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Environmental Reactivity of Solid State Hydride Materials: Modeling and Testing for Air and Water Exposure

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Abstract

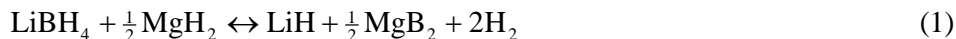
To make commercially acceptable condensed phase hydrogen storage systems, it is important to understand quantitatively the risks involved in using these materials. A rigorous set of environmental reactivity tests have been developed based on modified testing procedures codified by the United Nations for the transportation of dangerous goods. Potential hydrogen storage material, $2\text{LiBH}_4\cdot\text{MgH}_2$ and NH_3BH_3 , have been tested using these modified procedures to evaluate the relative risks of these materials coming in contact with the environment in hypothetical accident scenarios. It is apparent that an ignition event will only occur if both a flammable concentration of hydrogen and sufficient thermal energy were available to ignite the hydrogen gas mixture. In order to predict hydride behavior for hypothesized accident scenarios, an idealized finite element model was developed for dispersed hydride from a breached system. Empirical thermodynamic calculations based on precise calorimetric experiments were performed in order to quantify the energy and hydrogen release rates and to quantify the reaction products resulting from water and air exposure. Both thermal and compositional predictions were made with identification of potential ignition event scenarios.

Keywords: Hydrogen storage, Metal Hydride, Environmental Reactivity, Water Exposure, Air Exposure

Introduction

Although extensive studies exist on the safety properties of hydrogen gas itself [1-3] less is known about the reactivity of solid state hydrogen storage materials when exposed to the environmental surroundings (i.e.- water, water vapor, and air). It is important to understand the risks in using these materials such as in the case of a hydrogen storage tank being breached and hydride material that is exposed to the environment or dispersed onto the ground. The assessment of risks associated from hydrogen gas release and ignition; along with the flammability of resultant dehydrogenation products are critical. A number of early reports focusing on NaAlH_4 were made in preparation for handling and building prototype hydrogen storage systems [4a-4c]. This report generated and compiled data including the identification of gas and solid products resulting from air and water exposure. More recently, other publications have been published that discusses safety aspects of such materials as NaAlH_4 and $8\text{LiH}\cdot 3\text{Mg}(\text{NH}_2)_2$ [4, 5].

This report will discuss the environmental reactivity of two potential hydrogen storage materials: a *destablized* mixture of lithium borohydride (LiBH_4) and magnesium hydride (MgH_2) in a molar ratio of 2 to 1, respectively and the chemical hydride ammonia borane. For the destabilized LiBH_4 material, Vajo et al[6] showed that the formation of MgB_2 during dehydrogenation stabilizes the LiBH_4 and reduces the enthalpy of reaction. The “destabilized” mixture has been reported to have a >10wt% H_2 capacity and rechargeable under reasonable pressure and temperature (1 to 10 atm and 20 to 100°C) [6, 7].



The second material of interest, ammonia borane (NH_3BH_3), has been the subject of a number of studies as a chemical hydride due to its high hydrogen capacity (19 wt%) and low dehydrogenation temperature of 100°C (373 K) [9,10]. Furthermore, ammonia borane has good thermal stability and is readily available commercially.

The purpose of this paper is to explain the details related to an idealized computational model that was developed to explain the hazards associated with these materials being dispersed from a hydrogen storage tank for a breach-of-tank scenario. The model takes into account empirical thermodynamic data obtained using isothermal calorimetry, where each material can be exposed to various degrees of liquid water, water vapor, and air contact. Calorimetry allows for time resolved data such as heat and hydrogen generation and rate of reaction to be measured for various environmental exposure scenarios. These results are then input into the finite element model, to gain insight to the spatially resolved reaction rates with both thermal and compositional information. It will be shown that time and location for coincidental hydrogen minimum ignition temperature and minimum flammability concentration can be resolved. Such studies give insight into environmental exposure scenarios and, ultimately, will help reduce the number of experiments needed to explain the environmental reactivity behavior of different solid-state hydrogen storage materials.

