Development and Investigation of Novel Nanostructures and Complex Hydrides for Hydrogen Storage

by

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A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy Department of Mechanical Engineering College of Engineering University of South Florida

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Date of Approval: May 26, 2009

Keywords: polyaniline, chemisorption, kinetics, complex hydride, physisorption

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Dedication

This dissertation is dedicated to my parents, Dieter Horst Kunibert and Ursula Luzia Jurczyk as well as my wife Christine Victoria Niemann, my son Sebastian Eduard Gerhard Niemann and any other children I will hopefully have.

Acknowledgements

I would like to thank my research advisors, Dr. Ashok Kumar and Dr. Elias K. Stefanakos for providing me with the extraordinary opportunity of pursuing this research as well as for all the guidance they lent to me over the years. I would also like to thank Dr. Sesha S. Srinivasan for his invaluable help throughout the entire research as well as for helping me with anything I ever needed help with. Additionally, I would like to thank Dr. D. Yogi Goswami, Dr. Delcie Durham, Dr. Autar Kaw, and Dr. Matthias Batzill for being part of my dissertation committee, as well as Dr. John Wolan for being the chair of my Ph.D. defense.

Additionally, I am very grateful to the Department of Energy that provided funding for this research as well as QuantumSphere, Inc. for additional funding and material support.

I would also like to thank the outstanding people at the department of mechanical engineering, specifically, Sue Britten and Shirley Trevor for the many, many things they have done for me.

Finally, I would like to thank my family and friends for their patience and emotional support throughout this endeavor.
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Development and Investigation of Novel Nanostructures and Complex Hydrides for Hydrogen Storage

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ABSTRACT

Over the past few years, the need for a clean and renewable fuel has sharply risen. This is due to increasing fossil fuel costs and the desire to limit or eliminate harmful by-products which are created during the burning of these fuels. Hydrogen is the most abundant element in the universe and can be used in either fuel cells or traditional internal combustion engines to produce energy with no harmful emissions. One of the main obstacles facing the implementation of a hydrogen economy is its storage. Classical methods of storage involve either high and unsafe pressures or liquid storage involving a large amount of energy.

Two alternative hydrogen storage methods are investigated – physisorption, which is the weak chemical bonding to a material, as well as chemisorption, which is a strong chemical bond of hydrogen to a host material. Polyaniline, a conducting polymer, is investigated in both its bulk form as well as in nanostructured forms, more precisely nanofibers and nanospheres, to store hydrogen via physisorption. It is found the bulk form of polyaniline can store only approximately 0.5wt.% hydrogen, which is far short of the 6wt.% required for practical applications. Nanofibers and nanospheres, however, have
been developed, which can store between 4wt.% and 10wt.% of hydrogen at room temperature with varying kinetics.

A new complex metal hydride comprised of LiBH₄, LiNH₂ and MgH₂ has been developed to store hydrogen via chemisorption. While the parent compounds require high temperatures and suffer of slow kinetics for hydrogen sorption, the work performed as part of this dissertation shows that optimized processing conditions reduce the hydrogen release temperature from 250°C to approximately 150°C, while the addition of nano sized materials has been found to increase the kinetics of hydrogen sorption as well as further decrease the hydrogen release temperature, making this one of the first viable hydrogen storage materials available.

This is the first time that nanostructured polyaniline has been investigated for its hydrogen performance. Additionally, the thorough investigation of the effects of nano sized additives and processing parameter optimization of the multinary hydride are first reported in this dissertation.
Chapter 1 - Introduction

1.1. Hydrogen – A Clean and Renewable Fuel

Whether one believes that earth has reached peak oil or that humans are responsible for global warming due to the emissions caused by the burning of fossil fuels, or even if one just thinks that it is important to become energy independent to prevent future conflicts, there is consensus that the search for alternative clean and renewable energy should be a prerogative in the near future [1]. One of the many options is to use hydrogen as a fuel [2]. Hydrogen, provided it is produced using clean and renewable energy sources, such as solar energy, can either be combusted in an internal combustion engine or used in a fuel cell [3, 4] to produce energy that is free of any pollutant by-products, producing solely energy and water. Though there are many barriers towards realizing a hydrogen economy, one of the biggest challenges is to find a safe and efficient means of storing the hydrogen for use in mobile applications [5]. Current options include storing hydrogen in its liquid form or as a compressed gas. Both methods require a large amount of energy and can pose serious safety risks. Therefore, there is a push to find a material to chemically store hydrogen using, for example, metal hydrides [6] or complex hydrides [7]. There are, however, many challenges that these materials must overcome. Specifically, these are to have fast kinetics, a high capacity, e.g. more than 6wt.% hydrogen, and to be reusable for at least 1000 cycles [8].
Over the past few years, the scientific evidence for the inevitability of the so-called peak-oil has become almost overwhelming. Even the optimists [9] amongst the scientists studying peak-oil agree that alternatives to oil need to be found. And the sooner this happens, the better it will be for humanity. If one imagines the oil supply as a clock, peak oil would occur at roughly six o’clock [10]. And, according to many scientists, it is approximately 5:30 – peak oil is near. It is no longer a question of whether oil will run out, but when it will run out. This is only one reason for the need for a substitute to fossil fuels.

In addition to the peak-oil problem, the idea of global warming is finding more supporters in the scientific community than it ever has. It is widely agreed that an alternative to fossil fuels must be explored [11]. Hydrogen is one viable alternative to the black gold, and has been shown to successfully power both fuel cells as well as internal combustion engines [12]. All major automobile manufacturers such as BMW, Daimler, Volkswagen, Honda, General Motors, and Ford, to name a few, have successfully demonstrated the use of hydrogen as a chemical or ignition fuel, though the companies vary on the way the hydrogen is used. BMW, for example, is one of the few automobile manufacturers that uses a modified internal combustion engine as opposed to a fuel cell.

One of the main problems with the utilization of hydrogen as a fuel is its onboard storage. The Department of Energy of the United States of America and the Freedom Car Technology Team have set forth very specific guidelines as to the requirements that need to be met by a hydrogen storage material to successfully compete, and eventually replace, fossil fuels. The specific targets, as they apply to this dissertation are discussed in Section
1.2. A thorough review of current hydrogen storage research is given by Schlapbach and Züttel [13].

Hydrogen, the most abundant element in the universe, is a clean and renewable energy carrier. It 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. Figure 1.1 is a schematic representation of the ideal clean and renewable hydrogen cycle. It also represents the three main challenges facing the use of hydrogen as a fuel source:

(1) A clean and efficient production of hydrogen
(2) An efficient and safe storage system for hydrogen
(3) An efficient and inexpensive means of utilizing hydrogen as a fuel

The ideal production of hydrogen is achieved utilizing clean and renewable energy sources, such as wind energy, solar energy or geo-thermal means to produce electricity, which in turn can split water into oxygen and hydrogen, where the hydrogen is then processed and stored while the oxygen is either released to the atmosphere or bottled and sold for medical purposes, etc. The storage of the hydrogen on board of an automobile is the topic of this dissertation and will not be further elaborated in this section. Finally, the hydrogen needs to be used to produce energy. This can be achieved either by using a hydrogen fuel cell, where the hydrogen is used to produce electricity using, for example, a polymer electrolyte fuel cell or an internal combustion engine, which is modified to run on hydrogen instead of gasoline. Both of these technologies have their advantages as well as drawbacks and are still being optimized. In the end, the
water produced during either the burning of hydrogen or in a fuel cell is simply released back to the environment or collected for further use.

1.2. Obstacles Facing the Storage of Hydrogen

Under ambient conditions hydrogen is a gas, which is highly reactive with other compounds. Therefore, it is not generally found in its molecular form. In order to utilize hydrogen as a practical means for replacement of gasoline in automobiles, the U.S. Department of Energy (DOE) has established criteria that need to be met. These criteria
address not only the cost of the hydrogen storage system, but also the gravimetric and volumetric hydrogen storage requirements of any material to be used. The fueling time and delivery temperatures of hydrogen are also of utmost importance. Table 1.1 provides an overview of the requirements of any hydrogen storage system.

Table 1.1: Department of Energy hydrogen storage system requirements [8].

<table>
<thead>
<tr>
<th>Storage Parameter</th>
<th>Units</th>
<th>2007</th>
<th>2010</th>
<th>2015</th>
</tr>
</thead>
<tbody>
<tr>
<td>System Gravimetric Capacity</td>
<td>kg H₂/kg system</td>
<td>0.045</td>
<td>0.06</td>
<td>0.09</td>
</tr>
<tr>
<td>System Volumetric Capacity</td>
<td>kg H₂/L system</td>
<td>0.036</td>
<td>0.045</td>
<td>0.081</td>
</tr>
<tr>
<td>Storage system cost</td>
<td>$/kg H₂</td>
<td>200</td>
<td>133</td>
<td>67</td>
</tr>
<tr>
<td>Min/max delivery temperature</td>
<td>°C</td>
<td>-30/85</td>
<td>-40/85</td>
<td>-40/85</td>
</tr>
<tr>
<td>Cycle life</td>
<td>Cycles</td>
<td>500</td>
<td>1000</td>
<td>1500</td>
</tr>
<tr>
<td>Min/max delivery pressure from tank</td>
<td>atm (abs)</td>
<td>8/100</td>
<td>4/100</td>
<td>3/100</td>
</tr>
<tr>
<td>System fill time (5kg)</td>
<td>min</td>
<td>10</td>
<td>3</td>
<td>2.5</td>
</tr>
</tbody>
</table>

These specific targets were created to enable the use of hydrogen as a fuel for automotive applications by replacing an average gasoline tank with a hydrogen storage system. A gravimetric density of 6wt.% of hydrogen (0.06 kg H₂/kg system) is based on a driving range of approximately 300 miles with 6kg of hydrogen. Of course, the actual fuel economy of the hydrogen powered vehicle will vary based on whether it utilizes an internal combustion engine or a fuel cell to power the vehicle as well as the weight of the car, just like a gasoline powered vehicle. Since the hydrogen storage system includes the container that is used to hold the hydrogen storage material, the actual gravimetric density of the material should be at least 2wt.% higher. This means that the 2010 target really is considered to be 8wt.% of hydrogen for the hydrogen storage material. For
comparison, a typical gasoline tank onboard a car currently weighs approximately 74kg, of which 55.4kg is gasoline and the rest the actual canister.

Another important criterion for a practical hydrogen storage material is that the hydrogen should be absorbed and released between -40°C and 85°C. More specifically, this means that the temperature of the hydrogen should be within this range, as these are the practical temperature ranges for the current state of the art fuel cells. In all practicality, this means that a higher temperature can be used to release the hydrogen from its material, as long as the hydrogen is then cooled to within the previously mentioned temperature range. When using a hydrogen fuel cell, however, it is important to maintain the temperature of the fuel cell above 0°C since the water that is produced as a by-product would otherwise freeze and destroy the membrane within the fuel cell.

The refueling time of hydrogen into the system is equally as important. Approximately 5kg of hydrogen should be absorbed by the storage system in less than 5 minutes. It is estimated that approximately 5 to 13kg of hydrogen is required to power light duty vehicles. The specific system fill time listed in Table 1.1 is for 5kg, which means that the time to fill the system with more hydrogen would accordingly be scaled up.

While there are other targets that need to be met, the combination of the gravimetric density, hydrogen delivery temperature, and fueling time are the most difficult to combine for a hydrogen storage system. There has been success in meeting one or even two of these criteria in a hydrogen storage system, but so far no success in meeting all three of these. The most important developments are listed in Section 1.3.
1.3. Current State of Hydrogen Storage

Hydrogen storage by itself is nothing new. In fact, hydrogen does not occur naturally as an element or molecule, but instead is always bound chemically to another material. These chemical compounds can be gases such as methane, liquids such as water, or solids such as metal hydrides. Of course, hydrogen can easily be separated from its chemically bonded counterparts and stored in molecular or atomic form. NASA has been using liquid hydrogen, for example, to propel its shuttles into space for decades now. Hydrogen can be stored by four main methods – as a compressed gas, as a liquid, or via physisorption and chemisorption, the latter two of which are considered chemical storage. These four main methods of storage are discussed in further detail in the following subsections. Table 1.2 gives an overview of some of the most commonly used methods for hydrogen.

Table 1.2: Comparison of some hydrogen storage methods [14].

<table>
<thead>
<tr>
<th>Storage method</th>
<th>Gravimetric density (wt.%)</th>
<th>Volumetric density (kg H₂/m³)</th>
<th>Temp. (°C)</th>
<th>Press. (bar)</th>
<th>Phenomena and remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compressed</td>
<td>13</td>
<td>&lt;40</td>
<td>Room Temp.</td>
<td>300-1000</td>
<td>Compressed gas in light weight composite cylinders</td>
</tr>
<tr>
<td>Liquid</td>
<td>Size dep.</td>
<td>70.8</td>
<td>-252</td>
<td>1</td>
<td>Liquid H₂, boil off</td>
</tr>
<tr>
<td>Adsorbed hydrogen</td>
<td>~2</td>
<td>20</td>
<td>-80</td>
<td>100</td>
<td>Physisorption - large spec. surface area, reversible</td>
</tr>
<tr>
<td>Absorbed on interstitial</td>
<td>~2</td>
<td>150</td>
<td>Room Temp.</td>
<td>1</td>
<td>Atomic H₂ intercalation in host sites in metal, reversible</td>
</tr>
<tr>
<td>Complex compounds</td>
<td>&lt;18</td>
<td>150</td>
<td>&gt;100</td>
<td>1</td>
<td>High Temp., high Press.</td>
</tr>
<tr>
<td>Complexes with water</td>
<td>&lt;40</td>
<td>&gt;150</td>
<td>Room Temp.</td>
<td>1</td>
<td>Chemical oxidation of metals with water</td>
</tr>
</tbody>
</table>
1.3.1. Compressed Hydrogen - Gaseous Hydrogen Storage

One of the easiest ways of storing hydrogen is in the form of compressed gas. Since hydrogen has a density of approximately 0.09g/L, high pressures are required to store enough hydrogen in a reasonable volume for practical use. Thus, compressed hydrogen is generally stored with a pressure of approximately 300 to 1000bar, which can pose not only engineering design issues, but also safety risks. If hydrogen is stored at a pressure of 800bar at room temperature, the overall density of hydrogen is approximately 13wt.%, which does meet the DOE safety targets, but only has a volumetric density of less than 40kg H₂/m³, which ultimately is less than the 81kg H₂/m³ required by the DOE. Nevertheless, there is still a lot of research going on in the development of light weight and strong hydrogen cylinders by utilizing, for example, light weight composite materials with a tensile strength of 2000MPa. Ultimately, though, the relatively low volumetric density combined with the unsafe high pressure simply does not make compressed hydrogen a viable option for use in automotive applications. Compressed hydrogen might, however, still be used for large scale transportation, such as hydrogen tankers, as well as storage for hydrogen gas stations – places where there can be enough safety guaranteed by enclosing the tank to provide added safety. For automotive applications, however, compressed hydrogen simply cannot be considered as a viable option, mainly due to the safety aspects as well as the strict restrictions on volume and weight of the storage system.
1.3.2. Liquid Hydrogen Storage

Hydrogen can, of course, also be stored as a liquid. Since the boiling point of hydrogen is -252.87°C, the hydrogen must be cooled significantly. Cooling the hydrogen of course means that a very large amount of energy is required to do this. If, however, one were to ignore the energy required to achieve this, there are still several issues with using liquid hydrogen. One of the main issues is the so-called boil off [15]. Boil off occurs when the hydrogen is not uniformly maintained below the boiling point, which can easily occur when the hydrogen is not constantly stirred to ensure that there are no hot spots within the liquid storage container. Once part of the hydrogen boils, the hydrogen gas can then easily permeate the container walls and simply dissipate into the environment. The most advanced liquid storage tanks available to date still have significant boil off problems. BMW, for example, in its hydrogen powered test fleet, claims that a full tank of liquid hydrogen will be empty within approximately 7 days by simply sitting in the parking lot. In fact, boil off is such an issue, that BMW strongly discourages people from parking the cars inside a garage, as the hydrogen could accumulate and ignite once a source of ignition, as can be created from a light switch when it is turned on, is present.

Liquid hydrogen does have a few advantages [16], when compared with the DOE targets set forth. The pressure at which liquid hydrogen is stored is 1atm, which, in terms of pressure requirements, is an ideal pressure and also safe. The volumetric density of liquid hydrogen is 70.8kg H₂/m³, which almost meets the 2015 DOE targets. The gravimetric density, however, will depend on the size and type of container used to store. The cooling unit as well as any valves and tubing that might be used needs to be taken
into account when obtaining the gravimetric density. Since liquid hydrogen requires constant cooling as well as insulative material, the system weight quickly adds up, thereby greatly decreasing the gravimetric density.

1.3.3. Physisorption

Another commonly investigated method of storing hydrogen is by using physisorption. Through this process, gas molecules bond to the surface of the material via weak van der Waals bonds. Therefore, the amount of hydrogen that can be stored in a physisorption material is proportional to the surface area of the material. Theoretically, therefore, any material with a large specific surface area can be used to store hydrogen through the weak van der Waals bonds. The main class of material that has been investigated for physisorption is carbon since it possesses unique properties that are interesting for storing hydrogen. Due to the abundance of carbon and the simplicity of which one can produce various forms of it, such as carbon nanotubes, carbon nanofibers, nanobells, or graphene [17, 18], there is virtually an unlimited amount of materials that can be chosen for hydrogen storage. One of the most important advantages of carbon based materials is that they do not need to be kept in an inert atmosphere and also do not require a high pressure or strong cylinders to store the material. Virtually all carbon materials are environmentally friendly and benign to humans, which allows for a high safety aspect. Some work has been performed on investigating carbon-based materials for hydrogen storage. Graphite nanofibers, in its herringbone structure, have been shown to store hydrogen [19], though the exact structure required to store the hydrogen is still being investigated. Hydrogen storage in carbon nanotubes [20], carbon nanobells [21],
carbon nanofibers [22] and especially doped carbon nanotubes [23] have shown repeatable hydrogen storage of as much as 14wt.%, at least theoretically. Carbon materials can be readily decorated or modified to allow the modification of kinetics as well as capacity of these materials for use with hydrogen storage. Carbon-based materials possess another important feature, namely a hydrogen binding energy between 10 and 50kJ/mol H₂. This is an ideal value for the binding of hydrogen, since a material with hydrogen bonds less than this is not a suitable candidate material, as the hydrogen can be readily and accidentally released. More specific physisorption background information, as related to this work, is discussed at the beginning of chapter 3.

1.3.4. Chemisorption

Chemisorption of hydrogen is achieved when a material, such as a metal, forms a primary atomic bond with hydrogen, as is the case for metal hydrides. Metal hydrides, also known as interstitial hydrides, generally are metallic or graphite-like in appearance and generally are good conductors [14]. These materials bind the hydrogen in the form of strong primary chemical bonds. By changing the pressure or temperature of the metal hydrides, hydrogen is generally released. Metal hydrides, though investigated for decades, still do not provide an easy, reliable method for hydrogen storage. Almost all metal hydrides require an inert atmosphere from production to disposal to ensure that the material does not react with water or oxygen, which destroys or at the very least deteriorates the material. Often, a temperature of more than 250°C is required to release the hydrogen. Additionally, the hydrogen sorption kinetics are often very slow with low usable capacity (<2wt.%). Metal hydrides, however, do have a much higher volumetric
density than even liquid hydrogen. Mg$_2$FeH$_6$, for example, has a volumetric density of 150kg H$_2$/m$^3$. Since the maximum hydrogen to metal ratio known is 4.5, as is the case for BaReH$_9$ [24], it is essential to investigate only metal hydrides that consists of elements with an average molecular weight of less than 51.8g/mol to obtain a gravimetric density that is higher than 8wt.%, as required by the DOE. More specific examples of chemisorption, as it pertains to this dissertation are discussed in chapter 4.

1.4. Dissertation Outline

Chapter 2 discusses the details of the experimental part of this dissertation, more specifically, the details of the synthesis apparatuses, as well as the characterization techniques employed. The actual work performed as part of this dissertation can be separated into two parts – the investigation of physisorption phenomena and the investigation of chemisorption. Polyaniline, a conducting polymer, was chosen as the material to be investigated for physisorption and is described in chapter 3 both in its bulk form as well as in nanostructured form, more specifically nanofibers and nanospheres. Chapter 4 discusses the investigation and optimization of hydrogen performance of complex hydride structures composed of LiBH$_4$, LiNH$_2$, and MgH$_2$ with and without nano sized additives. Chapter 5 finally summarizes the work completed as part of this dissertation and offers some suggestions for future work.

1.5. Dissertation Goals and Significance of the Study

As traditional fossil fuel supplies are dwindling and carbon emissions derived from burning these fuels are being blamed for global weather changes, it is becoming increasingly important to find alternative energy sources. While there are clean and
renewable energy production methods, such as wind and solar energy, there is yet to be found a clean and safe means of propelling automobiles. Hydrogen is an ideal candidate since it can easily be refueled in automobiles in a manner similar to gasoline. Its onboard storage, however, is a significant barrier for utilizing hydrogen as a fuel. The materials developed as part of this dissertation provide a significant improvement in the hydrogen storage properties of solid state storage.

Two main approaches are investigated as part of this dissertation. The first is to tailor the nanostructure of polyaniline in its emeraldine form, a conductive polymer, so that the surface area of the polymer is increased, by creating nanospheres and nanofibers. The bulk form of polyaniline is also investigated for its hydrogen sorption properties as a comparison. The reason behind using a polymer for hydrogen storage is that polymers contain many hydrogen atoms which allow for the formation of weak secondary bonds between the hydrogen that is part of the polymer and the hydrogen that is meant to be stored. Since polyaniline is easily synthesized and is rather inexpensive, it is an excellent choice as a hydrogen storage material. The alteration of the physical structure of polyaniline into nanospheres and nanofibers allows for an increase in surface area, thereby exposing more material as potential bonding sites for the hydrogen. Since polyaniline is composed of quinoid and benzenoid rings and the emeraldine form is terminated with Cl⁻ ions, additional hydrogen bonding sites, in the form of stronger chemisorption of hydrogen, is made available. The advantage of having both chemisorption and physisorption sites is shown schematically in Figure 1.2. Hydrogen, as a molecule, can bond to the material through three main mechanisms. The simplest form is to simply bond weakly to the host material via physisorption as a molecule. This can
generally be achieved if the temperature is low enough, and is the main mechanism of storage for physisorption materials, but generally requires temperatures of approximately 77K. If additive materials, such as catalysts, are present, these materials can break up the molecule into ions which then allows for the diffusion through the relatively porous material to then chemically bond with the host material. Similarly, hydrogen molecules can also bond the host material.

