, this study showed that by combining Li-based systems, one can achieve dramatic improvements in performance. This was demonstrated best in the last experiment involving the molar ratio determined by Lewis et al. Lewis et al. established an ideal molar ratio of 6MgH₂ : 3LiBH₄ : 1LiNH₂. It was found that the hydrogen storage properties of this ideal molar ratio were further improved by varying preparation techniques and dopants. A high-throughput study varying preparation techniques would undoubtedly lead to further improvements in this hydrogen storage system. Utilizing the results of this work will lead to further advances. Continuing studies in this direction could lead to the development of a viable solid-state onboard hydrogen storage system.
Chapter 3
Investigation of the Interaction of LiBH₄ with TiCl₃ in Hydrogen Storage Systems

3.1 Introduction

It is important that the cycling data associated with any given hydrogen storage system be accurate. In some cases, it has been observed that the dehydrogenation kinetics of solid-state systems containing LiBH₄ are enhanced by the addition of Ti-compounds as catalysts. The effect associated with TiCl₃ additive was initially identified in the LiBH₄/MgH₂ system.⁴³ This kinetic enhancement in hydrogen released is only seen during the initial dehydrogenation. In the case of systems that do not cycle hydrogen (are not capable of rehydrogenation and dehydrogenation), it is not possible to say whether a given additive (such as TiCl₃, PtCl₂, NiCl₂ etc.) is actually functioning as a catalysts or simply taking part in a reaction that releases hydrogen (or other undesired gases).

Recently, a similar effect was seen by Au et al. although they concluded that TiO acts as a catalysts for the dehydrogenation of LiBH₄.⁴⁴

Given the need to overcome the kinetic limitations of dehydrogenation involving group I and II borohydrides, it is important to establish if titanium is actually exerting a catalytic effect. This study was carried out to determine whether Ti-compounds actually exert a catalytic effect. Furthermore, we have attempted to characterize the products that arise upon heating LiBH₄ with TiCl₃. Lastly, this study helped to explain why some systems are incapable of rehydrogenation.
3.2 Experimental

MgH₂, TiCl₃, and LiBH₄ used in this experiment were obtained commercially from Aldrich (95% purity except TiCl₃ which was 99.99% purity). TiB₂ and elemental boron, both crystalline and amorphous (boron), were obtained from Alfa Aesar at 99, 98, and 99% purity, respectively. Samples were chosen in order to provide the best chance of witnessing the reaction of LiBH₄ with an additive. The mixtures for the dehydrogenated study were synthesized via a slight variation of the method previously described in this work in which they were ball-milled. The preparation techniques used in this experiment are outlined in Table 3.1. Samples over eight mole % TiCl₃ were initially too reactive, often giving off H₂ during ball-milling. As a result, these samples were very susceptible to oxidation and potentially explosive. Thus, initially an 8 mol% TiCl₃ sample was prepared in order to maximize the chances of observing the desired reaction without causing oxidation or compromising safety. However, use of a different type of ball-milling container allowed us to increase the molar ratio of TiCl₃ to LiBH₄. This container consisted of a screw-on steel lid employing a rubber gasket. The resultant mixtures were then dehydrogenated using an Isuzu SS-K-300 PCT to obtain a pressure-composition isotherm. Other samples were prepared as outlined in Table 3.1.
Table 3.1 Summary of samples prepared to identify the products of the stoichiometric reaction seen in hydrogen storage systems involving LiBH₄ and TiCl₃.

Two forms of analysis were used to identify the species in the dehydrogenated mixture. The first being powder X-ray diffraction performed on a Phillips PX3040/60 X'Pert Pro diffractometer.²⁵ The second analysis, involving solid state $^{11}$B, $^1$H, $^7$Li, and cross-polarization MAS-NMR, was generated on a Bruker DSX-500.³⁵,³⁶
3.3 Results and Discussion

The stoichiometric effect that occurs with increased additive was first observed by Vajo et al. at 400°C. Vajo et al. noted that upon addition of 2 mol% TiCl₃ to LiBH₄/MgH₂ the temperature required for rapid dehydrogenation was lowered from 600°C to 400°C. However, as figure 3.1 shows, we observed this effect at much lower temperatures (170°C) using PCI measurement techniques. It is particularly striking that the increase in the rapidly released hydrogen correlates perfectly with increasing amounts of TiCl₃.