Experimental Procedures

Specimens were prepared by mixing commercially pure MgH_2 and LiBH_4 . Milling was conducted in a Spex mill for 1 hr., under an argon atmosphere with a ball-to-sample ratio of 20 to 3. Ammonia Borane was purchased commercially from Sigma Aldrich and used as-received. Approximately 3 grams of ammonia borane was discharged using a Sievert's apparatus at 180°C (heating rate of 10°C/min) and 1 bar of backpressure for 3 hours.

To quantify the heat released through contact with dry and humidified air and liquid water, oxidation and hydrolysis studies were performed in a Calvet calorimeter. Liquid water tests were performed using a mixing cell with pH-neutral water to react 5-10 mg of solid with 1 ml of water. Controlled humidity air reaction measurements were conducted at varying relative humidity levels (0-80%RH) and temperatures (40 and 70 °C). For these measurements, the calorimeter equipped with a flow cell utilizing either argon or air as the carrier gas with a flow rate of 10 ml/min reacting with 5-10 mg of solid. [8, 9]. Thermal Gravimetric Analysis (TGA) was utilized at various heating heats (0.8, 2, 5, and 10 °C/min) to determine the kinetics of ammonia borane, which was inputted into the modeling effort. In addition, residual gas analysis (RGA) was used to quantify the amount of impurities with respect to hydrogen for the gas released during testing.

Modeling

The governing equations solved for each analysis include mass, momentum, and energy balances, plus additional kinetics equations based on the chemical kinetics data. The following assumptions were made to simplify the analysis:

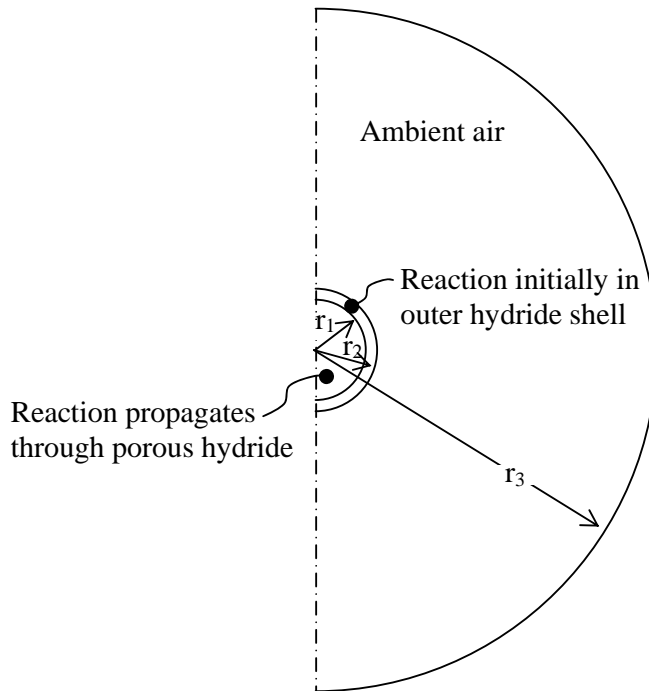


Figure 1: Schematic of sphere used in modeling of $2\text{LiBH}_4\cdot\text{MgH}_2$.

- The ambient fluid is dry air.
- The calorimetry data at 70 °C for the liquid water and $2\text{LiBH}_4\cdot\text{MgH}_2$ is assumed to be the worst case scenario with the fast reaction rate and highest heat of reaction for this system.
- The heat and mass generation source is based upon the worst case scenario as stated in the assumption above and is modeled as temperature, pressure, and material composition independent. Thus, the heat and mass generation source, which varies with time and position, will continue regardless of the fluid or material temperature, fluid pressure, or species concentrations.
- All reactions begin in the outer shell of the hydride sphere.

- The material is a uniform 50% porous sphere.
- Mass transport considerations and limitations within the porous sphere that would be present due to binders or other pelletization considerations are not addressed in this work.
- The material properties are constant during the simulation.
- The ambient air properties are allowed to change with temperature and pressure via the ideal gas law.