By increasing the surface area as well as the porosity, two main events can occur. The first is that the hydrogen has more bonding sites to the host material. The second is that the diffusion of hydrogen into the material is made possible. Since polyaniline cannot

![Figure 1.2: Schematic representation of physisorption and chemisorption with catalyst materials.](image)

By increasing the surface area as well as the porosity, two main events can occur. The first is that the hydrogen has more bonding sites to the host material. The second is that the diffusion of hydrogen into the material is made possible. Since polyaniline cannot
be simply modified to have smaller molecular size, the nanostructure can be altered to increase the surface area and also to increase the hydrogen diffusion pathways.

For the first time, polyaniline is shown to possess outstanding hydrogen storage properties by carefully modifying the nanostructure of the material. It is found that polyaniline combines both physisorption as well as chemisorption for storing hydrogen, which provides a significant improvement of hydrogen storage properties, since a usable capacity is achieved.

The second mechanism investigated as part of this dissertation is the route of chemisorption, or strong hydrogen atomic bonding, to complex hydride materials. Complex hydrides generally require a high temperature for hydrogen release as the hydrogen bonds are very strong. By reducing the crystallite size of the host material, specifically LiBH₄ and LiNH₄ and by further destabilizing the structure with MgH₂, the temperature can be reduced to allow for reversible hydrogen storage at a lower temperature. The reduction of crystallite size, as well as the exact processing technique is shown to be very important and have a large effect on the storage capacity.

Figure 1.3 shows general hydrogen absorption and desorption of complex hydrides. The unhydrided material absorbs hydrogen from the outside in until it is fully hydrided. By reducing the pressure on the sample or by increasing the temperature, the hydrogen is then released from the outside first until the material is fully unhydrided again. When the particles are too large, though, a hydrogen passivation layer can form during the initial hydrogen uptake, thereby reducing any further hydrogenation. Additionally, the kinetics, or rate, of hydrogen sorption is increased with particle size, as this means that the hydrogen has a larger distance to diffuse through. The effects of
particle size on hydrogen storage are shown in Figure 1.4. By employing mechanochemical milling, the particles are not only reduced in size, but dislocations and vacancies are created, thereby increasing the kinetics and capacity of the material. The interaction of the various particles that make up the hydrogen storage material are also of great importance, as this determines the interaction of the various compounds and either facilitates or hinders successful hydrogen sorption as will be shown.

Figure 1.3: Hydrogen storage mechanism in complex hydrides and the effect of particle size.

The complex hydrides that are developed are carefully investigated employing varying processing techniques, a deviation of the traditional means of producing complex hydrides. The nanostructure created with the varying techniques is carefully analyzed and
correlated with the material’s hydrogen performance. Additionally, the hydrogen storage properties are significantly improved by using optimized quantities of nano sized additives.

Figure 1.4: Particle size effects on hydrogen storage.
Chapter 2 - Experimental Equipment

This chapter is intended to give a general overview of the experimental equipment, materials, as well as some basic background information on these, employed within the scope of the dissertation work. More detailed information is presented in the beginning of chapter 3 and chapter 4, as any specifics may relate to the polymer or complex hydride.

2.1. Synthesis and Materials

With the exception of the starting materials, which are listed in Table 2.1, all materials that are described in this dissertation were synthesized in the laboratory in order to achieve the highest amount of flexibility on the tailoring of the materials’ properties to optimize the hydrogen performance of said materials.

Table 2.1: Materials used as part of this dissertation with their respective purity.

<table>
<thead>
<tr>
<th>Material</th>
<th>Company</th>
<th>Purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aniline</td>
<td>Sigma Aldrich</td>
<td>99%</td>
</tr>
<tr>
<td>Ammonium Persulfate</td>
<td>Sigma Aldrich</td>
<td>99%</td>
</tr>
<tr>
<td>Hydrochloric Acid</td>
<td>Sigma Aldrich</td>
<td>37%</td>
</tr>
<tr>
<td>Aluminum</td>
<td>Sigma Aldrich</td>
<td>98%</td>
</tr>
<tr>
<td>SnO₂</td>
<td>Sigma Aldrich</td>
<td>98%</td>
</tr>
<tr>
<td>LiBH₄</td>
<td>Sigma Aldrich</td>
<td>98%</td>
</tr>
<tr>
<td>LiNH₂</td>
<td>Sigma Aldrich</td>
<td>98%</td>
</tr>
<tr>
<td>MgH₂</td>
<td>Sigma Aldrich</td>
<td>98%</td>
</tr>
<tr>
<td>Cu</td>
<td>QSI</td>
<td>99%</td>
</tr>
<tr>
<td>Co</td>
<td>QSI</td>
<td>99%</td>
</tr>
<tr>
<td>Ni</td>
<td>QSI</td>
<td>99%</td>
</tr>
<tr>
<td>Mn</td>
<td>QSI</td>
<td>99%</td>
</tr>
</tbody>
</table>
2.1.1. Glove Box

The materials used for the complex hydrides were all stored in an Innovative Technology System One glove box. The glove box, shown in Figure 2.1, is filled with a 99.999% pure nitrogen atmosphere to protect all starting materials from oxidation and contamination. The atmosphere is constantly monitored and controlled so that the oxygen and moisture levels are constantly kept below 1ppm by providing a continuous flow of nitrogen. All sample preparation, whenever possible, was performed inside the glove box. This ensures that the hydrides do not react with any moisture or oxygen and also that the materials do not pick up any contamination, as might otherwise occur.

![Figure 2.1: Innovative Technology System One glove box.](image)

2.1.2. Polymerization

The polyaniline samples that are investigated as part of this research were synthesized in the laboratory rather than purchased. This was done to ensure the utmost flexibility in tailoring the characteristics of the polyaniline. The exact polymerization
procedure is described in detail in chapter 3. The polymerization was carried out inside of a fume hood, rather than the glove box, since the vapors emitted during polymerization could have damaged the glove box as well as brought the moisture and oxygen levels of the glove box to an unsafe amount, jeopardizing the purity of the materials stored within the glove box. The only experimental equipment used was glass ware and a stirring plate, as well as an electrospinning setup, described more closely in chapter 3.

2.1.3. Ball Milling

The complex hydrides were synthesized using ball milling, also known as mechano chemical synthesis. More specifically, a planetary ball mill, the Fritsch Pulverisette P5, was used for synthesis. The Fritsch Pulverisette P5, shown in Figure 2.2, contains a holder for a stainless steel bowl, which in turn contains 20 smaller stainless steel balls.

When the ball mill runs, the bowl rotates in a clockwise direction, while the base of the bowl rotates in the opposite direction. The sample to be milled is placed in the stainless steel bowl and then sealed. When the ball mill is running, the planetary action causes centrifugal forces that add and subtract alternatingly. Through these alternating forces, the balls roll halfway around the bowl and then are thrown across the container. This rotation, combined with translation of the balls, provides for a high impact of the grinding balls with the material that is being milled.
This means that ball milling allows not only for physical but also chemical changes of the material that is being processed. The physical aspects include:

1. particle size reduction through crushing
2. physical combination of materials
3. strengthening of particles through grain size reduction
4. specific surface area increase through crushing of the particles

The ball mill also allows for chemical interaction of the materials that are in the stainless steel container. Due to localized temperature increases created by the grinding action of the stainless steel balls with the material that is being milled, the materials that are being milled can form new chemical compounds. The stainless steel container used during synthesis also has an inlet and outlet vent, allowing for the addition of various processing gases, which is essential to the synthesis of the materials.
2.2. Thermal Characterization

Due to the nature of the materials investigated for hydrogen storage, the effect of temperature on the material’s characteristics is extremely important. The complex hydrides, for example, use temperature changes as a driving force for release. Therefore, it is extremely important to investigate the effects of temperature increases on the material. One of the first steps after synthesis of any new sample was therefore to perform thermal characterization. The three main techniques employed were thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and thermal programmed desorption (TPD), which are all discussed in this subsection.

2.2.1. Thermogravimetric Analysis (TGA)

Since the materials synthesized as part of this dissertation are all in their hydrided phase, a quick analysis of the material employing TGA can be very valuable. The data obtained from this quick screening tool can be used to obtain insight into the thermal stability, e.g. the usable temperature range of the material, as well as any phase changes that might be present such as melting. The TGA employed is a Thermal Analysis SDT (Simultaneous DSC and TGA) Q600, shown in Figure 2.3.
The Q600 possesses two alumina cantilever beams with built in thermocouples, as shown in Figure 2.4. This enables the simultaneous measurement of heat flow in a sample as well as weight loss, which might occur due to hydrogen release. An empty alumina beam is placed on one of the cantilever beams, while the sample is placed in another alumina pan on the other cantilever beam. Before loading the sample, both sample and reference pan are zeroed out to obtain the proper weight of sample. Approximately 5mg of sample was loaded into the sample pan – just enough to allow for an accurate measurement, but not enough for the sample to overflow and cause damage to the TGA. The TGA was placed in another glove box in order to minimize contact of the sample with the environment in order to obtain the most accurate results. While the furnace of the TGA can go up to 1200°C, none of the samples were ever heated above 500°C for two reasons. The first reason is to ensure that the TGA does not get damaged due to harmful vapor emissions. The other reason is that it would simply be impractical to use a hydrogen storage material at temperatures above 500°C.
Figure 2.4: Schematic representation of the most important parts of a TGA.

As Figure 2.4 shows, the main parts of the TGA are the two cantilever beams, a tube furnace, and a dual-balance mechanism coupled with photodiodes and sensors that actually measure the deflection of the beams due to weight loss or weight gain. In general, the samples were all analyzed in an argon atmosphere with a heating rate of 1°C/min to allow the sample to reach localized equilibrium and to obtain the most accurate material performance. Argon was chosen over nitrogen since it is an inert gas and since some of the samples that were characterized contained nitrogen, which might cause the sample to react with the nitrogen atmosphere, thereby giving inaccurate results. The TGA was calibrated in regular intervals for both heat flow as well as weight loss with standardized samples to provide the utmost accuracy.
A typical TGA plot, in this case for calcium oxalate, is shown in Figure 2.5 below. Calcium oxalate is often chosen as a reference material for calibrating the TGA since it exhibits three distinct weight loss regions. Typically, a weight loss of approximately 12.3% is observed below 200°C. This is then followed by a weight loss of 18.5% due to CO emission below approximately 500°C. Finally, the calcium oxalate loses approximately 30.3% of CO$_2$ below 800°C. The TGA measurements of the hydrogen storage materials are therefore used to determine the amount of gas released as a function of temperature. The slope of the weight loss curve can give an indirect indication of the rate at which the gas is released by the material, while the amount of weight loss can be directly correlated to the amount of gas released.

![Figure 2.5: Typical TGA profile - Calcium oxalate exhibiting weight loss due to water, carbon monoxide and finally carbon dioxide loss.](image)
2.2.2. Differential Scanning Calorimetry (DSC)

Even though the TGA contains a built-in DSC, several samples were characterized using Thermal Analysis’ DSC Q10, shown in Figure 2.6, for more accurate measurements. Similar to the TGA, two pans are used – one is an empty aluminum reference pan, the other is an aluminum pan with approximately 5mg of sample. The DSC then heats the sample and reference with a heating rate of approximately 1°C/min in a helium atmosphere. The DSC instrument ensures that both the sample pan as well as the reference pan is kept at the same temperature. If there is a temperature difference, due to an endo- or exothermic reaction, the instrument adds more energy to the cooler of the two pans and records this difference in heat flow.

![Figure 2.6: Thermal Analysis DSC Q10.](image)

A typical DSC profile is shown in Figure 2.7. It can be seen that there are four distinct thermal events that the material experiences while it is being heated. There are two endo- and two exothermic events. The glass transition, a phase change essentially, as well as the melting of the material are both endothermic events. The recrystallization and
decomposition of the material, however, are exothermic events. DSC analysis, combined with TGA analysis of the hydrogen storage materials is very important since it provides information as to the amount of energy required to release the hydrogen. Unfortunately, neither the TGA nor the DSC is capable of measuring the thermal performance of the material under high pressures of hydrogen. Therefore, it is not possible to determine the amount of energy required for rehydrogenation of the material.

2.2.3. Thermal Programmed Desorption (TPD)

The third and final thermal analysis of the hydrogen storage materials was performed using thermal programmed desorption, TPD. Quantachrome’s Autosorb 1 was used with the optional TCD (thermal conductivity detector) attachment, as shown in Figure 2.8. TPD works by heating the sample to be investigated within a u-shaped quartz.
tube at a controlled rate – generally 1°C/min was used for the work described in this dissertation. The mass of the sample is measured and then the sample is loaded inside the glove box. The quartz tube is then sealed with Parafilm® to prevent the sample from picking up moisture or oxygen. Once the quartz tube is installed in the TPD, the measurement is started. This includes the initial purging of any residual gas from the tube using helium for 20 minutes. After this, the sample is heated to 50°C and purged with nitrogen for another 30 minutes. After the purge, the sample is heated at a constant rate of 1°C/min up to a temperature of 350°C. Nitrogen was used as the purge gas since hydrogen and helium have similar thermal conductivities.

Figure 2.8: Thermal programmed desorption (TPD) with optional TCD controller.
The TPD measurements are used as a quick screening tool to obtain information about the temperature at which hydrogen, or any other gas, is released. The data can be used to verify any TGA or DSC data previously obtained. This provides an accurate and quick screening method for the hydrogen desorption properties of the investigated materials. Additionally, TPD data is collected at varying heating rates in order to obtain information about the activation energy associated with hydrogen release by employing Kissinger’s method [25].

A TPD plot showing the three step release of hydrogen of LiAlH₄ is shown in Figure 2.9. It is clear that there are three distinct peaks obtained at very distinct temperatures. This TPD data is easily confirmed either via literature or through other thermal characterization techniques such as TGA or DSC. Generally, the data is plotted as TCD signal versus temperature since TPD measurements are performed with a constant temperature ramping rate. One can, however, plot signal versus time to obtain some basic information about the kinetics of hydrogen release.
2.3. Structural Characterization

In addition to detailed thermal studies of the materials, the structural characteristics are of utmost importance. It is essential, for example, to confirm that the polymerization of polyaniline is indeed successful. The main tool employed for this is Fourier transform infrared spectroscopy (FTIR). Additionally, the microstructure of the materials for hydrogen storage is extremely important. As will be demonstrated, the surface area as well as the crystallite size of the material has a large effect on the hydrogen storage properties. In order to characterize this, scanning electron microscopy (SEM) is employed. Additionally, it is essential to know the nature of the chemical structure of the material after ball milling, which is determined employing x-ray...
diffraction (XRD). XRD allows for the confirmation of any chemical reaction that might occur during ball milling.

2.3.1. X-Ray Diffraction (XRD)

The chemical structure of the processed complex hydrides was analyzed using a Philips X’Pert XRD system, as shown in Figure 2.10. The polymer samples synthesized were not analyzed using the XRD since XRD can only be used to characterize and identify crystalline materials.

Figure 2.10: Philips X’Pert XRD used for characterizing the chemical structure of processed complex hydrides.

William Henry Bragg and William Lawrence Bragg won a Nobel Prize in 1915 after deriving a relationship between x-rays and crystal structure. This relationship is still used today and is known as Bragg’s law. Bragg’s law gives a relationship between the angle of the incident x-rays, \( \theta \), their wavelength, \( \lambda \), and the spacing between planes in an
atomic crystal lattice, $d$, as well as an integer determined by the order of the x-rays, $n$, as described in Equation 2.1:

$$n\lambda = 2d \sin \theta$$ (2.1)

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, $\theta$. 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, as shown in Figure 2.11 (a). 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, as shown in Figure 2.11 (b).

Figure 2.11: (a) X-rays not in phase causing a base line of XRD signal, (b) x-rays in phase causing a peak in XRD 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.
2.3.2. Fourier Transform Infrared Spectroscopy (FTIR)

Since the polymer samples that were synthesized were of amorphous nature, FTIR was employed to confirm that polyaniline actually was synthesized and to obtain information about its chemical nature, such as the presence of benzenoid and quinoid rings. A Perkin Elmer Spectrum One, as shown in Figure 2.12, was used to measure the FTIR spectra of the various samples. Since the polymer samples do not require any special consideration when performing measurements, as the complex hydrides require, all polyaniline samples were simply measured, after performing background scans, using the ATR powder accessory, which is also shown installed in Figure 2.12. Some of the complex hydrides were also characterized using the FTIR in order to determine the presence of BH\(^+\) ions, for example. Since the complex hydrides react with moisture and oxygen, the samples were pelletized after mixing with KBr powder and wedged between KBr windows to prevent contamination of the samples.

Figure 2.12: Perkin Elmer Spectrum One FTIR.
2.3.3. Scanning Electron Microscopy (SEM)

The surface morphology of both the polyaniline and complex hydride samples are of utmost importance to this research. Therefore, the materials were characterized using the Hitachi S800, shown in Figure 2.13. The polyaniline samples were simply placed on the sample holder using carbon tape and it was ensured that no excess material was loose, which might contaminate the SEM. The complex hydrides require more attention since these materials can react with moisture and oxygen. Therefore, all complex hydride samples were prepared inside the glove box and secured to the sample holder using carbon tape. The sample holder was then placed in a desiccator and transferred to the SEM. The only time the sample was exposed to the atmosphere was when loading the sample inside the SEM. The exposure was limited to a few seconds, which caused only minimal contamination. The main feature that was explored was the surface morphology.

Figure 2.13: Hitachi S800 SEM.
2.4. Hydrogen Sorption Measurements (PCT)

The most important characterization was the measurement of hydrogen sorption using a HyEnergy PCT Pro 2000, shown in Figure 2.14. The PCT Pro 2000 consists of a sample holder and a heater jacket for the sample holder along with carefully calibrated reservoirs for hydrogen. The equipment is capable of measuring hydrogen release and uptake from room temperature to 500°C with hydrogen pressure varying from vacuum to 200bar, though, for safety reasons, the highest pressure used was approximately 80bar. The PCT Pro 2000 is capable of performing two different types of hydrogen sorption:

(1) So-called PCT measurements, where the hydrogen is incrementally increased for absorption runs or decreased for desorption runs.

(2) Kinetics measurements where hydrogen absorption or desorption is measured with a constant pressure.
Most measurements are performed under isothermal conditions, though some of the measurements were run while increasing the temperature at a constant rate. The samples that were measured for their hydrogen performance generally had a mass of approximately 1 to 2g. The complex hydrides were loaded inside the glove box, while the polyaniline samples were loaded into the sample holder outside of the glove box. Before every measurement, the sample holder was purged with helium several times to remove any air or nitrogen that might be present. After the purging process, the volume of the sample was calibrated using a built in procedure. The accuracy of this calibration is of extreme importance since the equipment directly measures pressure and pressure drop. The change in pressure and the volume of the hydrogen was then correlated to the amount of hydrogen the material either absorbed or desorbed using the van der Waals equation, a modification of the ideal gas law. The van der Waals equation can be applied to fluids that is composed of particles with a non-zero size and that have a pairwise attractive force between particles. The equation is described by Equation 2.2:

\[
(p + \frac{n^2a}{V^2})(V - nb) = nRT
\]  

(2.2)

where \( p \) is the hydrogen pressure (measured directly), \( V \) is the volume that the hydrogen has available to expand into (obtained from the volume calibration), \( R \) is the gas constant (8.314J/(mol K)), \( a \) is the dipole interaction or repulsion constant (2.476x10^{-2}m^6Pa/mol^2), \( b \) is the volume occupied by the hydrogen molecules (2.661x10^{-5} m^3/mol), \( n \) is the number of moles of hydrogen, and \( T \) is the temperature of the sample during measurement in Kelvin. The temperature and the pressure are measured directly by the PCT Pro 2000. Since \( a \), \( b \), and \( R \) are constants, the measured data can be used to obtain the number of
moles of hydrogen that was absorbed or desorbed by the material. Multiplying this with the molecular weight of hydrogen (1.0079 g/mol) yields the equivalent mass of hydrogen that was sorbed. This can then be used along with the mass of the sample to obtain the amount of hydrogen in terms of weight percent (wt.%) as indicated by Equation 2.3:

$$\text{H}_2 \text{ concentration (wt.%) = } \frac{m_{\text{hydrogen}}}{m_{\text{hydrogen}} + m_{\text{sample}}} \times 100$$  \hspace{1cm} (2.3)

where $m_{\text{hydrogen}}$ is the mass of the hydrogen that is sorbed and $m_{\text{sample}}$ is the mass of the unhydrided material that sorbs the hydrogen.

As previously mentioned, the two main hydrogen sorption measurements performed on the samples are PCT and kinetics measurements. The PCT measurement is performed at a constant temperature with varying pressure. A basic absorption PCT is conducted by starting out with a low hydrogen pressure (0 to 1 bar) on the sample. A precalibrated reservoir is then filled with the same amount of hydrogen and the measurement is started. When the valve that separates the sample from the reservoir is opened, the change in pressure is recorded. From the gas law it is known what the equilibrium pressure should be. Any variation of the pressure is therefore due to the interaction of hydrogen with the material. If hydrogen is absorbed by the material, the pressure drops; if it is desorbed, or released, by the material, the pressure increases. After pressure equilibrium is reached, the valve between the reservoir and the sample is closed and the reservoir is filled with a certain amount of hydrogen – either more for absorption or less for desorption. The valve is then opened again and the previous procedure repeated. This is done with a variation of hydrogen pressure from 0 to 80 bar for absorption or from 80 to 0 bar for desorption in either 5 or 3 bar increments. The data that
is collected is then plotted as hydrogen pressure versus hydrogen concentration. Some materials exhibit a so-called plateau pressure – a pressure at which an optimal amount of hydrogen is released or absorbed. An example of a desorption PCT measurement exhibiting a plateau pressure around 15bar is shown in Figure 2.15.