![Figure 3.1 PCI showing dehydrogenation of MgH₂-LiBH₄ system with increasing amounts of dopants demonstrating the stoichiometric reaction between TiCl₃ and LiBH₄.](image)

Figure 3.1 PCI showing dehydrogenation of MgH₂-LiBH₄ system with increasing amounts of dopants demonstrating the stoichiometric reaction between TiCl₃ and LiBH₄.
It has been suggested that the species being formed as a result of the stoichiometric reaction is elemental boron. Since boron is observed in the crystalline form it was thought that X-ray analysis might reveal the presence of this compound. 2LiBH₄-MgH₂ doped with 8 mol % TiCl₃ was isolated for XRD analysis in the hopes of identifying the species formed in the stoichiometric reaction. This effort is reflected in figure 3.2. There was a great deal of overlap between the peaks associated with various species making characterization difficult. As a result, MgH₂ was eliminated from the mixture in order to reduce the number of species seen in the XRD and ideally, increase the likelihood of seeing the products of the stoichiometric reaction. The powder diffraction of the material obtained without MgH₂ is shown in figure 3.3. This experiment produced results very similar to figure 3.2. Analyses were performed on several samples but, as the spectra below indicate, the presence of crystalline boron was never observed. However, the presence of LiCl confirms that a metathesis reaction is indeed taking place between LiBH₄ and TiCl₃ however it gives little clue to the identity of the other product(s). In an attempt to obtain a XRD standard of crystalline boron, a sample was prepared consisting of LiBH₄ and crystalline boron. Despite the inclusion of elemental boron, no boron species were seen in the XRD.
Figure 3.2 X-ray diffraction spectrum of a sample of LiBH₄ and MgH₂ doped with 8 mol% TiCl₃ and heated to 400°C. Peak list at the bottom shows the positions of LiCl, LiBH₄, TiB₂, MgH₂.

For comparison purposes an XRD spectrum was obtained from a sample of pure crystalline boron. Upon analyzing this spectrum, it was found that identification of this species is further complicated by the overlap it has with the peaks associated with LiBH₄. However, the pure crystalline boron sample did show unique peaks at 2θ = 35 and 37.5° as seen in figure 3.4a. These were not seen in any samples of our materials that were analyzed with XRD. Based on this, the formation of crystalline boron in the presence of TiCl₃ and LiBH₄ is highly unlikely. This also suggests that during ball-milling and heating (processes that were performed on the aforementioned sample) the crystalline boron is converted into amorphous boron.
Figure 3.3 X-ray diffraction spectrum of a sample of LiBH₄ doped with 8 mol% TiCl₃ and heated to 400°C. Peak list at the bottom shows the positions of LiCl, LiBH₄, and TiB₂ peaks. Boron peaks are shown in figure 3.4a.

Figure 3.4 XRD spectra for (a) a sample consisting of pure crystalline boron and (b) a sample consisting of LiBH₄ doped with 8 mol% crystalline boron.
The XRD analysis gave no information about the boron containing product(s). Apparently the boron species become amorphous during the ball-milling process thus rendering them invincible to x-ray analysis. Thus, it can be said that no crystalline boron is present in these samples. However, the possibility that amorphous boron forms cannot be ruled out.

Since XRD yielded few clues as to the identity of the species in question, a solid-state NMR was performed. If the species resulting from the stoichiometric reaction were amorphous (thus invisible to XRD), $^{11}$B NMR should still provide a means of identification. Figure 3.5, below, compares the $^{11}$B NMR for several samples.

Comparing the unheated and heated samples of 8 mol% TiCl$_3$ doped LiBH$_4$, shows that upon heating, an unidentified peak forms at $\sim$15ppm. At the bottom of the figure are standards for LiBH$_4$ and TiB$_2$. As can be seen, there is a correlation between the central peak of the standard TiB$_2$ spectra and the peak seen in the heated TiCl$_3$ doped LiBH$_4$.

The TiCl$_3$ doped 2LiBH$_4$-MgH$_2$ forms a significantly greater portion of the unknown specie. However, the resolution was poor on this sample. The samples with more components proved to be more difficult to spin. As a result, MgH$_2$ was eliminated from further samples in order to increase $\omega$, the spinning speed, which improves resolution.
Figure 3.5 Results of $^{11}$B NMR performed at Jet Propulsion Laboratories. As can be seen, the sample consisting of heated LiBH$_4$ doped with 8 mol% TiCl$_3$ shows evidence of TiB$_2$ formation.