The built-in hydrogen-air reaction within FLUENT [9] is used to mark the hydrogen ignition even when/if it occurs. However, the model is only designed to capture the events leading up to the ignition event and is not designed to model the ignition event itself or the events following the ignition event

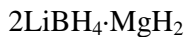
Results and Discussion

UN Derivative Testing

Six tests were adopted from United Nation's protocol on the Transport of Dangerous Goods [10] to evaluate the flammability and water reactivity of various solid state hydrogen storage materials. Table 1 is a summary of these test results. When describing the material's environmental reactivity, the tests are divided into two categories: Flammability and Water Contact. Flammability tests include pyrophoricity, self-heating, and burn rate. Water reactivity focuses on material contact with water, which includes water immersion, surface exposure (contact), and water drop. The $2\text{LiBH}_4\cdot\text{MgH}_2$ is less reactive by an order of magnitude, than data reported for $8\text{LiH}\cdot\text{Mg}(\text{NH}_2)_2$ and NaAlH_4 [4, 5] in both flammability (burn rate) and water reactivity. Ammonia borane is the least reactive hydrogen storage material with respect to $2\text{LiBH}_4\cdot\text{MgH}_2$, $8\text{LiH}\cdot\text{Mg}(\text{NH}_2)_2$, and NaAlH_4 based on the behavior observed during the environmental exposure involved in the series of UN tests. The only test ammonia borane failed was that of self-heating. The material self-heated to close to 300°C , possibly due to the oven temperature being close to the dehydrogenation temperature of ammonia borane and a large flux of hydrogen available. No water reaction was observed.

Table 1: UN Testing results for $2\text{LiBH}_4\cdot\text{MgH}_2$ and NH_3BH_3 .

Material / UN Test	State	Pyrophoricity	Self-Heat	Burn Rate	Water Drop	Surface Contact	Water Immersion
$2\text{LiBH}_4\cdot\text{MgH}_2$ SRNL	C	No ignition event. Hygroscopic material absorbed H_2O from air.	Self-heated $\sim 300^\circ\text{C}$ within 5 min as $T_{\text{oven}} = 150^\circ\text{C}$ is approached.	Flame propagated in 5 sec with burn rate of 52 mm/sec.	2 H_2O drops required for near-instant ignition.	Material ignited	No ignition event recorded. Gas evolved at longer times. (5 min)
NH_3BH_3 SRNL	C	No ignition event. Hygroscopic material absorbed H_2O from air.	Self-heated $\sim 300^\circ\text{C}$ within 10 min, 5 min at $T_{\text{oven}} = 150^\circ\text{C}$	Flame propagated in 6 sec with burn rate of 33 mm/sec	No reactivity detected	No ignition event recorded. Gas evolved at longer times. (5 min)	No reactivity detected



Calorimetry

Figure 2 displays the normalized heat flow (mW/mg) for the $2\text{LiBH}_4 \cdot \text{MgH}_2$ reaction with liquid water in a mixing cell compared with water vapor in a gas flow cell[8, 11]. The amount of total water addition in excess of stoichiometry is 32 times for liquid water and 4 times (after a reaction time of 12 hours) for the conditions of 40°C and 30% relative humidity. The qualitative difference observed for heat flow is believed to be due to the difference in gas/solid versus liquid/solid interfacial reactions and is currently under further investigation. The total energy release of the water vapor reaction was greater (-268 kJ/mol) than the energy release upon liquid water hydrolysis (-223 kJ/mol). In addition the final crystalline reaction products were different in the two cases: the reaction with 30% relative humidity air resulted in $\text{LiB}(\text{OH})_4$ and residual MgH_2 , while the liquid water hydrolysis resulted in $\text{LiB}(\text{OH})_4$, $\text{H}_6\text{B}_2\text{O}_6$ and $\text{LiB}(\text{OH})_2(\text{O}_2)$ phases along with amorphous components. Overall, in both the liquid mixing and gas flow reactions the trend is for a lower measured energy compared to the thermodynamically predicted reactions. As reported earlier, these discrepancies are to the fact that the actually observed products do not match those predicted from thermodynamics and often have a significant degree of amorphous character. Despite discrepancies in theoretical versus experimental heat release, the kinetics of energy release empirically determined for these materials via calorimetry will be used as input data for modeling the environmental reactivity under accident scenarios as described in the subsequent section.