![Desorption PCT plot of LiAlH₄ showing plateau pressure around 15bar.](image)

Figure 2.15: Desorption PCT plot of LiAlH₄ showing plateau pressure around 15bar.

The other main hydrogen sorption measurement performed is a kinetics measurement. For an absorption measurement, an example of which is shown in Figure 2.16, the sample is first either evacuated or charged with 1bar of hydrogen. A precalibrated reservoir is then filled with 80bar of hydrogen. When the valve between the reservoir and the sample is opened, the hydrogen immediately reaches an equilibrium pressure, which is determined automatically using the gas law. If hydrogen is absorbed,
the pressure within the sample holder drops until it finally reaches equilibrium. This pressure data is then used to obtain the amount of hydrogen that the material absorbed. A desorption kinetics measurement is performed the same way, except that the sample is first placed under 80bar of hydrogen pressure and the reservoir evacuated. If hydrogen is released, the pressure increases above the expected equilibrium and can then be related to the amount of hydrogen desorbed. Kinetics measurements are generally performed at constant temperatures to obtain information about the rate of hydrogen sorption. However, kinetics measurements can also be performed with increasing or decreasing temperature to obtain a relationship between the temperature and the amount of hydrogen sorbed.

![Figure 2.16: Kinetics plot of LiAlH₄ showing absorption kinetics.](image_url)
Chapter 3 - Physisorption in Polyaniline

3.1. Introduction

As mentioned in chapter 1, two main hydrogen storage approaches are investigated. This chapter investigates hydrogen storage via physisorption in polyaniline (PANI). PANI is a conducting polymer that has been well characterized. Its chemical structure is shown in Figure 3.1. The emeraldine base form of PANI consists of quinoid and benzenoid rings. This means that the theoretical hydrogen capacity of polyaniline is approximately 6wt.%. While this is too low to exceed the DOE targets mentioned in chapter 1, it is not the chemisorption aspect of PANI that is of interest, but instead the physisorption aspect.

![Figure 3.1: Chemical structure of emeraldine base polyaniline.](image)

To date, there has been very little research into hydrogen storage using polymers. Since polyaniline is rather simple to synthesize in a laboratory setting, while being relatively inexpensive, it was decided to investigate polyaniline in its bulk form as well as in nanostructured form with various additives for hydrogen storage. This nanocomposite material consists of a polyaniline matrix, which can be functionalized by either catalytic doping or incorporation of nano variants. It was reported that polyaniline could store as
much as 6 to 8wt.% of hydrogen [26], which, however, another team of scientists could not reproduce [27]. Yet another recent study revealed that a hydrogen uptake of 1.4 to 1.7wt.% hydrogen has been reported for polymers of intrinsic microscopy [28].

Most hydrogen storage investigations of polymers that have been conducted were performed at 77K and only involved pure physisorption, mainly by increasing the surface area of the polymer. One form of hydrogen storage in polymers is to use a polymeric foam for hydrostatic pressure retention of hydrogen [29]. In this method of storing hydrogen, the ideal tank contains spherical cells that act as microscopic pressure vessels, ideally in a homogeneous manner. However, no significant amount of hydrogen has been experimentally proved to be stored. As of the time of writing this dissertation, only theoretical work has been performed on hydrogen storage in polymer foams.

Hypercrosslinked polymers, such as styrenic polymer produced from polyvinylbenzylchloride, have also been investigated for their hydrogen sorption properties [30]. It was found that approximately 3wt.% hydrogen could be stored at 15bar, although a temperature of 77K was required to ensure that the weak hydrogen bonds created through physisorption did not break, thereby releasing the hydrogen. Polychloromethylstyrene-co-divinylbenzene [31], another hypercrosslinked polymer, was shown to reversibly store 1.6wt.% hydrogen at a temperature of 77K and a pressure of 12bar. Again, the surface area of the material played an important part in storing the hydrogen, as is expected for physisorption materials. The hydrogen storage mechanism was purely physisorption and lacked any chemisorption of hydrogen, an attribute that is needed to get away from the low temperatures required for pure physisorption materials.
Another polymer class that has been investigated for its hydrogen storage properties are polymers of intrinsic microporosity, known as PIMs. PIMs are polymers that have very large surface areas, generally in the range of 500 to 900 m$^2$/g and are generally prepared by using a benzodioxane formation reaction between suitable monomers. It has been shown, for example, that HATN-network-PIM can store about 1.6 wt.% hydrogen at a pressure of 10 bar and a temperature of 77 K [28, 32]. While this value is higher than that of metal organic frameworks, it is still too low for practical use and of course requires a temperature which is not only impractical but also requires a large amount of energy.

Polyaniline is a conductive polymer, with conductivity on the order of 10$^0$ S/cm. This is higher than that of typical non-conducting polymers, but much lower than that of metals [33]. In addition to its conductivity, polyaniline in its emeraldine base (EB) form is very simple and inexpensive to polymerize. It is because of this simplicity that it was chosen as a matrix material for the nanocomposite structure discussed in this paper.

Conducting polymer nanostructures combine the advantages of organic conductors and low dimensional systems having interesting physicochemical properties [33-36] and useful applications [37-39]. Among the conducting polymers, polyaniline was considered important because of its extraordinary properties of electrical and optical behavior. It was recently reported that polyaniline could store as much as 6 to 8 wt.% of hydrogen [26], which was later refuted by Panella et al. [27]. Polypyrrole, another polymer investigated for hydrogen storage had a similar fate, in that it was claimed to be able to store as much as 10 wt.% at room temperature [26], though this was also refuted [27]. Though many controversial results were reported in terms of hydrogen uptake [40-
43] in polymer nanocomposites, there are still a number of parameters, tailor-made properties, surface morphologies and their correlation with hydrogen sorption behavior to be investigated before these materials can be commercially deployed for onboard hydrogen storage. Similarly, nanotubes [20, 44], nanofibers [45] and nanospheres [46] have attracted more interest because of their novel properties and wide potential application for nanometer-scale engineering applications. It is known that the nanofibrallar morphology significantly improves the performance of polyaniline in many conventional applications involving polymer interactions with its environment [47]. This leads to faster and more responsive chemical sensors [39, 48], new organic/polyaniline nanocomposites [49] and ultra-fast non-volatile memory devices [50].

A graphical comparison of polymer structures investigated to date is shown in Figure 3.2. It can be seen that there has not been a lot of work performed on polymeric hydrogen storage, and that the work that has been reported to date mostly is performed at low temperatures of 77K. The polypyrrole and polyaniline with high capacity that are shown in that figure were later refuted by other teams of scientists, as previously mentioned. The polyaniline structures investigated in the following sections are all evaluated for their hydrogen performance between room temperature and 125°C, which correlates approximately with the temperature range required by the DOE for practical hydrogen storage.
3.2. Bulk Polyaniline

The first form of the emeraldine base polyaniline (PANI) to be investigated was bulk polyaniline. Bulk simply refers to the nanostructure of PANI, indicating that the PANI is used as-synthesized in its non nanostructured form. This means that the surface morphology was not adjusted into nanofibrous form. After some baseline characterization and hydrogen sorption experiments, filler materials could be added to the PANI. The addition of filler materials to the matrix material could be used to tailor an ideal nanocomposite material for hydrogen storage. Several different filler materials in various concentrations were added to the nanocomposite and its effect on the characteristics of

Figure 3.2: Previous work on hydrogen storage in polymers, mainly in polymers of intrinsic microscopy (PIM).
the material determined. A schematic representation of the use of filler materials and the mechanism of hydrogen storage for bulk polyaniline can be seen in Figure 3.3.

Figure 3.3: Hydrogen sorption mechanism of standard polyaniline composite material.

Since polyaniline is composed primarily of hydrogen and carbon atoms, it possesses a large number of both primary and secondary hydrogen bonding sites. Figure 3.3 shows a combination of both primary and secondary bonding sites as follows:

1. Hydrogen gas enters the hydrogen storage tank containing the polyaniline matrix material as hydrogen molecules in gaseous form.

2. Any added materials, such as SnO, then react with hydrogen molecule to break it up into hydrogen ions to facilitate the bonding to the host matrix.
(3) The hydrogen ions then bond to either filler materials such as 3a) carbon nanotubes, 3b) fullerenes, or simply to 3c) the host material through either primary atomic bonds, where and impurities or vacancies are present or to other primarily bonded hydrogen through weak secondary hydrogen bonding.

(4) By reducing the hydrogen pressure on the material or heating up the host matrix, the hydrogen is then released from storage.

(5) Finally, after recombining to hydrogen molecules, the hydrogen is used in either an internal combustion engine or in a fuel cell.

3.2.1. Synthesis of Bulk Polyaniline

The polyaniline used for this experiment was synthesized by following a well established method for the synthesis of the emeraldine base (EB) form of polyaniline [33]. 5.71g of ammonium persulfate were dissolved in a 100mL beaker with 50mL of de-ionized water. 5mL of aniline were mixed with approximately 35mL of de-ionized water. These two solutions were then slowly mixed with 10mL of 37% HCl acid in a large beaker. After the temperature rises to approximately 45°C, the polymerization is considered finished. The sample, however, is magnetically stirred for approximately 24 hours to ensure complete polymerization. After magnetic stirring, the sample was vacuum filtered through an 11μm filter, after which it was washed twice with HCl to ensure termination of any bonds and methanol. The sample was then vacuum dried at 100°C for approximately 24 hours. While most samples were polymerized at room temperature, which was approximately 23°C, a few samples, which will be discussed separately, were polymerized at approximately 0°C by placing the chemicals in a freezer
for several hours before polymerization and then mixing the chemicals inside an ice bath cooled beaker.

The so-called filler materials were added during the polymerization process, so as to ensure uniform distribution within the sample. Some of the filler materials added to the nanocomposite material included SnO$_2$ (obtained from Sigma Aldrich in nanopowder form), multi wall carbon nanotubes (with a purity of at least 60% before purification), as well as aluminum powder (obtained from Riedel-de Haën as fine powder with a purity greater than 93%). These materials were added in various concentrations, which will be discussed in the individual results section. All materials were added in terms of weight percent based on the expected yield.

3.2.2. Bulk Polyaniline Characterization

The as-synthesized nanocomposite samples were characterized before and after hydrogen sorption employing Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), as well as scanning electron microscopy (SEM). FTIR, which was performed on a Perkin Elmer Spectrum One, was utilized to ensure the proper polymerization of the sample as well as determine any chemical effect a filler material might have had. TGA was carried out on a TA SDT Q600, while DSC measurements were made with a TA DSC Q10P. TGA was employed mainly to determine the useful temperature range of the sample material, as well as to determine any hydrogen that might have bonded to the material chemically. The DSC measurement was used to determine any phase transitions that might occur as a result of the heat ramping process. Finally, the SEM was utilized to determine any
surface morphological changes of the materials, such as the formation of clusters as a result of hydrogen sorption.

As described, the polyaniline based nanocomposite materials were synthesized according to a standardized method. Initially, solely polyaniline in its emeraldine base form was synthesized. This sample is referred to as PANI-STD. It was decided to include multiwall carbon nanotubes into the polyaniline matrix material, as these have been shown to increase the conductivity of the conducting polymer [51]. This sample is referred to as PANI-MWCNT. Due to the availability and relatively low cost of multiwall carbon nanotubes, as compared to single wall carbon nanotubes, it was decided to only use multiwall carbon nanotubes, though there has been significant research on hydrogen storage in single wall carbon nanotubes [20]. The hydrogen sorption measurements for carbon nanotubes, however, are usually performed at a temperature of 77K [52].

10wt.% tin oxide was also added to the matrix material, since it was expected to act as a catalyst material in the capture of hydrogen, breaking the hydrogen molecule into ions. This sample is referred to as PANI-SnO₂ throughout this paper. Finally, fine aluminum powder was added to the matrix material during polymerization to determine any effect of the aluminum on hydrogen sorption. This sample is referred to as PANI-Al. It was thought that the aluminum would form alane or alanate, thus increasing the hydrogen sorption of the nanocomposite. All samples were prepared with varying concentrations of the filler materials. Therefore, the samples will be denoted not only by their abbreviation, but also labeled with the appropriate concentration of the material added to the nanocomposite, in weight percent.
3.2.3. FTIR Characterization Results

FTIR spectrum analysis was performed to identify the bonding environment of the as-synthesized materials, and to determine whether the filler materials chemically reacted with the polyaniline matrix material, or simply physically mixed with the polyaniline. Figure 3.4 shows a comparison of standard polyaniline, polyaniline with multiwall carbon nanotubes, polyaniline with SnO$_2$, and finally polyaniline with aluminum powder.

Figure 3.4: FTIR comparing standard polyaniline (PANI-STD), polyaniline with 10wt.% SnO$_2$, polyaniline with 10wt.% MWCNT and polyaniline with 30wt.% aluminum powder.

All four samples exhibit the same benzenoid and quinoid ring vibrations around 1500cm$^{-1}$ and 1600cm$^{-1}$, respectively. Figure 3.4 shows that the polyaniline that was synthesized is in fact polyaniline in its emeraldine base [53]. Additionally, all samples
exhibit peaks around 1306 cm\(^{-1}\), which is attributed to the \(\pi\)-electron delocalization induced in the polymer by protonation. The peak around 1375 cm\(^{-1}\) is attributed to the C-N stretch in the base. The peak around 822 cm\(^{-1}\) is due to C-H bond out of plane [54]. It can also be seen that the addition of tin oxide mainly caused a physical rather than a chemical reaction between the polyaniline and the tin oxide, as the FTIR spectrum is essentially unchanged. The addition of multiwall carbon nanotubes to the polyaniline matrix material also shows more of a physical mixing rather than a chemical mixing. This explains the results that are obtained in the hydrogen sorption measurements, to be discussed in the next section. The addition of aluminum to the sample, however, clearly shows a chemical reaction between the polyaniline and the aluminum powder. The large peak around 1150 cm\(^{-1}\) is a sign of increased conductivity and was described by Quillard et al. [55] as the “electron-like band.”

3.2.4. Thermogravimetric Results

Once the successful polymerization of the sample was confirmed, a TGA measurement was performed on the samples. The sample was heated from room temperature up to 400\(^\circ\)C. The main purpose for performing the TG analysis was to determine the maximum temperature possible for hydrogen sorption measurements, as well as to confirm the useful thermal range of the samples.

It can be seen in Figure 3.5 that all samples are stable up to at least 200\(^\circ\)C. The initial weight loss in the samples at around 100\(^\circ\)C is simply due to moisture contained within the nanocomposites. It is interesting to note that the sample with the multiwall carbon nanotubes exhibits a higher weight loss than the other samples. This could be
explained by the fact that the multiwall carbon nanotubes were not of 100% purity, but
instead contained soot or other forms of carbon, which were burned off during the
temperature increase.

![Thermogravimetric analysis of standard polyaniline, polyaniline with 10wt.%
multiwall carbon nanotubes, polyaniline with 10wt.% tin oxide, and polyaniline after
hydrogen sorption measurements.](image)

Figure 3.5: Thermogravimetric analysis of standard polyaniline, polyaniline with 10wt.%
multiwall carbon nanotubes, polyaniline with 10wt.% tin oxide, and polyaniline after
hydrogen sorption measurements.

While care was taken to purify the carbon nanotubes as much as possible before
synthesis of the nanocomposite material by using a combination of ultrasonication,
washing with de-ionized water, drying in air and washing with HCl [56], some impurities
must have remained in the sample, causing the observed drop. Additionally, the PANI-
MWCNT sample contained a higher amount of moisture, as it was observed that this
sample readily absorbed moisture, as the sample were handled and stored in atmospheric conditions.

3.2.5. Scanning Electron Microscopy Results

Figure 3.6 shows some SEM images of standard polyaniline before and after hydrogen sorption measurements. Figure 3.6 (a) and (b) clearly show the rough surface of the standard polyaniline. The images show a rock like surface structure, with sharp edges. Figure 3.6 (c) and (d), on the other hand, reveal that hydrogen interacted with the polyaniline during the PCT hydrogen sorption measurements. The interaction of hydrogen with the polyaniline caused a type of ballooning effect, in which the hydrogen seeped into the material and was stored in small pockets. This indicates that the hydrogen is stored physically, rather than chemically.
3.2.6. Hydrogen Sorption Measurements

The isothermal volumetric measurements were carried out by HyEnergy’s PCT Pro 2000 sorption equipment. This fully automated Sievert’s type instrument uses an internal PID controlled pressure regulator with maximum pressure of 170bar. It also includes five built-in and calibrated reservoir volumes of 4.66, 11.61, 160.11, 1021.30 and 1169.80mL. The volume calibration without and with the sample was performed at a constant temperature with an accuracy of ±1°C using helium. The software subroutines for hydrogen purging cycles, leak test, kinetics, PCT and cycling etc. were performed by
the HyDataV2.1 program. The data collected for each run was analyzed using the Igor Pro 5.03 program with a built in HyAnalysis Macro.

The amount of material loaded for hydrogen sorption measurements corresponds to approximately 2g. Before the experiment was run, the volume of the sample was determined at the appropriate temperature. The absorption measurement was generally performed at 60bar of hydrogen pressure at temperatures varying from 25°C up to 125°C. Desorption measurements have been carried out under vacuum.

Cho et al. [26] had reported hydrogen sorption of polyaniline at approximately 77K, which was shown to not be reproducible [27]. This low temperature, however, is not feasible for use in mobile applications. It would simply require too much energy to cool and maintain the hydrogen storage material at such a low temperatures. It was therefore decided to conduct the hydrogen sorption measurements between ambient temperature and 125°C. The absorption of hydrogen was carried out at 60bar hydrogen pressure, while the sample was initially just below ambient pressure. For desorption measurements, the sample was held at the pressure resulting from the absorption measurement, while the reservoir, into which the hydrogen was to flow, was evacuated.

Figure 3.7 shows the hydrogen sorption measurements of standard polyaniline. The pressure was raised in aliquots from 0bar hydrogen pressure to 60bar hydrogen pressure at different temperatures. It can be seen that the standard polyaniline does not absorb any hydrogen at room temperature. At 50°C, however, the sample can store approximately 0.075wt.% hydrogen at 60bar. As the temperature is increased, the sample can store more hydrogen. At 125°C, the standard polyaniline, as synthesized, is capable of storing 0.35wt.% hydrogen.
When tin oxide was added to the polyaniline, no change in the hydrogen sorption capabilities was observed, regardless of the amount of tin oxide, as seen in Figure 3.8. It is thought that the lack of hydrogen sorption increase is due to the measurement temperatures chosen. From hydrogen gas sensing research, it is known that a temperature of around 300°C is optimum for hydrogen to bind with SnO₂ [53]. The measurements followed the same hydrogen sorption behavior as observed for the standard PANI sample seen in Figure 3.7. An increase in pressure and temperature meant an increase in hydrogen sorption, provided the temperature of sorption was above 30°C. Regardless of
the amount of SnO$_2$ added to the polyaniline matrix, there was no change in hydrogen sorption, hence only the 10wt.% sample has been presented here.

![Hydrogen sorption measurements of polyaniline with 10wt.% SnO$_2$ at different temperatures and increasing pressure.](image)

Figure 3.8: Hydrogen sorption measurements of polyaniline with 10wt.% SnO$_2$ at different temperatures and increasing pressure.

Similarly, the amount of multiwall carbon nanotubes showed no effect on the hydrogen sorption capabilities of the material. Figure 3.9 shows the hydrogen sorption results of the polyaniline sample with 10wt.% multiwall carbon nanotubes. It can be seen that the same trend is evident – a higher temperature and a higher pressure means more hydrogen can be stored. The multiwall carbon nanotubes cause only a very slight increase in the hydrogen sorption capabilities, which can be accredited to an increase in the
porosity caused by the inclusion of nanotubes. Again, a minimum temperature of just above 30°C is needed for the material to absorb hydrogen.

Figure 3.9: Hydrogen sorption measurements of polyaniline with 10wt.% multiwall carbon nanotubes at different temperatures and increasing pressure.

Figure 3.10 shows the hydrogen sorption measurements performed on the polyaniline sample with 30wt.% aluminum powder. It can be seen that this nanocomposite material exhibits a much higher hydrogen sorption than the other samples. It is interesting to note that hydrogen sorption begins at 75°C, above approximately 50bar hydrogen pressure, as compared to 30°C for most other samples. The exact effect of the aluminum on the hydrogen sorption performance of the nanocomposite material is still
unclear, as well as the effect of different concentrations of aluminum. It is however clear that no hydrogen alanate is formed from this interaction.

![Figure 3.10: Hydrogen sorption measurements of polyaniline with 30wt.% fine aluminum powder at different temperatures and increasing pressure.](image)

3.2.7. Bulk PANI Summary

All experiments were conducted to mimic the U.S. Department of Energy’s goals as closely as possible. Hence, it was decided to keep the hydrogen sorption temperature range below 130°C, and above 0°C, which is reasonably close to DOE targets. Hydrogen sorption measurements were not performed below 0°C, as it is the author’s opinion that it is simply not feasible for use in automotive applications to store hydrogen at such low
temperatures, especially considering the freezing effects of fuel cells that would result from such a low temperature.

It has been shown that a polyaniline nanocomposite material can store just under 0.5wt.% hydrogen at 175°C. The inclusion of multiwall carbon nanotubes has little effect on the hydrogen sorption capabilities of the material, though the increase in porosity of the material causes a slight increase in the hydrogen sorption capabilities of the material. The carbon nanotubes cannot, however, be seen as the primary hydrogen storage material. SEM analysis shows that the hydrogen is mainly physically absorbed, in forms of small pockets of hydrogen. The inclusion of tin oxide has been shown to have no effect on the hydrogen sorption capabilities of the material either. Finally, the addition of aluminum to the nanocomposite matrix has shown the greatest effect on the material’s hydrogen capacity. The increase in hydrogen sorption capabilities caused by the inclusion of fine aluminum powder, as well as the exact chemical interaction between the aluminum and the polyaniline, is still unclear. The use of bulk polyaniline, however, is not a feasible or practical option for hydrogen storage.

3.3. PANI Nanospheres

Since the bulk polyaniline showed promise in that it was able to reversibly sorb hydrogen at slightly elevated temperatures, though with a low capacity, it was decided to investigate various nanostructures of polyaniline. As was previously mentioned, a higher surface area allows for more hydrogen bonding sites. Additionally, smaller particle sizes also mean faster kinetics, at least theoretically, since the hydrogen can diffuse through the
material with more ease. Hence, the first nanostructured polyaniline that was investigated was PANI nanospheres.