To better elucidate the correlation between pure TiB$_2$ and what is observed in the TiCl$_3$ doped LiBH$_4$ mixture, the NMR results were zoomed in to the range 100 to -100 ppm. The result of that is shown below in figure 3.6. Figure 3.6 shows a strong correlation between TiB$_2$ and the species seen in the LiBH$_4$ mixture. However, there is also a correlation with elemental boron, though not as strong as with TiB$_2$. 

---

**Figure 3.6** Zoomed NMR spectra showing the correlation between TiB$_2$ and the species seen in the LiBH$_4$ mixture.
Samples of 8 mol% boron and TiB₂ doped LiBH₄ were made for comparison to figure 3.6. It was proposed that the environment of the TiB₂ seen in figure 3.6 was different enough from the pure substance to have caused the shift in the spectrum. Figure 3.7, TiB₂ doped LiBH₄, does not show the shift from that of pure TiB₂ seen in figure 3.6. Figure 3.8, boron doped LiBH₄, bears little resemblance to figure 3.6. Thus, it is unlikely that boron is responsible for the peak seen at ~15ppm in figure 3.6. The shoulder peaks seen between 0 and 20 ppm in figures 3.6, 3.7 and 3.8 are attributed to oxidation formed during preparation.
Figure 3.7 MAS-NMR of 8 mol% TiB₂ doped LiBH₄ compared with pure TiB₂.

Figure 3.8 MAS-NMR of 8 mol% B doped LiBH₄ compared with pure amorphous boron.
Cross-polarization (polarization transfer) MAS-NMR (CPMAS) involves taking advantage of the dipolar coupling between rare spins (in this case $^{11}$B) and abundant nuclei for increased resolution. This experiment typically leads to an improvement in the signal to noise ratio. With this in mind, CPMAS-NMR was performed on a heated 8 mol% TiCl$_3$ doped LiBH$_4$. This is shown in figure 3.9 below.

![Figure 3.9 CPMAS-NMR of heated (400°C) 8 mol% TiCl$_3$ doped LiBH$_4$ shown in black. Spectra from figure 3.6 are also included for comparison.](image)

In liquid-state NMR a direct correlation between the cross-polarization results and those that do not take advantage of cross-polarization are to be expected. Nuclei in solution have a good deal of freedom to move and thus it is not required that the abundant nuclei, typically $^1$H, be bonded to the rare nuclei (in this case $^{11}$B however typically $^{13}$C) in order to use cross-polarization. In other words, in liquid-state NMR the success of a cross-polarization experiment is distance dependent. However, in solid-state, a strong
correlation, such as that seen in figure 3.9, supports the notion that a bond exist between rare and abundant nuclei due to the limited movement of nuclei in the solid-state. In addition, the sideband patterns seen in the CPMAS and MAS NMR in the range ±100-1000ppm are distinctive from TiB₂. (figure 3.10)

![Figure 3.10 Zoomed out CPMAS, MAS NMR of 8 mol% TiCl₃ doped LiBH₄ compared with pure TiB₂ MAS NMR. The overall shape of the sideband pattern of the CPMAS and MAS are distinctive from pure TiB₂.](image)

The information in figures 3.9 and 3.10 strongly reject the postulation that TiB₂ is forming during this decomposition. Most likely, the specie formed upon decomposition is of the form BₓHᵧ in addition to the LiCl identified with XRD. The BₓHᵧ is a higher order borohydride and thus unlike diborane it is not a gas at ambient temperatures.

The formation of a BₓHᵧ specie suggests a more complex mechanism for the decomposition of LiBH₄ and TiCl₃ than had been originally proposed. As a result, an *in-situ* type MAS-NMR experiment was performed. Samples were heated step-wise to
400°C and analyzed with NMR at various points during the heating. A striking result was found at 40°C. Two new peaks were seen at -42.5 and -18.6ppm.

![Figure 3.11 NMR-MAS spectrum of 8 mol% TiCl₃ doped LiBH₄ heated to 40°C. Spectrum shows two new peaks at -42.5 and -18.6ppm.](image)

The peak at -42.5ppm matches perfectly with a previously identified borohydride of the form Ti(BH₄)₃•solvent. This experiment involved mixing TiCl₄ and LiBH₄ in solution. The second peak, at -18.6ppm, matches that of elemental boron.

3.4 Conclusion

By examining mixtures of TiCl₃ doped LiBH₄ we were able to establish that there is indeed an irreversible reaction taking place between these compounds. This reaction,
being irreversible, gives a one-time boost in hydrogen desorption, but also leads to the decomposition of TiCl₃ and LiBH₄. Borohydrides that are dependent on Ti or Ni-additives will not be capable of full reversibility. The Ti or Ni-additives in these systems are not acting as a catalyst but simply as reactants.