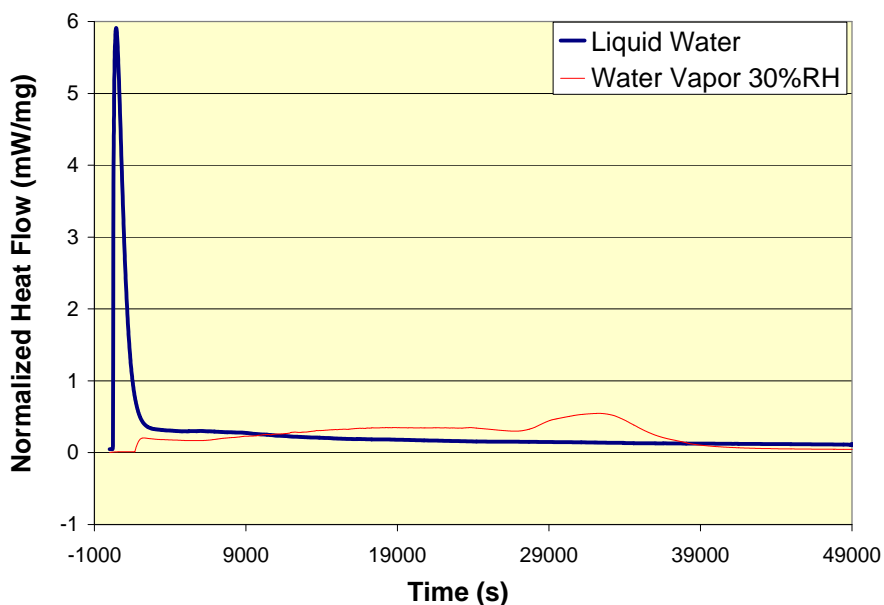


Figure 2: Normalized heat flow (mW/mg) during hydrolysis/oxidation of $2\text{LiBH}_4 \cdot \text{MgH}_2$ with liquid water at 40°C and with 30% relative humidity air at 40°C (10 ml/min flow rate).

Modeling

The first risk mitigation strategy for a self heating powder would be to pelletize it so that fine particles do not react with air and or ambient water vapor. In this instance it is important to identify what maximum diameter pellet would self heat to the point where the minimum hydrogen ignition temperature was reached. Two different “accident” scenarios were considered for material in a spherical pelletized form of varying radii: (i) air has completely

penetrated the intergranular space within the pellets and (ii) hydrogen still occupies the intergranular space.

For the first scenario, the hydride is initialized with ambient air filling the porous media. This scenario assume that the hydride has been released from its container for a short amount of time prior to any chemical reaction occurring, which allows all of the hydrogen gas to be expelled from the hydride prior to the reaction and be replaced with ambient air. Pertinent model parameters are summarized in Table 2, with results from these simulations shown in Figures 3 and summarized in Table 3. The smallest diameter hydride spheres (0.05 inch and ¼ inch models) never reach the lower flammability limit (LFL = 0.04) for hydrogen concentration, which means no reaction event occurs. For the larger spheres (½ inch and higher models), the LFL and/or the auto-ignition temperature (500°C or 571°C depending on the H₂ concentration) of hydrogen is reached and a reaction event occurs. Thus, there is a critical radius between ¼ and ½ inch that indicates the minimum amount of material necessary for a hydrogen reaction event to occur.

Table 2: Model Parameters for porous 2LiBH₄·MgH₂

Parameter	Value			
Material porosity (ϵ)	0.5			
Particle Diameter (D_p)	3.7×10^{-6} m			
Material density (ρ)	927 kg/m ³			
Material thermal conductivity (k)	0.5 W/m-K			
Material specific heat (C_p)	1583 J/kg-K			
Heat/Mass generation	Based on calorimetry data			
Reaction propagation	0.03 mm/s*			
Model dimensions:	Model	r ₁ (in)	r ₂ (in)	r ₃ (in)
	0.05 in	0.00	0.05	10.05
	¼ in	0.20	0.25	10.25
	½ in	0.45	0.50	10.50
	1 in	0.95	1.00	11.00
	1 ½ in	1.45	1.50	11.50
	2 in	1.95	2.00	12.00
	2 ½ in	2.45	2.50	12.50

Note: *based on contamination model [8]

Figure 2 shows the species concentration major components of the hydrogen-air reaction for the ½ inch sphere model. Note that as the H₂ and O₂ burn away, water vapor (H₂O) increases in their place. Similar results are seen for the larger spheres (1 inch and greater models), but are not shown.