3.3.1. Synthesis of Polyaniline Nanospheres

The polyaniline nanospheres (PANI-NS) were synthesized by oxidative polymerization of aniline monomer at 0°C in an ice bath using ammonium persulfate as the oxidant in the presence of surfactant. Aniline, ammonium persulfate, polyvinyl pyrroledene, cetyl ammonium bromide, and camphorosulfonic acid are used as received from Sigma-Aldrich. Camphorosulfonic acid surfactant as the dopant and ammonium persulfate as the oxidant were used in the present synthesis of polyaniline nanospheres (see flow chart in Figure 3.11). Calculated quantities of aniline monomer (0.005mol) were mixed with 50mL of distilled water and stirred using magnetic stirrer for 10 minutes. Meanwhile, calculated quantities of surfactant (0.75mol) and oxidant (0.005mol) were dissolved separately in distilled water and stirred for 10 minutes in an ice bath. The surfactant solution was first added to the aniline monomer aqueous solution and then the previously cooled oxidant solution was added drop wise after which the mixture was allowed to react for 10hr in an ice bath. The precipitate was filtered and washed several times with distilled water and methanol to terminate the polymerization reaction and then dried in vacuum at room temperature for 24hr. Later, the vacuum-dried precipitate was annealed at 100°C for 1hr. The dried polyaniline was characterized and tested for the hydrogen uptake and release measurements.
3.3.2. Scanning Electron Microscopy Results

The microstructure of the as-synthesized PANI nanospheres was studied by Hitachi S800 scanning electron microscope (SEM). A fixed working distance of 5mm and a voltage of 5-25kV were used. Sample preparation for the SEM measurement was carried out inside the glove box by covering the sample holder with Parafilm® for minimal exposure to oxygen while transferring it to the secondary emission chamber. EDAX Genesis software was used to analyze the SEM images.
It was found that the synthesis, as previously outlined, produced a virtually 100% yield of polyaniline nanospheres with an average diameter of 100nm, as can be seen in Figure 3.12. The nanospheres are not independent of each other, but instead are agglomerated. This is to be expected as the nanospheres are produced without templating and are simply formed through a chemical method. However, the nanospheres are very uniform and possess a better morphology than the bulk PANI previously discussed.

Figure 3.12: SEM of PANI nanospheres at a magnification of 25000.
3.3.3. FTIR Characterization Results

The quinoid and benzenoid bond stretches of the PANI-NS were compared to the bulk PANI with a Perkin Elmer Spectrum One FTIR spectrometer. The PANI-NS samples were pelletized and sealed in a specially designed KBr cell for infrared measurements to prevent any further moisture uptake. As Figure 3.13 indicates, the FTIR spectrum of the PANI nanospheres is virtually identical to the spectrum of the bulk counterpart. The relative intensities of the peaks to each other remain unchanged, with the exception of the out of plane C-H deformation peak observed around 800cm⁻¹. All other peaks, most importantly the characteristic quinoid and benzenoid peaks are virtually identical, therefore confirming the formation of the emeraldine base polyaniline.

![Figure 3.13: FTIR comparison of bulk PANI with PANI nanospheres.](image)
3.3.4. Hydrogen Sorption Results

The volumetric hydrogen sorption measurements are of paramount importance in understanding the hydrogen storage behavior of PANI-NS. Room temperature hydrogen absorption was executed at a high pressure ($H_2 \sim 80$ bar) with a pre-calibrated reservoir. These isothermal volumetric measurements were carried out by HyEnergy’s PCT Pro 2000 sorption equipment. This fully automated Sievert’s type instrument uses an internal PID controlled pressure regulator with maximum pressure of 170bar. It also includes five built-in and calibrated reservoir volumes of 4.66, 11.61, 160.11, 1021.30 and 1169.80mL, of which the 160.11mL reservoir was used, providing for a roughly 15:1 volumetric ratio of the hydrogen volume to available sample volume. The volume calibration with and without the sample was performed at a constant temperature with an accuracy of $\pm 1^\circ$C using helium. The software subroutines for hydrogen purging cycles, leak test, kinetics, PCT and cycling were performed by the HyDataV2.1 Lab-View program. The data collected for each run were analyzed using the Igor Pro 5.03 program with a built-in HyAnalysis macro.

As with the bulk polyaniline sample, it was decided to perform hydrogen sorption measurements close to room temperature. Since the nanospheres do not contain any hydrogen after synthesis, with the exception of the chemically bonded hydrogen that is part of the polyaniline chemical structure, the first hydrogen measurement performed was absorption. The sample was kept under vacuum and then exposed to 80bar of hydrogen pressure. Each absorption measurement was then followed by a desorption measurement at $30^\circ$C and given enough time to reach an equilibrium. The results of the kinetic absorption and desorption measurements are shown in Figure 3.14.
The first hydrogen absorption measurement at 30°C revealed an uptake of more than 5.5wt.%, a significant improvement over the bulk polyaniline. However, the kinetics of the hydrogen uptake were extremely slow as it took almost 5hr to absorb the full 5.5wt.%. The speed of hydrogen release during the second kinetics measurement was even slower, though, as it took nearly 20hr to release just over 4.5wt.%, meaning that approximately 1wt.% was irreversibly stored in the polymer nanostructure. Consecutive absorption and desorption cycles showed that the amount of hydrogen that was absorbed was always equal to the amount that was released during the previous desorption cycle. However, the amount desorbed continuously decreased as did the kinetics. After only 3
absorption and desorption cycles, the amount of hydrogen that was absorbed was well under 1wt.%. Since the previous work with the bulk PANI showed that a higher temperature also meant a higher capacity, an absorption kinetic measurement at 90°C was performed. The results of this kinetics measurement, shown in Figure 3.15, indicate that only approximately 0.6wt.% of hydrogen could be reversible sorbed. This data is in agreement with the best case scenario of the bulk polyaniline previously discussed.

![Figure 3.15: Absorption kinetics of PANI nanospheres at 90°C.](image)

The slow kinetics of the hydrogen absorption indicate that chemisorption is taking place, rather than physisorption, as physisorption is generally characterized by fast, almost instantaneous, hydrogen release or uptake. This is further confirmed by the fact
that the desorption of hydrogen is extremely slow, which is to be expected since the
temperature of measurement is relatively low, which means that there is not enough
energy to break the hydrogen bonds quickly enough. Furthermore, since the nanospheres
are not separated, but instead are agglomerated, there is a larger hydrogen diffusion path
which in turn also means slower kinetics.

3.3.5. Hydrogen Cycling Effects on PANI Nanospheres

Since the capacity of the nanospheres decreased from 5.5wt.% to 0.6wt.% with
consecutive hydrogen cycling, the nanospheres were investigated using SEM. A
representative image can be seen in Figure 3.16. Some remnants of the nanospheres can
be seen, though it is evident that the nanostructure was significantly deteriorated. The few
remnants of the nanospherical structure that are visible further show that the average
diameter has increased to approximately 200nm. This swelling confirms that the PANI-
NS chemically interacted with the hydrogen, thereby causing the increase in particle size.
Additionally, the nanostructure was broken down by the repeated cycling, which is not
due to any temperature effects that might cause the breakdown of the structure. Some
microcracks can also be seen in the SEM image, which is a typical sign of hydrogen
cycling in materials as the hydrogen diffuses through the material, thereby creating these
cracks. The PANI-NS morphology observed after hydrogen cycling is reminiscent of the
bulk PANI morphology. Since the nanospheres are virtually identical to the bulk PANI,
as evidenced by the FTIR analysis, the deterioration of the nanostructure explains why
the final hydrogen capacity is close to that of the bulk PANI samples.
Figure 3.16: SEM image of PANI nanospheres after hydrogen cycling.

3.3.6. PANI Nanospheres Summary

Emeraldine base polyaniline nanospheres were successfully synthesized with almost 100% yield and an average diameter of 100nm. The FTIR characterization confirms that the chemical structure of the PANI is virtually identical to the bulk PANI previously investigated. It was found that the nanospheres have an initial uptake of approximately 5.5wt.% hydrogen with slow kinetics requiring approximately 5hr for full absorption. The desorption kinetic measurement at 30°C, however, shows that only 4.5wt.% of hydrogen is released again, leaving approximately 1wt.% contained in the PANI nanospheres. With each further absorption and desorption the capacity diminished
further, leaving more hydrogen in the structure. The rate of hydrogen absorption and desorption also decreased with each cycle, indicating that the material essentially became saturated with hydrogen through chemisorption, as evidenced by the slow kinetics while making hydrogen diffusion more difficult. SEM analysis of the nanospheres after hydrogen cycling reveal that the nanostructure of the material deteriorated as a result of chemical bonding of hydrogen to the PANI material. Swelling of the few remaining nanospheres was also observed, as were microcracks within the structure, evidence of hydrogen diffusion in the material. Hydrogen cycling at higher temperatures, as was done for the bulk PANI, revealed no further significant hydrogen uptake or release, but instead essentially confirmed the hydrogen capacity of bulk PANI.

3.4. Chemically Grown PANI Nanofibers

Nanofibers with diameters of tens of nanometers appear to be an intrinsic morphological unit that was found to “naturally” form in the early stage of chemical oxidative polymerization of aniline. In conventional polymerization, nanofibers are subject to secondary growth of irregularly shaped particles that form the final granular agglomerates. The key to producing pure nanofibers is to suppress secondary growth. Based on this, two methods (interfacial polymerization and rapidly mixed reactions) have been developed that can readily produce pure nanofibers by slightly modifying the conventional chemical synthesis of polyaniline without the need for any template or structural directing material. With this nanofiber morphology, dispensability and processibility of polyaniline are now greatly improved. On the other hand, the template synthesis method is an effective way to grow the nanofibers of various conducting
polymers [57, 58]. The preparation conditions and their effect on morphology, size, and electrical properties of nanofibers have been reported previously in literature [59].

3.4.1. Synthesis of Polyaniline Nanofibers

The polyaniline nanofibers (PANI-NF) were synthesized by oxidative polymerization of aniline monomer at 0°C in an ice bath using ammonium persulfate as the oxidant in the presence of surfactant. Aniline, ammonium persulfate, dodecyl benzene sulfonic acid, acrylmethylpropyl sulfonic acid, and camphorosulfonic acid are used as received from Sigma-Aldrich. Sulfonic acid based surfactants as the dopant and ammonium persulfate as the oxidant were used in the present synthesis of polyaniline nanofibers (see flow chart in Figure 3.17). Calculated quantities of aniline monomer (0.05mol) were mixed with 50mL of distilled water and stirred using magnetic stirrer for 10 minutes. Meanwhile, calculated quantities of surfactant (0.75mol) and oxidant (0.05mol) were dissolved separately in distilled water and stirred for 10 minutes in an ice bath. The Surfactant solution was first added into the aniline monomer aqueous solution and then previously cooled oxidant solution drop wise and the mixture was allowed to react for 15 hours in an ice bath. The precipitate was filtered and washed several times with distilled water and methanol to terminate the polymerization reaction and then dried in vacuum at room temperature for 24 hours. Later, the vacuum-dried precipitate was annealed at 125°C for 3 hours. The dried polyaniline was characterized and tested for the hydrogen uptake and release measurements.
3.4.2. FTIR Characterization Results

The quinoid and benzenoid bond stretches of the PANI-NF were compared via Perkin Elmer Spectrum One FTIR spectrometer. The PANI-NF samples were pelletized and sealed in a specially designed KBr cell for infrared measurements. Fourier transform infrared (FTIR) spectra of standard PANI and PANI-NF prepared from chemical templating method are shown in Figure 3.18.
Figure 3.18: FTIR spectra of PANI nanofiber and standard sample indicating that the major bonding environment remains unchanged for both standard and nanofibrous polyaniline structures.

The major bonding environment remains unchanged for both standard and nanofibrous polyaniline structures. The presence of two bands in the vicinity of 1500 cm\(^{-1}\) and 1600 cm\(^{-1}\) are assigned to the non-symmetric C6 ring stretching modes. The higher frequency vibration at 1600 cm\(^{-1}\) is for the quinoid rings, while the lower frequency mode at 1500 cm\(^{-1}\) depicts the presence of benzenoid ring units. Furthermore, the peaks at 1250 cm\(^{-1}\) and at 800 cm\(^{-1}\) are assigned to vibrations associated with the C-N stretching vibration of aromatic amine out of plane deformation of C-H of 1,4 disubstituted rings. The aromatic C-H bending in the plane (1167 cm\(^{-1}\)) and out of plane (831 cm\(^{-1}\)) for 1,4
disubstituted aromatic ring indicates a linear structure. Independent of surfactant, complete formation of polyaniline has been observed always.

3.4.3. Scanning Electron Microscopy Results

The microstructure of the as-synthesized PANI nanofibers was studied by Hitachi S800 scanning electron microscope (SEM). A fixed working distance of 5mm and a voltage of 5-25kV were used. Sample preparation for the SEM measurement was carried out inside the glove box by covering the sample holder with Parafilm® for minimal exposure to oxygen while transferring it to the secondary emission chamber. EDAX Genesis software was used to analyze the SEM images.

It is clearly discernible from the scanning electron micrograph, shown in Figure 3.19, that the density of nanofiber formation remains rather constant, irrespective of the surfactant used during the synthesis of PANI-NF. Furthermore, it can be seen from Figure 3.19 that the average nanofiber diameter is approximately 250nm. It is important to note that the surface of the nanofibers is rather rough, which is typical of chemical nanofiber growth. Additionally, the nanofibers are rather inconsistent in length and overall appear to be fragmented. However, there is no evidence of bulk PANI observed, meaning that there is essentially a 100% yield of nanofibers. The nanofibers that were synthesized using camphorosulfonic acid, as seen in Figure 3.19 (c), were analyzed for their hydrogen sorption behavior because of their slightly rougher surface, as it was thought that they possess more potential hydrogen binding sites.
Figure 3.19: Scanning electron micrographs of polyaniline nanofibers grown at room temperature in aqueous medium with different surfactants (a) dodecyl benzene sulfonic acid, (b) acrymethylpropyl sulfonic acid, and (c) camphorosulfonic acid using ammonium persulfate as oxidizing agent.
3.4.4. Hydrogen Sorption Results

The volumetric hydrogen sorption measurements are of paramount importance in understanding the hydrogen storage behavior of PANI-NF. Room temperature hydrogen absorption was executed at a high hydrogen pressure of approximately 80bar with a pre-calibrated reservoir of 160.11mL, providing for roughly a 15:1 volumetric ratio of hydrogen to sample volume.

Figure 3.20 demonstrates the initial hydrogen uptake of PANI-NF with respect to time. From this figure it is seen that rapid absorption was achieved (i.e. 95% of total capacity 3-4wt.% in less than 10min) by the nanofibrous matrix. The absorbed hydrogen was then desorbed against 1bar and approximately 1-2wt.% hydrogen was released at room temperature (see Figure 3.20).
Figure 3.20: Hydrogen absorption and desorption kinetics of PANI-NF in the 1st and 13th cycle.

In order to confirm and ensure the effective hydrogen sorption, the Pressure-Composition-Temperature (PCT) measurements were carried out at room temperature for the PANI-NF from the 2nd cycle to the 6th cycle as shown in Figure 3.21 (a) and (b). Interestingly, a distinct plateau pressure region was observed, which is usually an identifier for effective hydride formation of chemisorption, around 30bar (up to 1.5wt.% hydrogen uptake) and a linear region (up to 2wt.%) with total absorption capacity around 3.5wt.%. In the consecutive hydrogenation cycles (3rd-6th), this plateau pressure region diminishes; nevertheless, the hydrogen absorption capacity remains the same as shown in Figure 3.21 (a). The initial plateau region observed most likely corresponds to
chemisorption of hydrogen into the material. The hydrogen initially bonds via physisorption to the nanofibers, but hydrogen also fills any vacancies and unterminated bonds that arose during the synthesis of the nanofibers, which is very common for chemically synthesized polymers. The fact that no desorption plateau region is observed further confirms hydrogen sorption via chemisorption, as room temperature does not provide the hydrogen with enough energy to break the hydrogen bonds produced through chemisorption. The reduction in the plateau pressure, as well as the reduction in the amount of hydrogen that is actually chemically sorbed during consecutive cycles, indicates that the nanofibers become saturated and terminated with hydrogen. Since hydrogen is still reversibly sorbed in the nanofibers without any plateau region, it is clear that the remaining 3.5wt.% of hydrogen is stored via physisorption.

The reversibility of hydrogen absorption and desorption of 3 to 4wt.% at room temperature was unambiguously demonstrated by Figure 3.21(a) and (b). It is also noticeable from this figure that by increasing the sorption temperature from room temperature to 50°C in the 5th cycle, the plateau pressure region disappears, which indicates that these nanofibers react with hydrogen more effectively at room temperature than at a moderate temperature of 50°C.
Figure 3.21: Pressure-Composition Isotherms (PCT) of PANI-NF at room temperature from 2\textsuperscript{nd} to 6\textsuperscript{th} (a) absorption (b) desorption cycles.
Furthermore, it is clear that the main driving force behind hydrogen sorption in these nanofibers is not temperature, but instead pressure. This means that a pressure of approximately 80bar is required to keep the hydrogen stored in the material. If the pressure is reduced from 80bar to near vacuum, the hydrogen is very quickly released, as is evident in Figure 3.22 – the kinetic behavior of the nanofibers. Conversely, if the pressure is increased instantaneously to 80bar, the hydrogen is quickly reabsorbed.

After several hydrogen sorption cycles, the absorption kinetics at the 13th cycle was recorded and compared with the 1st cycle. It was observed that the reaction kinetics in the 13th cycle remain the same as for the 1st cycle (Figure 3.20). Hydrogen absorption and desorption from the 14th to 25th cycle are shown in Figure 3.22. It is clearly seen from this figure that there was no deterioration in the hydrogen storage capacity of 3-4wt.% during these reversible cycles. Furthermore, it can be seen that it only takes approximately 6min to absorb the hydrogen. With increasing cycles, however, there is a slight reduction in the kinetics of the material, most notably in the desorption of hydrogen. While the absorption kinetics stay virtually unchanged, the desorption kinetics slow from 6min to about 30min for full hydrogen release with consecutive hydrogen absorption / desorption cycles.
Figure 3.22: Hydrogen sorption kinetics at room temperature from 14th cycle to 25th cycle showing little degradation in kinetics and no degradation in the storage capacity within the measured cycles.

3.4.5. Hydrogen Cycling Effects on PANI Nanofibers

This decrease in hydrogen kinetics can be explained when looking at the microstructure of the PANI nanofibers after hydrogen cycling, as seen in Figure 3.23. It is evident that the nanofiber structure that was initially present is no longer intact. The nanofibers are in fact wholly missing. The interaction of the hydrogen with the nanofibers, through repeated pressure changes at close to room temperature first caused chemical bonding to the PANI which resulted in termination of bonds. Additionally, the force caused by the pressure variations of the hydrogen essentially resulted in the nanofibers being repeatedly compressed and decompressed, thereby forcing the
microstructural changes. As can be seen in the SEM image, however, the PANI surface morphology is still characterized by a porous nature, created by the diffusion of hydrogen in and out of the structure. Since the microstructure changed so significantly, a surface area analysis was performed on the PANI nanofibers before and after hydrogen cycling to confirm the initial findings of unchanged surface area. The results of the BET surface area analysis are presented in Figure 3.24.

![SEM image of PANI nanofibers after hydrogen cycling.](image)
Figure 3.24: BET surface area analysis of PANI nanofibers (CM) before and after hydrogen cycling.

It can be seen that the surface area of the PANI nanofibers before hydrogen cycling was approximately 3.26m²/g and after hydrogen cycling actually increased slightly to 3.56m²/g. This surface area is significantly lower than most other porous polymers reported in literature, which often have areas larger than 100m²/g. The intrinsic nature of polyaniline, however, allows the hydrogen to bond with many different sites both through chemisorption and physisorption, as previously shown.

3.4.6. PANI Nanofibers (CM) Summary

In summary, polyaniline nanofibers (PANI-NF), synthesized by chemical templating technique using various surfactants as dopants and ammonium persulfate as the oxidant, were successfully shown to reversibly store hydrogen. The characteristics of
PANI-NF are understood regarding their structure, microstructure, bonding, and thermal stability behaviors. The signature bands of benzenoid and quinoid transitions in the frequency of 1500cm⁻¹ and 1600cm⁻¹, respectively, as evidenced from FTIR, confirms the formation of the polyaniline nano structure irrespective of the surfactants used in the precursor preparation. The rate of hydrogen sorption during the initial cycle is very rapid (95% hydrogen storage capacity (3-4wt.%) absorbed in less than 6min). Moreover, these PANI nanofibers demonstrate excellent reversibility (up to 25 cycles measured) at room temperature. This behavior has previously not been reported in literature. Another important feature discernible from the PCT isotherms was that during the second hydrogen absorption run, the plateau pressure occurred around 30bar, and it diminished in subsequent cycles. This means that hydrogen first bonded to vacancy sites and unterminated bonds created during the chemical synthesis. The reduction in the plateau pressure as well as the reduction in plateau capacity with subsequent cycles indicates that the chemisorption sites disappear as hydrogen is chemically bonded. This chemisorption is further proven by the lack of plateau regions in desorption cycles, as the low temperature (around room temperature) does not provide enough energy for the hydrogen to break the stronger chemical bonds. Nevertheless, the reversible capacity of 3-4wt.% was maintained throughout 25 cycles through physisorption with pressure changes as the main driving force in hydrogen absorption and desorption. Furthermore, it was shown that the nanofibrallar nature of the PANI nanofibers disappears through hydrogen cycling, most likely due to repeated compression of the structure from 0 to 80bar of hydrogen pressure. The surface area, however, remains virtually unchanged and even increases slightly. This means that the binding sites for the hydrogen remain intact, even
though the morphology is changed significantly. While a capacity of 3-4wt.% is not enough to meet the DOE targets for a practical hydrogen storage medium, the rapid kinetics and low temperature required for hydrogen cycling make these chemically synthesized nanofibers an attractive hydrogen storage medium for smaller applications.