It was initially proposed that LiBH₄ was simply reacting with TiCl₃ to form TiB₂. However, by performing the in-situ NMR experiment (figure 3.9), it was found that the reaction proceeds by the following multi-step mechanism:

\[
4\text{LiBH}_4 + \text{TiCl}_3 \rightarrow \text{LiTi(BH}_4)_4 + 3\text{LiCl} \quad (\text{eq } 3.1)
\]

\[
\text{LiTi(BH}_4)_4 \rightarrow \text{LiH} + \text{TiH}_3 + \text{B} + 6\text{H}_2 \quad (\text{eq } 3.2)
\]

\[
\rightarrow \rightarrow \rightarrow \text{B}_2\text{H}_6 \quad (\text{eq } 3.3)
\]

The in-situ experiment gave a picture of the reaction process. For a sample consisting of 8 mol% TiCl₃ doped LiBH₄ prepared according to table 3.1 anionic LiTi(BH₄)_4 is formed somewhere between 25-40°C. In this same temperature range a good deal of LiTi(BH₄)_4 has already decomposed forming the products shown in equation 3.2. The decomposition results in the formation of hydrogen gas, elemental boron, and LiH. The LiTi(BH₄)_4 has completely decomposed by 60°C. Elemental boron remains until about 180°C. By 400°C the boron has reacted with the TiH₃ to yield the B₆H₇ specie. It is likely that all borohydrides react with Ti and Ni-additives in this way. Although equation 3.3 may at first glance seem unlikely, it was shown with $^{11}$B NMR that heated LiBH₄ doped with catalytic amounts of boron showed greater decomposition than pure LiBH₄ at the same temperature. While some aspects of the above mechanism are difficult to confirm absolutely, the formation of LiTi(BH₄)_4 and elemental boron is strongly supported by NMR data.
CHAPTER 4

Future Directions

In order to further improve the performance of the systems discussed in chapter 2 (thus making it viable for on-board storage), it would be necessary to find a compound that releases greater amounts of NH₃. Although the release of NH₃ gas is typically undesirable, the appeal of this system is that it rapidly consumes this normally toxic gas. This has recently been explored with LiNH₂ as a NH₃ donor, with favorable results. Additionally, other molar ratios of LiNH₂ and LiBH₄ yield greater amounts of NH₃ than the α and β-phases. Combinations involving these compounds need to be explored. These studies will be particularly effective if done in conjunction with the Lewis et al. combinatorial method. Finally, it may be possible to utilize other undesirable products (e.g., diborane) that result from the decomposition of solid-state compounds to improve the performance of hydrogen storage systems.

Solid-state NMR was a powerful tool in determining the identity of the products resulting from the reaction of TiCl₃ and LiBH₄. Further use of MAS NMR will allow us determine the full details of this reaction. Complete understanding of the reaction between these two compounds will give great insight into the decomposition of borohydrides in general.
REFERENCES


25. XRD analysis performed at Howard Research Laboratories of Malibu, CA. Samples analysis was performed by Dr. John Vajo and Dr. Sky Skeith.

26. Samples are sealed under vacuum with a glass tube sealer and an O2-natural gas torch. This allows for a near perfect seal and thus prevents oxidation of samples during transport. Samples were sent away for XRD and solid-state NMR analysis.

27. Samples were analyzed by Dr. Walter Niemczura at the University of Hawaii Chemistry Department in Honolulu, HI.

28. Tunstall, D. Royal Society


32. Dr. Greg Lewis performs his high-throughput experiments at UOP, LLC in Des Plaines, Ill. Figure 2.10 is unpublished and was given to us by Dr. Lewis.


35. Principles of Solid State Magic-Angle spinning NMR are discussed briefly in the experimental section of Chapter 2.

36. Samples were analyzed by Dr. Sonjong Hwang at the Jet Propulsion Laboratory on the campus of the California Institute of Technology in Malibu, CA.

37. It should be noted that this sample was performed at JPL. NMR samples run at the University of Hawaii use a different standard than the JPL NMR. As a result, the ppm position of peaks is shifted downfield by 20ppm. Thus, the peak seen here at ~15ppm will occur at ~35ppm in a NMR run at UH.


40. The temperature at which LiTi(BH₄)₄ forms varies greatly depending on the concentration of LiBH₄ and TiCl₃. Godwin Severa was able to show that a mixture consisting of 6LiBH₄ : 1TiCl₃ or greater will form LiTi(BH₄)₄ during ball-milling with no heating required.