For the second scenario, the hydride is initialized with hydrogen gas filling the porous media. This scenario assume that the chemical reaction occurs immediately after the hydride is released from its container, which means the porous space within the hydride is still full of 100% hydrogen gas at the start of the numerical simulation. It was observed that due to the high dissipation rate of H₂ into the ambient atmosphere, most of the hydrogen has been expelled from the hydride prior to the start of the chemical reaction (mass/heat generation) within the simulation. Thus, the hydrogen-initialized hydride models yielded similar results to the air-initialized hydride models and are not shown.

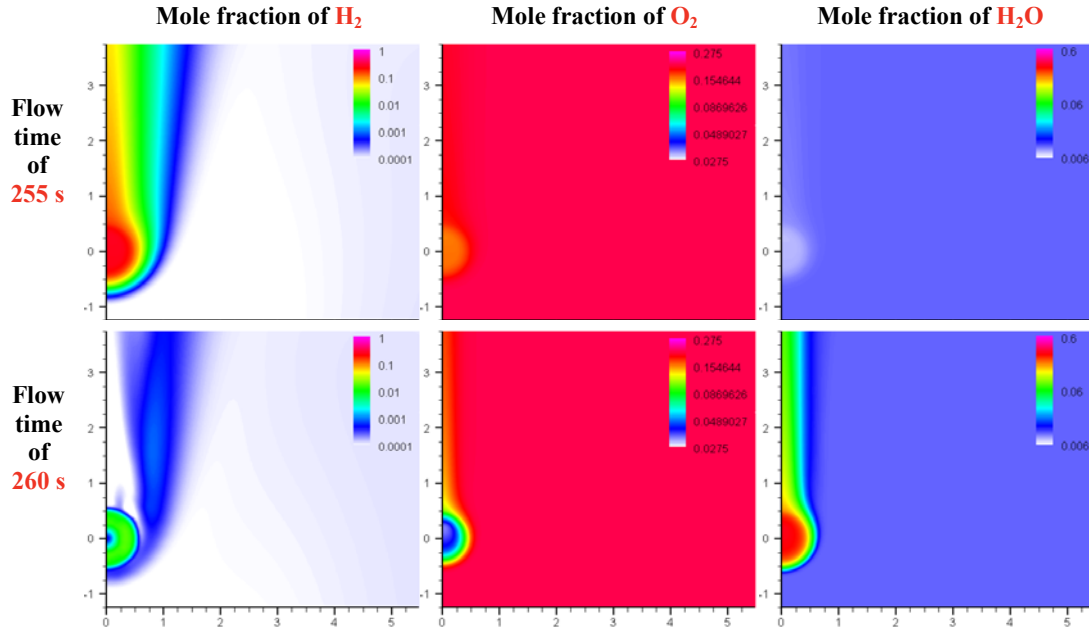


Figure 3: Mole fractions of H₂, O₂, and H₂O before and after hydrogen ignition (255s and 260s, respectively) for the axi-symmetric sphere with a ½ inch radius.