3.5. Electrospun PANI Nanofibers

In this section, the synthesis and characterization of polyaniline nanofibers by electrospinning process of polymer solution on a collection substrate is investigated. These as-deposited nanostructures were characterized using Fourier transform infrared (FTIR) spectroscopy for determination of stretching modes and vibrations. An important aspect of hydrogen adsorption and desorption behavior in these nanofibers was estimated by high pressure hydrogen sorption measurements. Microstructural changes due to hydrogen sorption were observed by scanning electron microscopy (SEM) in the imaging mode.

3.5.1. Synthesis of Electrospun Polyaniline Nanofibers

As with the chemically grown nanofibers, the polyaniline nanofibers (PANI-NF-ES) were grown by oxidative polymerization of aniline monomer at 0°C in an ice bath using ammonium persulfate as the oxidant in the presence of surfactant, though with slightly different conditions. Aniline, ammonium persulfate, dodecyl benzene sulfonic acid, acrylmethylpropyl sulfonic acid, and camphorosulfonic acid are used as received from Sigma-Aldrich. Sulfonic acid based surfactants as the dopant and ammonium persulfate as the oxidant were used in the present synthesis of polyaniline nanofibers (see flow chart in Figure 3.25).
Calculated quantities of aniline monomer (0.01mol) were mixed with 50mL of distilled water and stirred using magnetic stirrer for 10min. Meanwhile, calculated quantities of surfactant (0.75mol) and oxidant (0.01mol) were dissolved separately in distilled water and stirred for 10min in an ice bath. The surfactant solution was first added into the aniline monomer aqueous solution and then the previously cooled oxidant solution was added drop wise after which the mixture was allowed to react for 15hr in an ice bath.

Figure 3.25: Flow chart for the synthesis of electrospun polyaniline nanofibers.

Calculated quantities of aniline monomer (0.01mol) were mixed with 50mL of distilled water and stirred using magnetic stirrer for 10min. Meanwhile, calculated quantities of surfactant (0.75mol) and oxidant (0.01mol) were dissolved separately in distilled water and stirred for 10min in an ice bath. The surfactant solution was first added into the aniline monomer aqueous solution and then the previously cooled oxidant solution was added drop wise after which the mixture was allowed to react for 15hr in an ice bath.
The obtained polymer solution was then sprayed by the electrospun method schematically represented in Figure 3.26. In the electrospinning process, a high electric field is applied to the viscous polymer solution, held in a capillary tube, inducing a charge density on the liquid surface. The distance between the tip of the needle and the substrate was optimized to 20cm with a voltage to 15kV.

Mutual charge repulsion causes a force directly opposite to the surface tension. When the electric field is sufficiently high, the surface of the solution in proximity of the tip of the capillary tube elongates and forms a cone, named Taylor cone, which in turn
allows for the formation of randomly arranged nanofibers. These polyaniline nanofibers are collected and then dried in vacuum at room temperature for 24hr. Later, the vacuum-dried sample is annealed at 125°C for 3hr. Finally, the dried electrospun nanofibers are characterized and tested for the hydrogen uptake and release measurements.

3.5.2. Scanning Electron Microscopy Results

The microstructure of the as-synthesized PANI nanofibers was studied by Hitachi S800 scanning electron microscope (SEM). A fixed working distance of 5mm and a voltage of 5-25kV were used. Sample preparation for the SEM measurement was carried out inside the glove box by covering the sample holder with Parafilm® for minimal exposure to oxygen while transferring it to the secondary emission chamber. EDAX Genesis software was used to analyze the SEM images.

The electrospun nanofibers were successfully grown and can be seen in Figure 3.27. It is important to note that the nanofibers are more or less of the same dimensions. The average diameter is approximately 1.5μm, thereby not technically nanofibers. The fibers have very large aspect ratios, with lengths of several μm. Additionally, the fibers are very smooth in appearance, which is typical of electrospun grown fibers. No bulk PANI is visible from the SEM images, meaning that there is essentially a 100% yield of nanofibers.
3.5.3. FTIR Characterization Results

Fourier transform infrared (FTIR) spectra of electrospun polyaniline nanofibers (PANI-NF-ES) before hydrogen sorption are shown in Figure 3.28. The major bonding environment remains unchanged for both the pristine and hydrogenated PANI-nanofibrous structures. The presence of two bands in the vicinity of 1500cm⁻¹ and
1600 cm$^{-1}$ are assigned to the non-symmetric C6 ring stretching modes. The higher frequency vibration at 1600 cm$^{-1}$ is for the quinoid rings, while the lower frequency mode at 1500 cm$^{-1}$ depicts the presence of benzenoid ring units. Furthermore, the peaks at 1250 cm$^{-1}$ and at 800 cm$^{-1}$ are assigned to vibrations associated with the C-N stretching vibration of aromatic amine out of plane deformation of C-H of 1,4 disubstituted rings. The aromatic C-H bending in the plane (1167 cm$^{-1}$) and out of plane (831 cm$^{-1}$) for a 1,4 disubstituted aromatic ring indicates a linear structure.

Figure 3.28: FTIR spectra of bulk PANI and electrospun PANI nanofibers.
It is interesting to note that the quinoid ring stretch around 1650 cm\(^{-1}\) is significantly more pronounced relative to the other peaks and also shifted by 50 cm\(^{-1}\) as compared to the bulk polyaniline. Additionally, the benzenoid ring stretch around 1450 cm\(^{-1}\) is not as broad, but instead composed of several individual smaller peaks. Overall, the FTIR spectrum confirms that polyaniline in its emeraldine form is present, as all the major characteristic peaks are observed. However, there is a definite difference in the FTIR spectra of the electrospun nanofibers as compared to even the chemically grown nanofibers, which essentially had an identical spectrum to the bulk chemically grown polyaniline.

3.5.4. Thermogravimetric Results

The thermal stability of PANI nanofibers (both CM and ES methods) and the standard samples were characterized using TA Instrument’s simultaneous DSC and TGA (SDT-Q600) tool. A pre-weighed sample was loaded into the ceramic pan and covered with the ceramic lid inside the glove box to prevent moisture from getting into the sample during transfer. The ramp rate of 5°C/min was used for all the measurements. TA’s Universal Analysis 2000 software program was used to analyze the TGA and DSC profiles.

This TGA comparison is shown in Figure 3.29. The initial weight loss up to 15% is due to moisture that was absorbed during regular storage, since the polyaniline samples were all kept in sealed, but non-inert containers. After the release of the stored moisture, it can be seen that the PANI nanofibers (ES) are stable up to 150°C. This is to be expected, as the sample preparation includes annealing of the PANI at 125°C. A
temperature of higher than 150°C is not required any way as this would be too high a temperature for practical hydrogen storage. It should be noted, however, that the electrospun nanofibers are less thermally stable than the bulk or chemically grown counterparts. This is most likely due to the slight chemical differences that were observed during FTIR analysis, as previously mentioned.

![Thermogravimetric weight loss analysis of PANI samples in both bulk and nanofiber form.](image)

3.5.5. Hydrogen Sorption Results

The electrospun PANI nanofibers were subjected to both kinetic and PCT hydrogen measurements. Figure 3.30 demonstrates the hydrogen sorption life cycle kinetic curves of PANI-NF at two different temperatures, 30 and 100°C. As with previous
samples, the first hydrogen sorption measurement was performed at 30°C. However, when the nanofibers were subjected to a high hydrogen pressure of 80bar the hydrogen uptake was found to be less than 0.75wt.%, which is reminiscent of the bulk PANI samples. Additionally, there was no real desorption observed at this low temperature. It was therefore decided to perform the hydrogen measurements at various temperatures, and finally at 100°C (see Figure 3.30) hydrogen was absorbed. Surprisingly, a hydrogen uptake (A1 in Figure 3.30) of close to 11wt.% with rapid adsorption kinetics (approximately 95% hydrogen adsorption within 5-10min) was observed at 100°C. The desorption cycle of the same sample at 100°C then exhibited a hydrogen release of close to 8wt.%. This means that the other 3wt.% of hydrogen that was previously absorbed remained in the structure. Interestingly, the desorption (labeled as D1 in the figure) was composed of both a rapid hydrogen release step in which approximately 4wt.% was released within a few minutes and a slower hydrogen release step, accounting for another 4wt.% in approximately 45min. When the desorption equilibrium pressure was reached, hydrogen was reabsorbed into the sample. This time (A2) the full 8wt.% that was previously released was reabsorbed as rapidly as had occurred in the first hydrogen absorption. After this, only about 5wt.% hydrogen was released, again in a two-step process. Only this time the slower release step released only about 1wt.%, while the fast release regime remained at a capacity of 4wt.%. The full 5wt.% was then reabsorbed, though this time the kinetics of the hydrogen uptake decreased from about 5min to 25min.
After this cycle, the hydrogen capacity and kinetics dropped very quickly until finally virtually no hydrogen could be sorbed. The two-step release observed for the electrospun nanofibers is clearly evidence that both physisorption as well as chemisorption are taking place in the structure, exactly as was hoped at the outset of this work. The physisorption, again driven mainly by pressure changes, allowed for very rapid hydrogen release and uptake, while the slower second step during release was due to chemisorption, as more energy or more time in lack of a higher temperature, is required to release the hydrogen. The decrease in the hydrogen absorption capacity from cycle to cycle is clearly due to chemisorption of the hydrogen to the nanofibers. Once the
strong primary bond between the structure and the hydrogen is formed, it is virtually impossible to get the hydrogen back out without destroying the polymeric structure, as a temperature of more than 150°C has been shown to start the decomposition process.

Since only kinetic measurements were performed on the nanofibers and also in order to confirm the initial hydrogen uptake of 10wt.% that resulted from these measurements, a new batch of electrospun nanofibers was loaded into the PCT reactor. The hydrogen PCT absorption and desorption behavior of this batch is shown in Figure 3.31 and Figure 3.32, respectively. It is important to note that only PCT measurements were made on this batch and no kinetics measurements.

It was observed that virtually no hydrogen was absorbed or desorbed until a measurement temperature of approximately 50°C. After the initial hydrogen uptake of about 2.5wt.% at 50°C, the hydrogen capacity was found to increase with increasing temperature up to 125°C in various cycles as seen in Figure 3.31. At approximately 100 to 125°C a two fold increase of capacity (6-8wt.%)) was invariably obtained at various hydrogenation cycles. At the end of each adsorption PCT, desorption experiments were performed and the results are depicted in Figure 3.32. A hydrogen storage capacity of 2-10wt.% was obtained at temperature range of 50-125°C.
While it might appear that the amount of hydrogen that is released from the nanofibers is larger than the amount that is absorbed, this is in fact not the case. The data presented in Figure 3.32 is actually the amount of hydrogen released without taking the hydrogen itself into account which means that the numbers are slightly higher than they should be. It should be regarded as raw data. When one actually takes into account the weight of the material plus the weight of hydrogen stored in it, the maximum amount of hydrogen released changes from 8.5wt.% to approximately 7.5wt.%, thereby corresponding to the amount of hydrogen previously absorbed.
Figure 3.32: Hydrogen desorption PCT curves for the PANI-NF-ES at different temperatures.

The nanofibers that were tested for their capacity using PCT only are from the same synthesis batch and have absolutely no difference in terms of their chemical or physical composition to the batch of sample that was subjected only to kinetics measurements. However, the type of measurement that was employed made a large difference in capacity. As previously mentioned, hydrogen through physisorption or chemisorption is often based on diffusion. When one performs a kinetics measurement, the sample is subjected to either a high (80bar) or a low (0bar) hydrogen pressure. A PCT measurement, however, allows the sample to experience gradual pressure increase as opposed to this sudden pressure change. The hydrogen, therefore, has enough time to
diffuse through the material as the pressure is incrementally increased or decreased for absorption or desorption, respectively. While this has not affected any previous samples, the electrospun nanofibers were much more sensitive to the type of measurement. Most likely, this is due to the difference in chemical structure, as was shown by the FTIR spectrum in Figure 3.28.

3.5.6. Hydrogen Cycling Effects on Electrospun PANI Nanofibers

In order to confirm the hypothesis of chemisorbed hydrogen from the kinetic measurements, scanning electron microscopy was performed on the cycled nanofibers. The SEM image of the electrospun PANI nanofibers before hydrogen sorption, shown in Figure 3.33 (a) is compared to the SEM image of the nanofibers after hydrogen cycling, as shown in Figure 3.33 (b). It becomes evident that the density of the nanofibers was not altered significantly. The SEM micrographs of the hydrogenated and dehydrogenation samples show nanofibrallar swelling, breakage of fiber length and precipitations, which is most likely the cause for hydrogen loading saturation and poor cyclic reversibility. In addition to the swelling of the nanofibers due to the chemical bonding of hydrogen to the PANI, it is clear that the nanofibers also break into smaller pieces, thereby losing the high aspect ratio and returning more to the bulk form of polyaniline previously described.
After hydrogen cycling, FTIR was performed to observe any possible changes in the structure of the nanofibers. As can be seen from Figure 3.34, there is absolutely no change in the nature of the chemical bonds. The quinoid and benzenoid ring vibrations and stretches are all intact. Due to the nature of sample preparation, though, the intensity of the transmittance does vary between the measurements. The relative intensities of the individual peaks remains constant, though, indicating no chemical change after hydrogen interaction.
Figure 3.34: FTIR spectra of electrospun PANI nanofibers before and after hydrogen cycling.

3.5.7. Electrospun PANI Nanofibers Summary

Conducting polyaniline nanofibers were synthesized using chemical templating method followed by an electrospinning process. The FTIR spectra of these PANI nanofibers reveal the presence of two bands in the vicinity of 1500 cm$^{-1}$ and 1600 cm$^{-1}$, which are assigned to the non-symmetric C6 ring stretching modes. The lower frequency vibration at 1500cm$^{-1}$ is for the benzenoid rings, while the higher frequency mode at 1600cm$^{-1}$ corresponds to benzenoid to quinoid transition indicating the synthesized polymer was polyaniline in oxidized form. These nanofibers have been compared with their standard bulk counterpart and found to be stable up to 150°C, slightly lower than
their bulk chemical counterparts. It was found that electrospun polyaniline nanofibers have a high hydrogen uptake of 10wt.% at around 100°C in the first absorption run. However, in the consecutive hydrogenation and dehydrogenation cycles, the capacity diminishes. This is due to a combination of chemisorption and physisorption during kinetic measurements where the sample is exposed to varying extreme pressures. Eventually, the electrospun PANI nanofibers become saturated with hydrogen during kinetic loading. When the nanofibers are exposed to PCT measurements, though, where the pressure is either gradually increased or decreased, the nanofibers exhibit a reversible hydrogen storage capacity of 3-8wt.% at different temperatures. This is due to the fact that the hydrogen is given enough time to diffuse and reach local equilibrium at the varying pressures. Unfortunately, this also means that a larger time is required to either absorb or desorb the hydrogen. The surface morphologies before and after hydrogen sorption on these PANI nanofibers encompass significant changes in the microstructure such as nanofibrallar swelling and slight deterioration in the length of the fibers.

It was confirmed that the hydrogen data is reproducible with high hydrogen storage capacity of 3-8wt.% at different temperatures, as summarized in Table 3.1. From this table, it is discernible that the hydrogen capacity increases with an increase of temperature. However, in order to attain this higher capacity, the nanofibers need to be exposed to gradual pressure changes rather than be exposed to large pressure changes, as would be typical with kinetics measurements.
Table 3.1: Hydrogen sorption capacity of electrospun nanofibers at various temperatures and sorption cycles.

<table>
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<th>Cycle Number</th>
<th>Adsorption/Desorption</th>
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<th>Hydrogen Concentration (wt.%)</th>
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<td>100</td>
<td>6.5</td>
</tr>
<tr>
<td>8</td>
<td>Desorption</td>
<td>100</td>
<td>6.5</td>
</tr>
<tr>
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<td>Adsorption</td>
<td>50</td>
<td>3</td>
</tr>
<tr>
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<td>Desorption</td>
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</table>

3.6. Polyaniline Hydrogen Storage Summary

Polyaniline, in its emeraldine form, was successfully synthesized through chemical means. The bulk, or as synthesized form, as well as three different nanostructures of PANI were characterized for physical, chemical and hydrogen sorption characteristics. It was found that the inclusion of additives to the bulk form PANI had virtually no effect on its hydrogen sorption characteristics. Bulk PANI was found to have a hydrogen capacity of less than 0.5wt.% at a temperature of 100°C. It was observed that the capacity of hydrogen in this standard sample increased slightly with increasing temperature. This increase with temperature is due to the expansion of PANI, which in turn allows for the hydrogen to diffuse readily into the polymer. While others have claimed that standard PANI can absorb as much as 8wt.%, this was refuted by Panella et al., as well as this research.

The nanostructured PANI nanospheres, with an average diameter of 100nm, were synthesized by slightly modifying the chemical synthesis technique used to produce the standard PANI. FTIR analysis, however, shows that the nanospheres do possess the same chemical composition as the standard PANI. While an initial hydrogen uptake of 5.5wt.%
of hydrogen was observed at 30°C, the capacity of each consecutive desorption cycle was reduced by roughly 1wt.%, though the desorbed hydrogen was reabsorbed. Since the kinetics of hydrogen uptake were on the order of several hours, with slower kinetics for each consecutive cycle, it was found that the main driving force behind the hydrogen sorption of the nanospheres was chemisorption, most likely in the form of hydrogen reacting with unterminated bonds that were a result of the synthesis. Finally, a capacity of only 0.6wt.%, virtually identical to that of bulk PANI, was observed at a temperature of 90°C. SEM analysis showed that the repeated hydrogen cycling caused the nanospheres to swell after hydrogen reaction and also to agglomerate until it finally had an appearance reminiscent of bulk polyaniline. The interaction of hydrogen with the sample also led to the formation of microcracks, which are caused by the diffusion of hydrogen through the material.

By again slightly modifying the chemical synthesis technique, chemically grown PANI nanofibers were created. FTIR investigation again proved that the nanofibers were of the emeraldine form. The fibers had an average diameter of 250nm with varying lengths. The nanofibers were also characterized by a rough surface. Hydrogen cycling of the nanofibers showed that an initial capacity of 3-4wt.% was absorbed in less than 10min, while approximately 1-2wt.% hydrogen was released at room temperature. PCT measurements performed on the nanofibers showed that roughly 3.5wt.% hydrogen was reversibly stored in the nanostructures. The initial hydrogen absorption showed a hydrogen plateau pressure around 30bar, indicative of chemisorption. Through repeated cycling, however, the plateau pressure region disappeared, though the capacity remained unchanged at 3.5wt.% for many cycles. SEM analysis of the chemically grown
nanofibers after hydrogen cycling showed no evidence of the initial nanofibrous morphology. Instead, the fibers had virtually disappeared and a rather porous material remained. Surface area analysis revealed that the surface area remained unchanged after hydrogen cycling. Unlike the nanospheres, whose structure also disappeared, the nanofibrous nature of the PANI allowed for it to agglomerate into a porous material, thereby losing the initial physical characteristics, but still maintaining the surface area. This is an important factor for hydrogen storage materials, as was previously discussed.

Finally, electrospun nanofibers were investigated for their hydrogen performance. By using a well known electrospinning technique, the nanofibers were synthesized with average diameters of 1.5μm and lengths of several microns. The nanofibers were, unlike the chemically grown nanofibers, rather smooth. While FTIR again confirmed the presence of the typical benzenoid and quinoid rings of emeraldine base PANI, it was observed that the quinoid peak was much larger in relation to the other FTIR peaks. The quinoid peak was also shifted by approximately 50cm⁻¹, making it unique among all the polyaniline structures investigated. Hydrogen kinetic measurements on the electrospun nanofibers at 30°C showed no hydrogen sorption, but absorption at 100°C revealed a very promising initial uptake of over 10wt.% in less than 10min. The desorption that followed showed an almost instantaneous release of 4wt.% hydrogen and another 4wt.% with much slower kinetics. Each consecutive absorption cycle reabsorbed the previously released hydrogen with slightly lower kinetics, but still in a matter of minutes rather than hours. The desorption capacity decreased by roughly 2wt.% for each cycle, but the fast hydrogen desorption remained until finally, after approximately 3 absorption / desorption
cycles, virtually no hydrogen was sorbed. While the fast kinetics of the absorption measurements clearly indicate that physisorption is taking place, the desorption cycles are clearly a combination of both chemisorption (slower kinetics) and physisorption (faster kinetics). The combination of physisorption and chemisorption is also evidenced by the breakage and swelling of the nanofibers, though overall they do remain intact. Hydrogen PCT measurements on a new batch of this sample, however, revealed that approximately 8wt.% hydrogen could be reversibly stored in the electrospun nanofibers as long as the pressure was gradually increased or decreased. This slow exposure to hydrogen is essential in that the nanofibers are not exposed to pressure extremes, which can result in the destruction of the nanofiber morphology. Additionally, the hydrogen is allowed enough time to diffuse into the material and bond. While this method of storage requires a higher amount of time, it is still the most preferential method of storing hydrogen in polyaniline. The capacity of 8wt.% along with the relatively low temperature of 100°C makes the electrospun polyaniline an ideal candidate for hydrogen storage.

It appears that the main factor in storing hydrogen in polyaniline is less the surface area, as was previously thought for polymers, but in fact lies more in the exact chemical composition. Unterminated bonds, which provide chemisorption sites for hydrogen are an excellent initial hydrogen storage site, but require an amount of energy that is simply too high for practical purposes, therefore requiring high temperatures that would in fact destroy the chemical structure of the polyaniline. The relative intensity of the quinoid ring vibration with respect to the other FTIR peaks appears to play a vital role in the hydrogen storage behavior of polyaniline. Also, the form of hydrogen storage, namely exposure of the material to hydrogen, is extremely important when dealing with
relatively weak materials such as PANI. Though it might require more time to store and release the hydrogen, a gradual pressure change is essential to maintaining the hydrogen characteristics of the material.

The work on these polymers is the first to investigate various nanostructures of polymers at temperatures above 77K. A comparison of the results obtained from this research with other work that was previously conducted on hydrogen storage in polymers is shown in Figure 3.35. The significant results described within this chapter are highlighted in red boxes, showing a closing in on the DOE goals with the PANI nanofibers produced via electrospinning method almost meeting the DOE targets.

Figure 3.35: Comparison of novel PANI results with previous polymer hydrogen storage research.
Chapter 4 - Complex Hydrides LiBH₄/LiNH₂/MgH₂

4.1. Introduction

As briefly mentioned in chapter 1, only complex hydrides composed of elements with less than an average molecular weight of 51.8g/mol (Cr) provide a sufficient enough gravimetric hydrogen density to meet or exceed the DOE targets for a practical hydrogen storage system. The group I, II and III light metals, such as Li, K, Be, Na, Mg, B, Ca and Al are excellent candidates as they form a large variety of metal hydrogen complexes. The most common of these metal hydrogen complexes consists of borohydride (BH₄⁻), amide (NH₂⁻) and alanate (AlH₄⁻) ions, which are accompanied by cations such as Li⁺ or Na⁺. The hydrogen is generally stored in the corners of a tetrahedron within these systems. Some previously investigated materials in this class are listed in Table 4.1.

Table 4.1: Physical characteristics of some previously investigated complex hydrides.

<table>
<thead>
<tr>
<th>Material</th>
<th>Molecular Weight (g/mol)</th>
<th>Density (g/cm³)</th>
<th>Melting Temperature (°C)</th>
<th>H₂ Release Temperature (°C)</th>
<th>H₂ Capacity (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiBH₄ [60]</td>
<td>21.784</td>
<td>0.66</td>
<td>268</td>
<td>380</td>
<td>18.4</td>
</tr>
<tr>
<td>NaBH₄ [61]</td>
<td>37.83</td>
<td>1.074</td>
<td>505</td>
<td>400</td>
<td>10.6</td>
</tr>
<tr>
<td>LiAlH₄ [61]</td>
<td>37.95</td>
<td>0.917</td>
<td>125</td>
<td>125</td>
<td>9.5</td>
</tr>
<tr>
<td>KBH₄ [61]</td>
<td>53.94</td>
<td>1.178</td>
<td>585</td>
<td>500</td>
<td>7.4</td>
</tr>
<tr>
<td>NaAlH₄ [62]</td>
<td>54.0</td>
<td>1.27</td>
<td>178</td>
<td>210</td>
<td>7.4</td>
</tr>
<tr>
<td>Mg₂NiH₄ [63]</td>
<td>111.3</td>
<td>2.72</td>
<td></td>
<td>280</td>
<td>3.6</td>
</tr>
<tr>
<td>Mg₂FeH₆ [24]</td>
<td>110.5</td>
<td>2.72</td>
<td></td>
<td>320</td>
<td>5.4</td>
</tr>
<tr>
<td>Mg₃MnH₇ [24]</td>
<td>134.9</td>
<td>2.30</td>
<td></td>
<td>280</td>
<td>5.2</td>
</tr>
<tr>
<td>BaReH₉ [24]</td>
<td>332.5</td>
<td>4.86</td>
<td></td>
<td>100</td>
<td>2.7</td>
</tr>
</tbody>
</table>
Most alanates are extremely stable and often decompose in two- or three-step reactions, limiting the amount of hydrogen that can be released, since often a higher temperature is required for the release of hydrogen from the second step. Borates are also extremely stable and therefore often require high temperatures for hydrogen release, but do so in a one-step reaction, thereby eliminating the need for extremely high temperatures and also increasing the kinetics of hydrogen release.

Lithium borohydride (LiBH₄) and lithium amide (LiNH₂) were chosen as the two primary hydride materials to be investigated for hydrogen storage in the form of complex hydrides. These two materials were chosen due to their high gravimetric hydrogen densities and their initial investigation for hydrogen storage. LiBH₄ has been studied extensively for its chemical properties as well as its hydrogen storage characteristics. It has been determined that LiBH₄ possesses an orthorhombic crystal structure [64], as is shown in Figure 4.1. Each Li⁺ ion is surrounded by four BH₄⁻ ions in a tetrahedral configuration. The gravimetric hydrogen density of LiBH₄ is 18.5wt.%, significantly more than the material requirements set forth by the DOE. While hydrogen is generally not released until above 470°C [65], it was found that additives can reduce the hydrogen release temperature to as low as 200°C as is the case for SiO₂ [66], but the kinetics of the reaction are very slow, making the material impractical for hydrogen storage use in automobiles.
Figure 4.1: Boron (top) and lithium (bottom) coordinations in orthorhombic LiBH₄ at room temperature [64].

As early as 1910, it was found that Li₃N reacts with hydrogen to form LiNH₂ [67], though LiH is also formed as a by-product. LiNH₂ has a theoretical hydrogen capacity of 8.1wt.% and releases hydrogen after melting at a temperature of 380°C. While the temperature is too high for hydrogen release, there has been significant improvement in the hydrogen behavior of LiNH₂ by using either catalysts to reduce the hydrogen release temperature or by destabilizing LiNH₂ with other compounds. Additionally, the release of ammonia (NH₃) poses a large problem since NH₃ can poison fuel cells. However, the formation of ammonia can be suppressed through the addition of either catalysts or by destabilizing LiNH₂ with other compounds. It was shown, for example, that the addition of LiH to LiNH₂ can suppress any ammonia formation. This is accomplished due to the LiH reacting with NH₃, which is a very fast reaction [68]. Furthermore, the temperature of hydrogen release of LiNH₂ has been reduced to approximately 150-250°C through the addition of TiCl₃ [69].
There has been a lot of work in finding complex hydrides for hydrogen storage, the most important and recent of which are summarized in Figure 4.2 [66, 70-95]. While this figure certainly represents only a small portion of research performed on these systems, it nevertheless clearly illustrates that most materials either require temperatures that are too high for practical use or simply have a capacity that is too low. This figure summarizes mainly borohydride- and amide-based materials for hydrogen storage, as this is the main focus of this dissertation.

![Figure 4.2: Hydrogen sorption capacity and temperature of selected complex hydrides and chemical hydrides with DOE target range highlighted.](image)

While it appears that there are several materials that would meet the DOE guidelines, the amidoborane samples [91], such as LiNH₂BH₃ or NaNH₂BH₃ are non-
reversible, thereby making the systems impractical for mobile use, as required by the DOE. Mg(NH$_2$)$_2$ + 2MgH$_2$ was found to release 7.6wt.% around room temperature during ball milling [73], but exhibited such a low enthalpy that a high pressure (much higher than that required by the DOE) would be required to rehydrogenate the material, thereby also making the material impractical for use as a reversible hydrogen storage system. A promising system for hydrogen storage has been magnesium amide (Mg(NH$_2$)$_2$) with a capacity of between 5.6wt.% and 9.2wt.% [79, 82, 94], though all of these systems require temperatures of close to 200°C with a reduction in capacity directly proportional to the reduction in temperature.

By combining the advantages of some of these systems, namely the borohydride family of materials with the magnesium amide systems, it is thought that a combinatorial effect can be achieved with a reduction in hydrogen sorption temperature, reversibility, as well as a high hydrogen capacity. The overall goal of the investigation of complex hydrides for hydrogen storage is to reduce the hydrogen release temperature, which can be accomplished by either reducing the particle size, as is the case for MgH$_2$ or by destabilizing the material through the addition of catalysts or other additives. Ball milling is the chosen processing technique, as this combines both chemical and mechanical synthesis of the material. By ball milling, a homogenous mixture with reduced particle size can be achieved, as schematically indicated by Figure 4.3. The parent compounds are combined in the ball mill container and through milling at high speeds the materials grind each other down to smaller particle size and produce a homogenous mixture, possibly with a new chemical composition.
Furthermore, by combining several materials, whether they are in small quantities, so as to count as a catalyst, or in larger quantities, to be considered destabilizers, the activation energy for hydrogen release or absorption can be altered and ideally brought to a point where a low temperature is enough to release the hydrogen. When a material is destabilized, it can react with the additive during dehydrogenation to form a new compound, one that requires a lower energy, as schematically shown in Figure 4.4. An additive, B, can allow the hydrogenated material, A, to form an intermediate compound, AB, while releasing hydrogen, thereby lowering the activation energy required for desorption. Various nano additives are investigated for the complex hydride LiBNH as well as MgH$_2$, which is added in larger quantities. The details are described in the specific upcoming sections, as appropriate.
4.2. Quaternary Complex Hydride LiBH₄/LiNH₂ (LiBNH)

It has previously been shown that LiBH₄ combines with LiNH₂ to form a new quaternary structure when either heated for several hours or milled for several hours. This new quaternary structure, identified as Li₄BN₃H₁₀ is formed when LiNH₂ and LiBH₄ are combined in a 3:1 molar ratio [84]. While the material was found to release approximately 6wt.% hydrogen at a temperature of well over 250°C, it was also observed that the structure is non-reversible, therefore disqualifying it as a practical hydrogen storage system. Since this new structure exhibits hydrogen release at a temperature lower than its parent compounds, it was chosen as the ideal material for investigation, as the addition of various materials as well as various processing conditions had not been previously reported.

4.2.1. Synthesis of the Quaternary LiBNH

As mentioned in chapter 2, mechano chemical synthesis, or ball milling, is used to synthesize all complex hydrides investigated within this chapter. Since ball milling has
many variables, such as rotational speed, sample mass to ball ratio, the type of purge gas (or lack thereof), as well as milling duration, these parameters had to be optimized before commencing milling.

The milling speed was kept at a constant speed of 300 rpm, since this is the most commonly used milling speed employed and therefore the sample properties can be easily compared with other complex hydrides synthesized. The milling container used is made of stainless steel and has a volume of 80mL and contains 30 10mm diameter stainless steel balls. It was found that a total sample mass of 2g was the optimum amount for milling. This amount was chosen as it was found that more than 2g of sample leads to agglomeration of sample in the mill, producing a smaller yield and incomplete mixing. Additionally, it was found that using an Ar/H₂ (95%/5%) gas mixture with which the container was purged before milling commenced and then every two hours during milling further led to a reduction in agglomeration of sample, thereby increasing the yield to virtually 100%. The use of this Ar/H₂ gas mixture also enables the synthesis of larger sample masses, up to 4g, though the 2g limit was kept to keep the synthesis parameters constant.

Finally, the most important milling variable was the milling time. If a sample is milled for a short time, the parent compounds only physically mix, which is used for catalyst addition, but there is no chemical reaction. Since it was desired to produce a new chemical structure to eliminate the poor hydrogen sorption properties of LiBH₄ and LiNH₂, optimal milling duration was needed. Figure 4.5 shows the effect of milling duration on the quaternary material investigated. The bottom two curves show the XRD spectrum of the parent compounds LiBH₄ and LiNH₂ in their as-received (non-purified)
form. After milling $2\text{LiNH}_2$ with $\text{LiBH}_4$ for 30min, a new peak at approximately $29^\circ$ and $48^\circ$ emerge, indicating the formation of a new chemical structure. However, $\text{LiNH}_2$ is still clearly visible. Therefore, the milling duration was increased to 1hr and finally to 5hr, as the 1hr milling still showed the presence of $\text{LiBH}_4$. After 5hr of milling, there was no trace of the parent compounds, but new peaks were observed, verifying the formation of a new chemical structure. A milling duration of more than 5hr did not yield any changes in the chemical structure of the compound, and therefore would only lead to more costly and time-intensive synthesis.

![Figure 4.5: XRD pattern comparing parent compounds LiBH$_4$ and LiNH$_2$ for different milling durations.](image)

Figure 4.5: XRD pattern comparing parent compounds LiBH$_4$ and LiNH$_2$ for different milling durations.
Fourier transform infrared spectroscopy was used to further characterize the effect of milling duration on the samples. The parent compounds LiBH$_4$ and LiNH$_2$ are shown as the top two data sets in Figure 4.6. The FTIR spectrum of LiBH$_4$ shows BH$_2$ deformation bands at around 1100 and 1200 cm$^{-1}$ and B-H bonding stretches around 2300 cm$^{-1}$. LiNH$_2$ has both symmetric and asymmetric amide stretches at around 3250 and 3300 cm$^{-1}$. After milling for 5 hr, the new quaternary structure still exhibits the BH$_2$ deformation bands, the B-H bond stretch and the symmetric and asymmetric amide stretch. This indicates that the new structure that is formed, a new chemical compound as was shown in Figure 4.5, is composed of borohydride and amides, but is a new chemical structure, meaning neither of the parent compounds are present in their initial form. Additionally, it can be seen that the B-H stretch peak widens significantly with increased milling time. This is advantageous to hydrogen sorption as there is essentially more space for the hydrogen to bond to the material.
4.2.2. Hydrogen Characteristics of the Quaternary LiBNH

The optimum quaternary structure, referred to from here on out as LiBNH, which consists of a 2:1 molar ratio of LiNH$_2$:LiBH$_4$, ball milled for 5hr, was investigated for its hydrogen sorption characteristics. As Figure 4.5 indicates, there is no trace of either of the parent compounds, LiBH$_4$ and LiNH$_2$, present and instead a new quaternary phase consisting of Li, B, N, and H was formed.
After following the typical hydrogen sorption measurement procedures outlined in chapter 2, the hydrogen desorption and absorption of the structure was investigated starting at a temperature of 175°C. As can be seen from Figure 4.7, there is no significant hydrogen release until approximately 250°C. Only approximately 0.5wt.% of hydrogen is released at 175°C and 200°C, while 0.7wt.% of hydrogen is released at approximately 225°C. Finally, at 250°C, about 3.5wt.% of hydrogen is released from the material. It is interesting to note the presence of two hydrogen plateau regions, which most likely results from the release of hydrogen from borohydride and amide part of the new quaternary structure.
Each desorption measurement was followed by an absorption PCT measurement at the same temperature. However, as can be seen from Figure 4.8, only less than 0.3 wt.% of hydrogen could be reabsorbed, with more absorption occurring at lower temperatures, as should be expected. This is because a higher temperature means that the material contains more energy, and therefore the hydrogen bonds are broken. Because of the requirements of the DOE, it was decided not to investigate the hydrogen sorption of any material discussed as part of this work above 250°C. Repetition of these measurements with other batches yielded the same results as those presented in Figure 4.7 and Figure 4.8. This means that the quaternary structure that was formed is non-reversible, thereby making it unusable for automotive applications. Additionally, the
kinetics of absorption, as can be seen in Figure 4.9, are too slow to be useful. It takes almost 2 hours to reabsorb only 0.7 wt.% of hydrogen.

![Figure 4.9: Absorption kinetics at 250°C of LiBNH after dehydrogenation.](Image)

4.2.3. Activation Energy of the Quaternary LiBNH

To understand why this new quaternary structure does not reversibly store hydrogen, it was decided to investigate the activation energy of the structure. The TPD was used along with various heating rates to obtain peak data of the material which could then be correlated using Kissinger's method, as described in chapter 2, to the activation energy of the material. Figure 4.10 shows the data obtained for heating rates of 1, 5, and 10K/min. It can be seen that there is no significant hydrogen release until approximately
250°C, which verifies the PCT data previously discussed. As is typical of increased heating rates, the peak of the hydrogen evolution shifts upward as the material does not have enough time to reach localized equilibrium.

Figure 4.10: TPD plot of the quaternary LiBNH for heating rates of 1, 5, and 10K/min.

The temperature of the peak of each heating rate was then correlated to the activation energy by plotting the \( \ln(\text{heating rate/peak temperature}) \) versus \( 1/\text{temperature} \), as can be seen in Figure 4.11. This is based on Kissinger’s equation, which relates the heating rate to the activation energy of sample as:

\[
\frac{d}{d\left(\frac{1}{T_m}\right)} \ln\left(\frac{\beta}{T_m^2}\right) = -\frac{E}{R} \tag{4.1}
\]
where $\beta$ is the heating rate of the sample in K/min, $T_m$ is the peak temperature in K, $E$ is the activation energy of the hydrogen release, and $R$ is the gas constant. By obtaining the slope of the best fit linear line, it was found that the activation energy for the hydrogen release of the quaternary structure is approximately 145kJ/mol. As was previously described, this activation energy is too high to allow for reversible hydrogen storage at usable temperatures. Therefore, the new quaternary structure had to be destabilized further. As the ball milling was already optimized, it was decided to investigate various nano sized additives to the material, as is described in the next section.

Figure 4.11: Kissinger plot of the quaternary structure LiBNH.
4.2.4. Destabilization of the Quaternary LiBNH with Nano Sized Additives

Since the activation energy for the release of hydrogen of the quaternary structure was found to be 145kJ/mol, a value which is too high for practical reversible hydrogen sorption at usable temperatures, it was decided to investigate the effect of various nano sized additives to the quaternary structure. Since particle size plays an important role in hydrogen sorption, as previously mentioned, it was decided to use pre-prepared nano sized additives such as nickel (Ni) and zinc (Zn) in various concentrations as well as the co-addition of these additives. Initially, TGA measurements were performed to get an insight into the role that these nano additives have on the quaternary structure and their hydrogen release.

Figure 4.12 shows the TGA and DSC data of 1, 3, and 5 mol% of Ni. It can be seen that the amount of catalyst is important on the hydrogen release temperature of the material. While the DSC data does not show significant difference, it can be seen that the addition of 5mol% of Ni provides for a slight decrease in hydrogen release temperature, as compared to 1 and 3mol%. All samples were prepared in the same manner - the nano additive was added to the bulk quaternary structure in the previously described manner for synthesis and, after purging with an Ar/H₂ mixture, milled for 15 minutes. Since obtaining reliable TGA data proved difficult due to contamination of the material with either oxygen or moisture, it was decided to use TPD to obtain information about the effect of additives to the hydrogen storage material for any further materials.
One of the first samples that was investigated for its hydrogen storage behavior was the quaternary structure (LiBNH) with 3mol% of nano sized Zn. Figure 4.13 shows the desorption of hydrogen from the material with increasing temperature. Each desorption measurement was followed by a PCT absorption measurement at the same temperature. It can be seen that virtually no hydrogen is released from the material until approximately 250°C. At this temperature, however, 6wt.% of hydrogen is released in a three step reaction, compared to 3.5wt.% in a two-step reaction as was found for the quaternary structure, shown in Figure 4.7. After this desorption, however, no hydrogen is reabsorbed, as can be seen in Figure 4.14. Conversely, no significant amount of hydrogen
is released in subsequent cycles, as shown by the second desorption PCT measurement in Figure 4.13.

Figure 4.13: Hydrogen PCT desorption of LiBNH with 3mol% nano Zn.
Figure 4.14: Hydrogen PCT absorption of LiBNH with 3mol% nano Zn.

According to the TGA optimization of nano sized Ni in Figure 4.12, the effect of the addition of 5mol% of nano Ni on the quaternary LiBNH was investigated. Again, the hydrogen sorption measurements were investigated starting at 100°C, with each desorption followed by an absorption measurement at the same temperature. Figure 4.15 shows that the addition of 5mol% of Ni greatly reduces the temperature required for hydrogen release. At 175°C approximately 5.6wt.% of hydrogen is released. As can be seen, though, two separate desorption measurements had to be performed. This is because the maximum time allowed for a desorption measurement is 24hr. Hence, while the temperature of hydrogen release was reduced from 250 to 175°C, the kinetics were also significantly reduced to well over 24hr for the desorption of hydrogen. However, it can
be seen that, compared to the addition of Zn, the hydrogen release is performed in a one-step process with a plateau pressure less than 5bar of hydrogen pressure. As with the previous quaternary samples, however, there is virtually no reabsorption of hydrogen within the material.

Since Ni not only reduced the temperature for hydrogen release by approximately 75°C, but also reduced the kinetics of hydrogen release, it was decided to investigate the additive effect of using both nano Ni and nano Zn. Initially, 3mol% of nano Zn and 3mol% of nano Ni were added to the quaternary structure. Figure 4.16 shows that the addition of 3mol% of nano Ni and 3mol% of nano Zn does not improve the temperature of hydrogen release, as is seen for nano Ni. However, the three-step hydrogen release that
was observed with just nano Zn is preserved, though the plateau pressures are reduced from 60, 35, and 2bar to 25, 18, and 5bar of hydrogen pressure, an important improvement. However, the addition of Ni along with Zn did allow for almost 8.5wt.% of hydrogen to be released – a significant improvement compared to any of the other materials. Despite this improvement, though, the material is still not able to reabsorb the hydrogen that is released initially. The reabsorption of hydrogen essentially followed that of the quaternary structure, as depicted previously in Figure 4.8 or that of the Zn-doped quaternary that was shown in Figure 4.14.

Figure 4.16: Hydrogen PCT performance of LiBNH with 3mol% nano Ni and 3mol% nano Zn.
Since a concentration of 5mol% Ni was found to greatly reduce the temperature for hydrogen release, while allowing for a one-step hydrogen release at about 5bar, another sample, this time with 5mol% Ni and 3mol% Zn was investigated for its hydrogen characteristics. Figure 4.17 shows that hydrogen is released in a one-step reaction at approximately 3bar of hydrogen pressure with a total capacity of 6.5wt.% at 200°C. Hence, the larger amount of Ni took over the hydrogen performance of the material and allowed for the reduction of temperature from 250 to 200°C while the Zn allowed for the increased kinetics, as compared to the quaternary structure containing only nano Ni.

Figure 4.17: Hydrogen PCT performance of LiBNH with 5mol% nano Ni and 3mol% nano Zn.
4.2.5. Quaternary LiBNH Summary

Through XRD measurements, it was found that a 2:1 molar ratio of LiNH$_2$:LiBH$_4$ formed a new quaternary compound after approximately 5hr of ball milling. Furthermore, a purge with Ar/H$_2$ (95%/5%) before milling, as well as every 2hr of milling ensures that the resultant material does not agglomerate, thereby producing a homogenous yield of sample, provided that only 2g of sample are milled at a time.

PCT hydrogen sorption measurements of the quaternary structure, LiBNH, indicate that a temperature of 250°C is required to release approximately 4wt.% of hydrogen in a two-step release at pressure of 25 and 15bar. The addition of 5mol% nano sized Ni was shown to lower the hydrogen release temperature from 250 to 175°C in a one-step release at a pressure of 5bar, but with kinetics that require more than 24hr to release the hydrogen. The addition of 3mol% nano sized Zn had no effect on the temperature, but allowed for a release of 6wt.% of hydrogen at 250°C at the cost of hydrogen desorption kinetics. Finally, the addition of 3mol% nano sized Zn and 3mol% nano sized Ni enabled the quaternary structure to release 9wt.% of hydrogen at 250°C in a three-step process. The main hydrogen results of the quaternary structure are summarized in Table 4.2 and in Figure 4.18.

Table 4.2: Hydrogen performance of quaternary LiBNH with and without nano Zn and nano Ni.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Hydrogen release temperature (°C)</th>
<th>Hydrogen release pressure (bar)</th>
<th>Hydrogen capacity (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>250</td>
<td>25, 15</td>
<td>4</td>
</tr>
<tr>
<td>5mol% Ni</td>
<td>175</td>
<td>5</td>
<td>5.8</td>
</tr>
<tr>
<td>3mol% Zn</td>
<td>250</td>
<td>60, 35, 1</td>
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<tr>
<td>3mol% Zn + 3mol% Ni</td>
<td>250</td>
<td>28, 18, 5, 1</td>
<td>9</td>
</tr>
<tr>
<td>3mol% Zn + 5mol% Ni</td>
<td>200</td>
<td>2</td>
<td>5.2</td>
</tr>
</tbody>
</table>
4.3. Destabilization of LiBH$_4$/LiNH$_2$ with MgH$_2$

Magnesium hydride, MgH$_2$, has a theoretical hydrogen capacity of 7.6wt.%, an ideal value for practical hydrogen storage applications. However, a temperature of 350 to 400$^\circ$C is required to release hydrogen from this material. Additionally, the kinetics of release and uptake of hydrogen are too slow for practical use [96]. It was found that hydrogen pressure change on MgH$_2$ is the driving force for hydrogen absorption [97]. This means that a higher pressure leads to a higher rate of absorption of hydrogen by pure magnesium. However, a limiting factor in the rate of hydrogen, as well as the final capacity of hydrogen absorbed, is the formation of a surface shell of magnesium hydride,
essentially a diffusion barrier layer, which prevents any further hydrogen uptake. This is found to especially be the case for pressures above 30bar, where the rate of hydrogen uptake is found to be a maximum [97]. The hydrogen absorption kinetics were found to be controlled by diffusion of hydrogen atoms [98], especially the diffusion of hydrogen in the hydride-metal interface. If the hydride layer exceeds 30 to 50μm, hydrogen diffusion, and therefore uptake, is found to decrease due to the coalescence of the hydride nuclei on the magnesium surface which form a compact hydride layer [99].

In order to prevent this passivation layer, which not only slows the uptake of hydrogen, but also prevents full hydrogenation of the magnesium, the particle size of MgH₂ can be reduced so as to prevent the formation of this hydride layer. If the particles are smaller than 30μm, the hydrogen diffusion should therefore be able to continue allowing for more rapid and full hydrogen uptake of magnesium. As already mentioned, the use of ball milling allows for the reduction of particle sizes. Hence, it was decided to investigate the particle size reduction and some basic thermal studies of MgH₂ that result from this purely physical aspect of mechano chemical synthesis. In order to keep the MgH₂ hydrided during the milling process, the sample was kept in a hydrogen atmosphere by purging the sample holder with hydrogen before milling as well as every 2hr of milling for 15min.

Solid state synthesis pertaining to the destabilization of LiBH₄ and LiBH₄/LiNH₂ [100] with MgH₂ has been found to enhance the reversible hydrogen storage characteristics. The multinary complex hydride Li-Mg-B-N-H possesses a theoretical hydrogen capacity of approximately 8 to 10wt.%. However, it has been reported that only about 3wt.% of hydrogen was reversibly released between 160-200°C [101, 102]. It was
reported that the MgH$_2$ acts as a catalyst and assists in self-catalyzing the material to release hydrogen with three main reactions:

\[ \sim 175^{\circ}C: 2\text{Li}_4\text{BN}_3\text{H}_{10} + 3\text{MgH}_2 \rightarrow 3\text{Li}_2\text{Mg(NH)}_2 + 2\text{LiBH}_4 + 6\text{H}_2 \quad (4.2) \]

\[ \sim 200^{\circ}C: \text{Mg(NH)}_2 + 2\text{LiH} \rightarrow \text{Li}_2\text{Mg(NH)}_2 + 2\text{H}_2 \quad (4.3) \]

\[ \sim 300^{\circ}C: 3\text{Li}_2\text{Mg(NH)}_2 + 2\text{LiBH}_4 \rightarrow 2\text{Li}_3\text{BN}_2 + \text{Mg}_3\text{N}_2 + 2\text{LiH} + 6\text{H}_2 \quad (4.4) \]

Keeping these aspects in view, the current study aims to develop high capacity nanocomposite multinary hydrides (e.g. Li-Mg-B-N-H) by an inexpensive mechano-chemical process. The effects of the processing technique used to create the multinary hydrogen storage system have so far not been investigated. Therefore, the effects of commercial and nanocrystalline forms of MgH$_2$ on the multinary hydride structure formation and overall hydrogen decomposition characteristics are investigated to obtain a better understanding of the effects that processing conditions have on the hydrogen performance of the material. Additionally, the synergistic effects of nanocrystallinity on these hydrides have been investigated with a view to establish structure-property relations. Extensive analytical tools, as well as activation energy evaluations, have been employed to obtain insights into the nanocrystalline enhancement of the hydrogenation properties in these solid state multinary hydrides.

4.3.1. Synthesis of the Multinary Hydrides

The parent compounds, LiBH$_4$ and LiNH$_2$, were purchased from Sigma Aldrich with a purity of at least 95%, while MgH$_2$ was obtained from Alfa Aesar with a purity of at least 98%. All materials were kept in the inert atmosphere of the glove box and used without further purification. The investigated samples were created in 4g batches with a
constant molar ratio of 2LiNH\textsubscript{2}:LiBH\textsubscript{4}:MgH\textsubscript{2}, while taking into account the purity of the parent compounds, by employing high energy ball milling (Fritsch Pulverisette 6) for 5hr at 300rpm with intermittent hydrogen/argon (5%/95%) purges for 20min before milling and after 2 and 4hr. This was done to ensure that as little hydrogen as possible was released during the milling process and to reduce the agglomeration of the hydride that occurs when pure hydrogen is used as compared to the hydrogen/argon mixture, as was previously mentioned. The MgH\textsubscript{2} was either added as received or was added as a so-called nano MgH\textsubscript{2}. The nano MgH\textsubscript{2} (nMgH\textsubscript{2}) was created by ball milling the commercial MgH\textsubscript{2} (cMgH\textsubscript{2}) for 12hr with intermittent hydrogen/argon purges every 2hr. This ensured the reduction of particle size as well as the decrease in hydrogen release temperature, as previously reported [96]. The two main processing schemes that were used are shown in Figure 4.19. The first processing scheme was to add all parent compounds and mill for 5 or 10hr using either commercial or nano MgH\textsubscript{2}. This is the scheme that is generally used in reported literature and the materials serve as a sort of reference material. The second processing scheme was to first create the quaternary structure Li\textsubscript{4}BN\textsubscript{3}H\textsubscript{10} (referred to as LiBNH in the rest of the text) by milling LiBH\textsubscript{4} with 2LiNH\textsubscript{2} for 5hr and then adding either commercial or nano sized MgH\textsubscript{2}, after which the quaternary and the MgH\textsubscript{2} were milled for an additional 5hr. All milling was carried out in an inert atmosphere and the samples were purged with the hydrogen/argon mixture every 2hr. In total, five different samples were created. The samples are referred to in this chapter according to the naming convention shown in the bold boxes of Figure 4.19.
4.3.2. X-ray Diffraction Results

Figure 4.20 shows the XRD pattern comparing the five differently processed complex hydrides. The parent compounds, LiBH$_4$, LiNH$_2$, as well as both commercial and nano MgH$_2$ are in the lower half of the figure as a reference. The peak around 21° is from the Parafilm® used to protect the samples during measurement. Neither LiBH$_4$ nor LiNH$_2$ peaks are observed in any of the five samples. 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 Li$_4$BN$_3$H$_{10}$ [84]. The addition of commercial MgH$_2$ does not cause the formation of a new complex structure, but instead indicates that the quaternary structure is preserved, while the MgH$_2$ simply intermixes with the material. When the nano sized MgH$_2$ is added
to LiBH₄ and LiNH₂ or to the quaternary LiBNH, the MgH₂ peaks are barely picked up by the XRD. This indicates that the small size of the MgH₂ 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 LiNH₂ and LiBH₄. All samples are a physical, rather than a chemical, mixture of the quaternary structure LiBNH with MgH₂.

Figure 4.20: XRD profile of the five differently processed materials as well as the parent compounds, LiBH₄, LiNH₂, commercial MgH₂, and nano MgH₂.

4.3.3. FTIR Characterization Results

The five differently processed samples were characterized using FTIR to obtain information about the B-H and NH₂ stretches and BH₂ deformation, as seen in Figure
4.21. The data clearly shows that the amide, NH$_2^-$, and borohydride, BH$_4^-$, anions remain intact, as observed previously for the quaternary LiBNH samples [103]. The peaks of the symmetric and asymmetric amide anions are shifted from the expected 3312 and 3259cm$^{-1}$ to 3302 and 3244cm$^{-1}$, respectively. Furthermore, the peak around 1560cm$^{-1}$ is characteristic of the amide ion. The B-H stretches, usually found at 2225, 2237, 2293, and 2387cm$^{-1}$, overlap in the samples to form one large B-H stretch with a peak around 2320cm$^{-1}$. Finally, the BH$_2$ deformation peaks found at 1120 and 1092cm$^{-1}$ in LiBH$_4$ are observed at 1120 and 1082cm$^{-1}$, respectively, though the peak around 1120cm$^{-1}$ is extremely weak. However, there is no observable shift in any of the main stretches between the different samples, 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 [103]. 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 4.20.
4.3.4. Thermal Programmed Desorption Results

Upon producing the complex hydrides, each sample was characterized for its thermal characteristics using TPD with a heating rate of 1, 5, 10, and 15°C/min. As compared to the quaternary structure, the multinary structure containing MgH₂ showed a three-step hydrogen release mechanism, as is shown in Figure 4.22. This three-step release has previously been reported for the sample that is referred to as LicMgBNH in this paper. Our TPD analysis confirms the previously reported data, but also shows that the processing condition of the material does have an effect on the thermal decomposition characteristics. The first hydrogen release peaks between 157.7°C for the 10hr LicMgBNH and 165.2°C for LinMgBNH, which is a relatively small difference in
temperature. When investigating the second or main peak, of the various samples, it is interesting to note that the temperature range for main hydrogen release varies from 287°C for the 10hr LicMgBNH and 306.6°C for LinMgBNH.

Figure 4.22: TPD comparison of investigated processing variations showing the two main hydrogen release regions around 160°C and 300°C.

4.3.5. Activation Energy Results

The activation energy of each sample was experimentally determined using Kissinger's method, based on TPD data taken at 1, 5, 10, 15°C/min for the two peaks and correlated to the hydrogen release temperature. When investigating the first peak, around 160°C, it is interesting to note that the 10hr LicMgBNH sample has the lowest activation
energy (109.8 kJ/mole) at 157.7°C, but LiBNH+nMgH2 has the lowest peak hydrogen release temperature (153.3°C), as seen in Figure 4.23. Although these samples exhibit comparable decomposition temperatures, their activation energies vary by ~20 kJ/mol. A plausible reason is that the reaction pathways of ad-mixing MgH2 either in the first place (10hr LicMgBNH) or after the quaternary formation (LiBNH+nMgH2) proceeds with fine distribution of nanocrystalline MgH2 in the host matrix of multinary hydrides. It has been recently claimed that the nanocrystallization of MgH2 has significant impact on lowering the enthalpy of formation and enhancement of the reaction kinetics [46, 104]. The high temperature main hydrogen release peak (300°C) for all the processed materials and the reference LiBNH quaternary hydride are shown in Figure 4.22. While comparing the activation energies and decomposition temperatures of all the samples, it can be clearly inferred that the quaternary hydrides LiBNH combined with either commercial (LiBNH+cMgH2) or nanocrystalline MgH2 (LiBNH+nMgH2) milled for 5 hours show lower values, e.g. 145-148 kJ/mol at ~300°C. At this juncture, it is slightly difficult to justify from both Figure 4.23 and Figure 4.24, which sample or the processed material possesses an optimum hydrogen release characteristic at these two main decompositions. Again, it is undoubtedly clear that both the steps occur at two different temperature regimes such as 160 and 300°C for drive-off the hydrogen either surface adsorbed or bulk absorbed species. At the low temperature first step hydrogen release, the nanoMgH2 acts as a catalyst to speed up the reaction, hence 10hr LicMgBNH and LiBNH+nMgH2 materials demonstrated lower activation energies (Figure 4.23). On the other hand, in the high temperature main hydrogen release (Figure 4.24), temperature of 300°C act as a driving force to release hydrogen from the bulk structures of both LicMgBNH and
LinMgBNH milled only for 5hr. Hence, these materials exhibit lower activation energies which are comparable to pristine LiBNH. Based on the detailed analysis, we draw the conclusion that an additional 5hr of ball milling, either of the all-in-one hydride (10hr LicMgBNH) or the quaternary/nanocrystalline hydride mixture (LiBNH+nMgH₂), will alter the decomposition characteristics, especially the activation energy which is very vital for hydrogen storage.

Figure 4.23: Activation energy, as calculated from the TPD data using Kissinger’s method, compared with the first peak hydrogen release temperature.
141

Figure 4.24: Activation energy, as calculated from the TPD data using Kissinger’s method, compared with the main peak hydrogen release temperature.

4.3.6. Pressure-Composition-Temperature Isotherms

Figure 4.25 represents the PCT isotherms of multinary complex hydrides created with different processing conditions. The dehydrogenation PCT of LiBNH quaternary hydride is plotted for reference. The PCT studies of the multinary samples are carried out under the following conditions: temperature, $T=150-175^\circ C$; pressure difference between aliquots, $\Delta P=3\text{bar}$; absorption pressure limit, $P_a=80\text{bar}$; desorption pressure limit, $P_d=0\text{bar}$; and reservoir volume, $V_r=160\text{cm}^3$. Since all these samples are in hydride phases, the dehydrogenation experiment was followed by the rehydrogenation for at least
10hr. The PCT characteristics and their observations are given with respect to the sample processing conditions as follows.

(1) Quaternary hydride, LiBNH: A dehydrogenation capacity of ~4wt.% was found at 250°C. A two step plateau pressure region, $P_p$ (low plateau at $P<20$bar and high plateau at $P<30$bar) was observed and might pertain to the two phase components of LiBH$_4$ and LiNH$_2$. Although the hydrogen release capacity of 4wt.% at 250°C seems promising, these quaternary hydrides are not reversible at these temperatures.

(2) LicMgBNH and LinMgBNH: The multinary complex hydrides processed with either commercial or nanocrystalline MgH$_2$ and milled all-in-one for 5hr reveal reproducible hydrogen capacity of 3-4wt.%. It is noteworthy to mention that LinMgBNH possesses at least 1wt.% higher capacity and 25°C reduction in temperature as compared to the LicMgBNH counterpart. This could be achieved because of the uniform distribution of fine MgH$_2$ nanoparticles which might act as catalytic centers for lowering the hydrogen dissociation temperatures. Yet another difference between these two processed materials is the tailoring of the plateau pressure (hydrogen/hydride equilibrium region), which is crucial for a hydrogen storage system to be viable for mobile applications. The LinMgBNH material exhibits reduction in the absorption plateau pressure by 20bar in contrast to the LicMgBNH due to nanoparticulate formation.

(3) LiBNH+cMgH$_2$ and LiBNH+nMgH$_2$: Surprisingly, a greater reversible hydrogen storage capacity of 5.3-5.8wt.% was found at temperatures of 150-175°C for the quaternary hydrides LiBNH either milled with commercial or nano MgH$_2$ for 5hr.
The nano MgH$_2$ loaded LiBNH outperformed its commercial counterpart with a higher hydrogen capacity of 5.8wt.% at 150$^\circ$C as compared to 175$^\circ$C. There exist inflections of plateau pressure regions; however, they are not as clearly defined as the LicMgBNH and LinMgBNH samples. Moreover, the sorption plateau of these samples resembles greatly the pristine LiBNH which is the precursor material for the multinary hydride formation confirming XRD data. Overall, it is unambiguously claimed that LiBNH admixed either with commercial or nano MgH$_2$ and milled for 5hr, exhibits a high reversible hydrogen storage capacity of ~6wt.% at temperatures less than 175$^\circ$C.

(4) 10hr LicMgBNH: The extended milling duration of 10hr for the three component systems, 2LiNH$_2$+cMgH$_2$+LiBH$_4$ show poor hydrogen performance as depicted in Figure 4.25. A low hydrogen desorption capacity of 2wt.%, a low plateau pressure region of less than 5bar with less or no reversibility was obtained in this material. The crystallite agglomeration or the amorphous phase during the prolonged milling is expected to be the limiting factor for the absence of plateau and overall storage capacity. Though these materials exhibit lower activation energy (~109kJ/mol), in the first hydrogen release (see Figure 4.23), the effective hydrogenation needs systematic optimization strategies which are currently under investigation.
4.3.7. Crystallite Size Effects on Hydrogen Capacity

In order to better understand the hydrogen performance of the differently processed materials, the hydrogen capacity was investigated with respect to the crystallite sizes of the quaternary phase, LiBNH, and the MgH$_2$. The crystallite sizes were calculated from the XRD data (Figure 4.20) of each material using Scherrer’s method [105]. The initial crystallite sizes of LiNH$_2$, LiBH$_4$, MgH$_2$, nano MgH$_2$ and LiBNH were determined to be 138, 152, 212, 27, and 60nm, respectively. As seen from Figure 4.25, the nano size MgH$_2$ has an effect on the initial hydrogen release temperature. Both samples synthesized with nano MgH$_2$ release hydrogen at 150°C as compared to 175°C.
for all the other samples, which were synthesized with its commercial counterpart. The MgH$_2$ crystallite size for the nano MgH$_2$ samples are both approximately 10nm, whereas the crystallite size of the commercial MgH$_2$ samples vary from 35-75nm, as seen in Figure 4.26. It is important to note that the crystallite size of both MgH$_2$ and LiBNH are largest for the 10hr LicMgBNH sample, which explains the poor hydrogen performance of the sample, since it is well known that larger particles, and therefore a smaller surface area, correspond to poorer hydrogen performance (less than 2wt.% capacity). A milling duration of more than 5hr is in fact counterproductive and allows for the crystallite size to increase, as both the LiBNH and MgH$_2$ particles agglomerate. When looking at the correlation between crystallite size and hydrogen concentration, as shown in Figure 4.26, it becomes evident that the size of the LiBNH crystallites plays an important role on the hydrogen concentration. If the LiBNH crystallites have a size of approximately 28nm and the MgH$_2$ crystallites are approximately within 15nm (13-43nm) of this size, the highest possible hydrogen concentration is achieved (5.5wt.%). When the MgH$_2$ and LiBNH crystallites are either too similar in size, as in the case for the LicMgBNH sample (3.3nm difference), or if they are too different in size, as in the case for the 10hr LicMgBNH sample (32.9nm difference), the hydrogen concentration of the sample is reduced.
4.3.8. Surface Morphology

In order to perform SEM imaging, the samples were pressed into pellet form with a uniform thickness and pressure. The SEM images at 2,200 magnification are shown in Figure 4.27 for the five main samples. Figure 4.27(a) and Figure 4.27(b) show the two samples that were milled for a total duration of 5hr. The sample prepared using the commercial MgH$_2$ (Figure 4.27(a)) contains visibly larger particles than the sample prepared using nano MgH$_2$ (Figure 4.27(b)). This is due mainly to the fact that the commercial MgH$_2$, which does not form a chemical bond with the quaternary structure, but instead is intermixed with the material, is made up of larger particles than the nano
MgH$_2$. When the sample is milled for 10hr, however, as seen in Figure 4.27(c), the material is composed of uniformly agglomerated nanoparticles. This is surely due to the fact that the commercial MgH$_2$ has enough time, upon formation of the quaternary structure, to be ground into smaller particles and then given enough time to coalesce.

When MgH$_2$ was added to the quaternary structure LiBNH, the commercial MgH$_2$ produced comparable particle size distribution (Figure 4.27(d)) to the sample containing nano MgH$_2$ (Figure 4.27(e)).
Figure 4.27: Surface morphology of the five samples at 2200x magnification of (a) LicMgBNH, (b) LinMgBNH, (c) 10hr LicMgBNH, (d) LiBNH + cMgH₂, and (e) LiBNH + nMgH₂.
4.3.9. MgH₂ Destabilized LiBH₄/LiNH₂ Summary

A reversible hydrogen storage capacity of ~5-6wt.% was achieved at 150°C in the multinary complex hydrides comprising LiBH₄, LiNH₂ and MgH₂. Various processing conditions and optimization strategies were adapted to prepare these complex hydrides in a solid state. Among the various reaction pathways, the pre-processed quaternary hydride LiBNH ad-mixed with either bulk or nanocrystalline MgH₂ (LiBNH+cMgH₂ and LiBNH+nMgH₂) milled for 5hr shows pronounced hydrogen storage characteristics in reversible sorption cycles and lower activation energy of 145-148kJ/mol at ~300°C.

Irrespective of the processing scheme employed, it was found that all samples were intimate mixtures of the quaternary structure, referred to as LiBNH, with MgH₂ and that no new chemical compound was formed. It was found that the samples prepared with nano MgH₂ exhibited MgH₂ crystallites sizes of approximately 10nm, as compared to sizes of 35-75nm for those samples prepared with commercial MgH₂. The small MgH₂ crystallites enable the sample to release hydrogen at temperatures as low as 150°C as compared to 175°C for the larger MgH₂ crystallites. Furthermore, it was found that the size of the LiBNH crystallites plays an important role on the hydrogen concentration. If the LiBNH crystallites have a size of approximately 28nm and the MgH₂ crystallites are approximately within 15nm (13-43nm) of this size, the highest possible hydrogen concentration is achieved. When the MgH₂ and LiBNH crystallites are either too similar in size, as in the case of the LicMgBNH sample (3.3nm difference), or if they are too different in size, as in the case of the 10hr LicMgBNH sample (32.9nm difference), the hydrogen concentration of the sample is reduced.
The structural, microstructural and thermal desorption and activation energy calculations of all processed materials, as tabulated in Table 4.3, cumulatively suggest that synergistic effects of destabilization, nanocrystallization and process optimization lead to high hydrogen capacity materials for tomorrow’s fuel cell cars.

Table 4.3: Comparison of the results for the multinary complex hydrides developed by different processing conditions (the best results are shown in bold).

<table>
<thead>
<tr>
<th></th>
<th>LiBNH</th>
<th>LicMgBNH</th>
<th>LinMgBNH</th>
<th>10hr LicMgBNH</th>
<th>LiBNH + nMgH₂</th>
<th>LiBNH + nMgH₂</th>
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4.4. Destabilization of LiBH₄/LiNH₂/MgH₂ with Nano Sized Additives

Based on the previous experimental work on the optimization of the processing conditions as well as some previous insight into the role of nano sized additives on the quaternary LiBNH structure, it was decided to systematically investigate the effect of various nano sized additives on the multinary structure LiBNH + nMgH₂, as described in the previous section.
4.4.1. Synthesis of Destabilized Multinary Hydride

After the multinary hydride was synthesized, as described in chapter 4.3.1, various concentrations of nano additives were added to 0.4g of sample. The samples were loaded in the glove box and the same stainless steel milling container used for other synthesis was employed. The samples were then purged with the same hydrogen/argon mixture, as previously described, for 15min before being milled. Initially, the samples were milled at 300rpm for 15min to obtain a comparison of the effect of the nano additives on the multinary hydride. This milling duration allows for a thorough mixing of the parent compound with the nano additive without allowing the two to react and form a novel chemical structure. After a quick screening comparison of the various nano additives available, the samples that showed an increase in kinetics and the samples that showed a decrease in hydrogen release temperature were chosen to be optimized. Initially, 2mol% of various nano sized additives, obtained from QuantumSphere Inc., was investigated. The materials available were nickel, copper, manganese, cobalt and iron.

4.4.2. Thermal Programmed Desorption Results

TPD was used to obtain information about changes in the parent material’s hydrogen characteristics. Specifically, the temperature of hydrogen release as well as some general information about the kinetics of hydrogen release can be ascertained from this type of measurement. The peak temperature indicates the optimal hydrogen release temperature, whereas the width of the peak can be used to get insight into the rate at which hydrogen is released, at least qualitatively. A wide peak indicates a low rate of hydrogen release, whereas a narrow and sharp peak indicates rapid hydrogen release. As
can be seen from Figure 4.28, it is clear that all of the additives allow for a lower hydrogen release temperature. As previously described, the parent compound, LiBNH + nMgH₂, exhibits a three-step hydrogen release. While the TPD measurements are used for quick-screening the effect of the additives on the hydrogen performance of the material, it can be seen that each additive material either affects the rate of hydrogen release, as depicted by a sharp and narrow peak (especially iron) or significantly lowers the temperature required for hydrogen release.

![TPD comparison](image)

Figure 4.28: TPD comparison of LiBNH+nMgH₂ without additive and with 2mol% Ni, Cu, Mn, Co and Fe at a constant ramping rate of 1°C/min.
4.4.3. Hydrogen Sorption Screening Results

Since the TPD measurements only give an indication of the hydrogen sorption results, ramping kinetic measurements, where approximately 0.1g of sample are loaded into the PCT and then ramped at a rate of 1°C/min, were performed on all samples. Figure 4.29 shows the more detailed hydrogen performance of the standard sample, LiBNH+nMgH₂ without any additives, as well as with 2mol% of the aforementioned additives. It becomes clear that while cobalt seemed promising from the TPD data, it in fact has such slow kinetics, that cobalt is no longer of interest as an additive. The kinetics measurement do confirm the TPD data in that manganese and iron have the fastest kinetics, as indicated by the slope of the desorption curves. Furthermore, the significant reduction in hydrogen release temperature of nickel is confirmed.
Figure 4.29: Ramping kinetics measurements of LiBNH+nMgH2 without and with 2mol% nano Mn, Fe, Co, Cu, Ni and Fe+Ni.

Figure 4.30 shows a comparison of the hydrogen release rate and hydrogen release temperature of the standard sample without and with 2mol% of nano sized additives. Since the nano sized nickel showed the lowest hydrogen release temperature of just under 200°C and nano sized iron showed the highest release rate (0.2wt.%/min) at a comparatively low temperature of 245°C, these two additives were chosen to be optimized in terms of their concentration.
Figure 4.30: Comparison of hydrogen release temperature and hydrogen release rate of the standard LiBNH+nMgH$_2$ and LiBNH+MgH$_2$ with 2mol% of various nano additives.

TPD measurements were used to obtain information about the effect of various concentrations of nano nickel and nano iron, but are not shown here, as the optimum concentration of these additives were investigated for their hydrogen sorption properties. The effect of 2, 4, and 10mol% of nano nickel on the material can be seen in Figure 4.31. While 2mol% reduce the hydrogen release temperature as previously mentioned, any further amount of nickel does not further lower this temperature, but instead leads to much slower kinetics of hydrogen release, as is evident by the hydrogen desorption of the standard sample with 10mol%. 

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Figure 4.31: Ramping desorption kinetics of LiBNH+nMgH2 without and with 2mol%, 4mol% and 10mol% nano nickel.

Nano sized iron, on the other hand, maintains its kinetic advantage, but the hydrogen release temperature is further reduced with increasing iron amounts, as seen in Figure 4.32. A capacity of 6wt.% of hydrogen can be achieved with 0.2wt.%/min at a temperature of around 200°C for 10mol% nano iron, as compared to 6wt.% at 300°C at a rate of 0.08wt.%/min without any additive. This is a significant improvement and is most likely due the interaction of iron with magnesium which allows for a rapid hydrogen release at lower temperatures as the iron bonds with the magnesium, thereby forming a magnesium-iron alloy.
Further detailed hydrogen cycling measurements were being carried out on the 2mol% nano nickel and 10mol% nano iron samples, but the data is not presented in this dissertation due to time constraints. The data will be submitted to the International Journal of Hydrogen Energy and can be found when referencing the author’s name.

4.5. Complex Hydrides Storage Summary

A novel complex hydride system consisting of LiBH$_4$, LiNH$_2$, and MgH$_2$ was developed and presented in this chapter. All starting compounds had a capacity higher than the DOE targets so that the combination of the three compounds could only lead to a material with a higher theoretical value than that required for practical applications.
Initially, a new quaternary compound, referred to as LiBNH, was developed by optimizing the synthesis conditions of the solid state mechano chemical milling. It was found that a 2:1 molar ratio of LiNH₂:LiBH₄ produced a new chemical compound when milled for 5hr at 300rpm in an 80mL stainless steel container. The samples were purged before milling and every 2hr of milling with a 95%/5% Ar/H₂ gas mixture which was found to reduce agglomeration of sample during milling and to ensure the hydrogenation of the material. FTIR and XRD spectra of the samples indicate that the borohydride and amide stretches and bands are still intact, but that neither of the parent compounds are present. The quaternary structure exhibited hydrogen release at temperatures as low as 175°C, when destabilized with nano sized nickel, but irrespective of any additive, the quaternary structure was only able to reabsorb approximately 0.75wt.%.

The quaternary structure was destabilized further with the addition of MgH₂. Two main processing schemes were investigated:

(1) The addition of nano sized MgH₂ or commercial MgH₂ to the previously formed quaternary structure.

(2) The addition of nano sized MgH₂ or commercial MgH₂ to LiBH₄ and LiNH₂ in the stoichiometric ratio necessary to form the quaternary structure.

It was found that the addition of MgH₂ in a molar ratio of 1:1 LiBNH:MgH₂ did not form any new chemical compound with the quaternary structure, but that even in the case of the second processing scheme, the quaternary structure was formed alongside the MgH₂. All samples created with MgH₂ were found to reversibly store hydrogen at temperatures as low as 150°C with capacities ranging from 2-5.5wt.%.

The main driving force behind the hydrogen sorption properties of these materials was determined to be the
interaction of crystallite sizes of both the quaternary phase and the MgH₂. In fact, a size difference of approximately 15nm was found to be optimum and was observed in the LiBNH+nMgH₂ sample milled for 5hr. The second best performing material was found to be LinMgBNH milled for 5hr. Both samples with the nano sized MgH₂ were able to release hydrogen at temperatures as low as 150°C as compared to 175°C for the commercial MgH₂ samples. A comparison of the materials created as part of this dissertation with previously published results is shown in Figure 4.33.

![Figure 4.33: Complex hydride storage materials comparison with other published materials.](image)

Figure 4.33: Complex hydride storage materials comparison with other published materials.

The addition of various nano-sized additives, especially nickel and iron, further improve the hydrogen sorption behavior of the multinary hydride. While iron mainly
enhances the kinetics of hydrogen release in small (2mol\%) concentrations, it can also significantly reduce the temperature required for hydrogen release to close to 200°C. Nickel, on the other hand, has a large effect on reducing the temperature of hydrogen release in small concentrations (2mol\%) but has no effect on the rate of hydrogen release. A larger concentration of nickel was found to have no further effect on the material’s properties, but did lead to a significant reduction in hydrogen release kinetics due to the formation of a magnesium-nickel alloy.
5.1. Overview

A systematic study of two potential hydrogen storage systems has been carried out. The first system, polyaniline, was synthesized in its bulk form as well as in nanostructured forms of nanofibers and nanospheres. This system was investigated for its physisorption of hydrogen through weak secondary atomic bonds. The second main system was investigated for its strong primary atomic bonding of hydrogen and consisted of LiBH₄, LiNH₂, and MgH₂. Various nano sized additives were added to both the polyaniline and the complex hydride systems, though mainly the complex hydride system was found to destabilize to allow for hydrogen storage at lower temperatures and with faster kinetics.

5.2. Physisorption in Polyaniline – Summary and Conclusions

Polyaniline, in its emeraldine form, was successfully synthesized through chemical means. The bulk, or as-synthesized form, as well as three different nanostructures of PANI were characterized for physical, chemical and hydrogen sorption characteristics. It was found that the inclusion of additives to the bulk form of bulk PANI had virtually no effect on its hydrogen sorption characteristics. Bulk PANI was found to have a hydrogen capacity of less than 0.5wt.% at a temperature of 100°C. It was observed that the capacity of hydrogen in this standard sample increased slightly with increasing
temperature. This increase with temperature is due to the expansion of PANI, which in turn allows for the hydrogen to diffuse readily into the polymer. While others have claimed that standard PANI can absorb as much as 8wt.%, this was refuted by another group [27], as well as this research.

The nanostructured PANI, in the form of nanospheres with an average diameter of 100nm, was synthesized by slightly modifying the chemical synthesis technique used to produce the standard PANI. FTIR analysis, however, shows that the nanospheres do possess the same chemical composition as the standard PANI. While an initial hydrogen uptake of 5.5wt.% hydrogen was observed at 30°C, the capacity of each consecutive desorption cycle was reduced by roughly 1wt.%, though the desorbed hydrogen was reabsorbed. Since the kinetics of hydrogen uptake were on the order of several hours, with slower kinetics for each consecutive cycle, it was found that the main driving force behind the hydrogen sorption of the nanospheres was chemisorption, most likely in the form of hydrogen reacting with unterminated bonds that were a result of the synthesis. Finally, a capacity of only 0.6wt.%, virtually identical to that of bulk PANI, was observed at a temperature of 90°C. SEM analysis showed that the repeated hydrogen cycling caused the nanospheres to swell after hydrogen reaction and also to agglomerate until the sample finally had an appearance similar to bulk polyaniline. The interaction of hydrogen with the sample also led to the formation of microcracks, as shown in Figure 3.16, which are caused by the diffusion of hydrogen through the material.

By again slightly modifying the chemical synthesis technique, chemically grown PANI nanofibers were created. FTIR investigation proved that again the nanofibers were of the emeraldine form. The fibers had an average diameter of 250nm with varying
lengths. While this does not technically qualify them as nanofibers, the term is still employed to indicate the sub micron size of the fibers. The nanofibers also exhibited a rough surface. Hydrogen cycling of the nanofibers showed that an initial capacity of 3-4 wt.% was absorbed in less than 10 min, while approximately 1-2 wt.% hydrogen was released at room temperature. PCT measurements performed on the nanofibers showed that roughly 3.5 wt.% hydrogen was reversibly stored in the nanostructures. The initial hydrogen absorption showed a hydrogen plateau pressure around 30 bar, indicative of chemisorption. Through repeated cycling, though, the plateau pressure disappeared, though the capacity remain unchanged at 3.5 wt.% for many cycles. SEM analysis of the chemically grown nanofibers after hydrogen cycling showed no evidence of nanofibers. Instead, the fibers had virtually disappeared and a rather porous material remained. Surface area analysis revealed that the surface area in fact remained unchanged after cycling. Unlike the nanospheres whose structure also disappeared, the nanofibrous nature of the PANI allowed for it to agglomerate into a porous material, thereby losing the physical characteristics, but still keeping the surface area. This is an important factor for hydrogen storage materials as was previously discussed.

Finally, electrospun nanofibers were investigated for their hydrogen performance. By using a well know electrospinning technique, the nanofibers were synthesized with average diameters of 1.5 μm and lengths of several microns. The nanofibers were, unlike the chemically grown nanofibers, rather smooth. While FTIR again confirmed the presence of the typical benzenoid and quinoid rings of emeraldine base PANI, it was observed that the quinoid peak was much larger in relation to the other FTIR peaks. The
quinoid peak was also shifted by approximately 50cm⁻¹, making it unique among all the polyaniline structures investigated. Hydrogen kinetics measurements on the electrospun nanofibers at 30°C showed no hydrogen sorption, but absorption at 100°C revealed a very promising initial uptake of over 10wt.% in less than 10min. The desorption that followed showed an almost instantaneous release of 4wt.% hydrogen and another 4wt.% with much slower kinetics. Each consecutive absorption cycle reabsorbed the previously released hydrogen with slightly lower kinetics, but still in a matter of minutes rather than hours. The desorption capacity decreased by roughly 2wt.% for each cycle, but the fast rate of hydrogen release remained until the capacity of hydrogen sorption decreased to virtually zero after approximately 3 absorption / desorption cycles. While the fast kinetics of the absorption measurements clearly indicate that physisorption is taking place, the desorption cycles are clearly a combination of both chemisorption (slower kinetics) and physisorption (faster kinetics). Furthermore, breakage and swelling of the nanofibers was observed, though overall they do remain intact. Hydrogen PCT measurements on a new batch of this sample, however, revealed that approximately 8wt.% hydrogen could be reversibly stored in the electrospun nanofibers as long as the pressure was gradually increased or decreased. This slow exposure to hydrogen is essential in that the nanofibers are not exposed to pressure extremes, which can result in the destruction of the nanofiber morphology. Additionally, the hydrogen is allowed enough time to diffuse into the material and bond. While this method of storage requires a higher amount of time, it is still the most preferential method of storing hydrogen in polyaniline. The capacity of 8wt.% along with the relatively low temperature of 100°C makes the electrospun polyaniline an ideal candidate for hydrogen storage.
It appears that the main factor in storing hydrogen in polyaniline is less the surface area, as was previously thought for polymers, but in fact lies more in the exact chemical composition. Unterminated bonds, which provide chemisorption sites for hydrogen are an excellent initial hydrogen storage site, but require an amount of energy that is simply too high for practical purposes, therefore requiring high temperatures which would in fact destroy the chemical structure of the polyaniline. The relative intensity of the quinoid ring vibration with respect to the other FTIR peaks appears to play a vital role in the hydrogen storage behavior of polyaniline as quinoid rings allow for a more readily delocalization of electrons, thereby enabling the attachment of hydrogen atoms to the material. Also, the form of hydrogen storage, namely exposure of the material to hydrogen, is extremely important when dealing with relatively weak materials such as PANI. Though it might require more time to store and release the hydrogen, a gradual pressure change is essential to maintaining the hydrogen characteristics of the material.

The work on these polymers is the first to investigate various nanostructures of polymers at temperatures above 77K. A comparison of the results obtained from this research with other work that was previously conducted on hydrogen storage in polymers is shown in Figure 3.35. While all the previously published polymers were investigated for pure physisorption at room temperature, the polymers investigated as part of this dissertation were also investigated for combinatorial physisorption / chemisorption of hydrogen. It was found that the many unterminated bonds of the as-synthesized polymers allow for a rather large amount of hydrogen to be stored as part of the polymer. When adjusting the hydrogen cycling conditions, the hydrogen sorption behavior of the
materials was affected significantly. Therefore, it is important to not only consider the chemical structure of the material, but also the testing methodology.

5.3. Complex Hydride – Summary and Conclusions

A reversible hydrogen storage capacity of 5-6wt.% was achieved at 150°C in the multinary complex hydrides comprising LiBH₄, LiNH₂ and MgH₂. Through XRD measurements, it was found that a 2:1 molar ratio of LiNH₂:LiBH₄ formed a new quaternary compound after approximately 5 hours of ball milling. Furthermore, a purge with Ar/H₂ (95%/5%) before milling, as well as every 2 hours of milling ensures that the resultant material does not agglomerate, thereby producing a homogenous yield of sample, provided that only 2g of sample are milled at a time.

PCT hydrogen sorption measurements of the quaternary structure, LiBNH, indicates that a temperature of 250°C is required to release approximately 4wt.% of hydrogen in a two-step release at pressure of 25 and 15bar. The addition of 5mol% nano Ni was shown to lower the hydrogen release temperature from 250°C to 175°C in a one-step release at a pressure of 5bar, but with kinetics that require more than 24 hours to release the hydrogen. The addition 3mol% nano Zn had no effect on the temperature, but allowed for a release of 6wt.% of hydrogen at 250°C. Finally, the addition of 3mol% nano Zn and 3mol% nano Ni enabled the quaternary structure to release 9wt.% of hydrogen at 250°C in a three-step process, requiring approximately 24hr. The main hydrogen results of the quaternary structure are summarized in Table 4.2 and in Figure 4.18.
Various processing conditions and optimization strategies were adapted to prepare these complex hydrides in a solid state. Among the various reaction pathways, the pre-processed quaternary hydride LiBNH ad-mixed with either bulk or nanocrystalline MgH2 (LiBNH+cMgH2 and LiBNH+nMgH2) milled for 5 hours shows pronounced hydrogen storage characteristics in reversible sorption cycles and lower activation energy of 145-148 kJ/mole at ~300°C.

Irrespective of the processing scheme employed, it was found that all samples were intimate mixtures of Li₄BN₃H₁₀ with MgH₂ and that no new chemical compound was formed. It was found that the samples prepared with nano MgH₂ exhibited MgH₂ crystallites sizes of approximately 10nm, as compared to sizes of 35nm to 75nm for those samples prepared with commercial MgH₂. The small MgH₂ crystallites enable the sample to release hydrogen at temperatures as low as 150°C as compared to 175°C for the larger MgH₂ crystallites.

It was found that the size of the LiBNH crystallites is an essential factor in determining the amount of hydrogen that can be released at any given temperature. If the LiBNH crystallites have a size of approximately 28nm and the MgH₂ crystallites are approximately within 15nm (13nm to 43nm) of this size, the highest possible hydrogen concentration is achieved. When the MgH₂ and LiBNH crystallites are either too similar in size, as in the case of the LicMgBNH sample (3.3nm difference), or if they are too different in size, as in the case of the 10hr LicMgBNH sample (32.9nm difference), the hydrogen concentration of the sample is reduced. Unlike most other research, which focuses on quick screening materials for their hydrogen capacity, the work described within this dissertation shows that even theoretical investigation of hydrogen storage
materials is insufficient in finding the optimum material. Factors such as the crystallite size are routinely ignored, even though they can double the amount of hydrogen stored by the material.

The structural, microstructural and thermal desorption and activation energy calculations of all processed materials, as tabulated in Table 4.3, cumulatively suggest that synergistic effects of destabilization, nanocrystallization and process optimization lead to high hydrogen capacity materials for tomorrow’s fuel cell cars.

5.4. Future Work Recommendation

While significant improvements have been made on the hydrogen sorption characteristics of the polyaniline system as well as the complex hydride system, more detailed chemical analysis into the exact mechanism of its hydrogen sorption characteristics are needed. Additionally, there has been some indication that Nb2O5 can be used to further destabilize MgH2, which would be an interesting topic of research as an additive to the complex hydride that has been investigated and developed as part of this dissertation.

More detailed investigation of polyaniline and its various forms should be carried out to obtain proper insight into the role of processing conditions on the structure, both chemically as well as physically, as well as the hydrogen storage characteristics of PANI. The complex hydrides investigated as part of this dissertation should definitely be investigated further and destabilized, as all the storage characteristics appear to be extremely promising. Furthermore, a scaled-up process should be designed and built to test the materials in real-life conditions.
Finally, theoretical modeling of both systems using state of the art molecular dynamics simulation would further be of great value to further understand the elaborate processes involved in hydrogen storage and thereby allowing for a quick screening and development of practical hydrogen storage systems.
References


About the Author

Michael Ulrich Niemann was born February 24th, 1980 in Böblingen (Baden-Württemberg), Germany as the fifth son of Dieter Horst Kunibert Jurczyk and Ursula Luzia Jurczyk (née Niemann). He attended Kindergarten in Schopfloch (Kr. Freudenstadt) and then Higgins Elementary School in Poughkeepsie, NY until 3rd grade after which he finished the Grundschule in Schopfloch and the Progymnasium in Dornstetten, followed by 11th grade at the Wirtschaftsgymnasium in Freudenstadt, Germany. He obtained his Abitur equivalence at Venice High School in Venice, FL and then went on to the University of South Florida, Tampa, FL, USA. There, he obtained his Bachelor of Science degree in Mechanical Engineering and completed his Masters of Science in Mechanical Engineering with a thesis entitled “Shape Based Stereovision Assistance in Rehabilitation Robotics” under guidance of Dr. Rajiv Dubey. He joined Dr. Kumar and Dr. Stefanakos to pursue his Ph.D. in mechanical engineering, of which this dissertation is the culmination.

Michael married Christine Victoria Woodard during his Ph.D. studies on January 5th, 2005 in Bogota, Colombia. Both Christine and Michael are now proud parents of Sebastian Eduard Gerhard Niemann, who was born on February 27th, 2009 in Tampa, Florida. Upon graduation, Michael plans to return to his native Germany to pursue a career in industry, though a position in academia is not out of the question.