Table 3: Axisymmetric Sphere Results for air-initialized hydride

Model	H ₂ Ignition Event	H ₂ mole fraction (mf)	Temperature
0.05 in	None	Maximum value of 0.0123 at t = 160s	Maximum temperature of 164.2°C at t = 300s
¼ in	None	LFL reached between t = 55s and 60s Max of 0.135 at t = 230s	Maximum temperature of 752.4°C at t = 370s
½ in	Between t = 255s & 260s: H ₂ mf = 0.266 and 0.015 Temp = 569°C and 571°C	LFL reached between t = 30s and 35s Max of 0.266 at t = 255s	Maximum temperature of 1422°C at t = 540s
1 in	Between t = 200s & 203s: H ₂ mf = 0.323 and 0.0503 Temp = 327°C and 361°C	LFL reached at t = 25s Max of 0.323 at t = 200s	Maximum temperature of 2184°C at t = 963s
1.5 in	Between t = 180s & 185s: H ₂ mf = 0.343 and 0.0939 Temp = 263°C and 316°C	LFL reached between t = 20s and 25s Max* of 0.343 at t = 180s	Temperature reaches 2250°C at t = 1000s (and still rising)
2 in	Between t = 170s & 175s: H ₂ mf = 0.361 and 0.117 Temp = 234°C and 293°C	LFL reached between t = 20s and 25s Max* of 0.361 at t = 170s	Temperature reaches 2563°C at t = 1000s (and still rising)
2.5 in	Between t = 180s & 183s: H ₂ mf = 0.410 and 0.209 Temp = 255°C and 668°C	LFL reached between t = 20s and 25s Max* of 0.410 at t = 180s	Temperature reaches 2312°C at t = 1000s (and still rising)

Ammonia Borane (NH_3BH_3)

Figure 4 shows the calorimetric behavior of ammonia borane in the charged and discharged of the as-received and dehydrogenated material for exposure to dry and humid air (30%RH) at 40°C over an 18 hour period. In the case of dry air, endothermic behavior is observed with a calculated enthalpy of 5.9 and 32.1 kJ/mol NH_3BH_3 for the charged and discharged state respectively[9]. This behavior is attributed to ammonia borane having a low, initial dehydrogenation temperature (70°C) and oxidation from exposure to air. The discharged material has a higher enthalpy value due to material stability. However, the introduction of 30% water vapor to the system initiates an exotherm of -15.2 and -49.4 kJ/mol NH_3BH_3 for the charged and discharged states respectively. The behavior in the discharged state is related to the decomposition of ammonia borane and the stability of the material after discharge. X-ray diffraction analysis showed pure crystalline ammonia borane starting material, Figure 5(a). However, amorphous material was identified as the resultant material after exposure to air and water vapor. This is similar to the XRD pattern of dehydrogenated material shown in Figure 5(b).

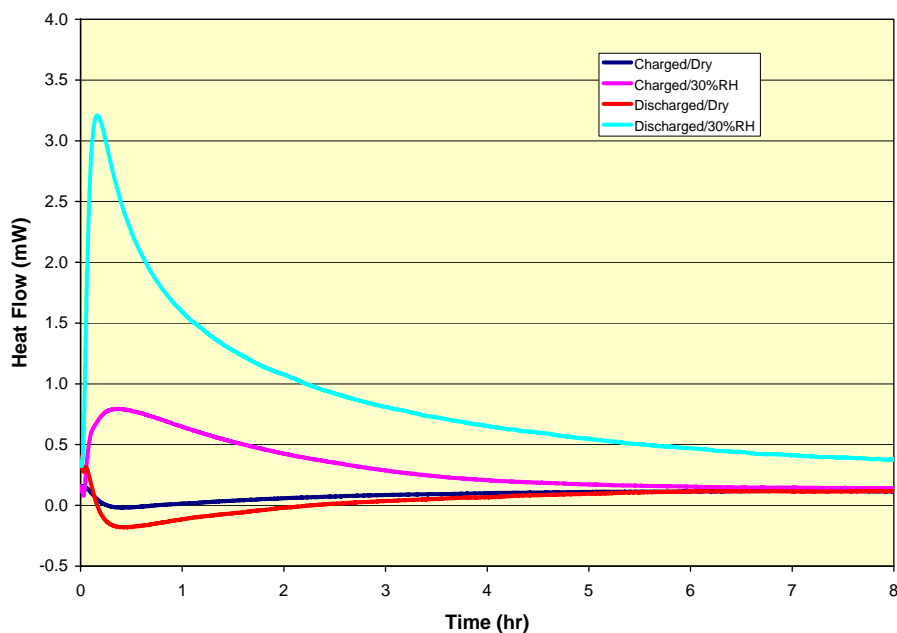


Figure 4: Heat Flow of charged and discharged Ammonia Borane for an 18 hour period in the charged and discharged state in dry air and 30%RH environment

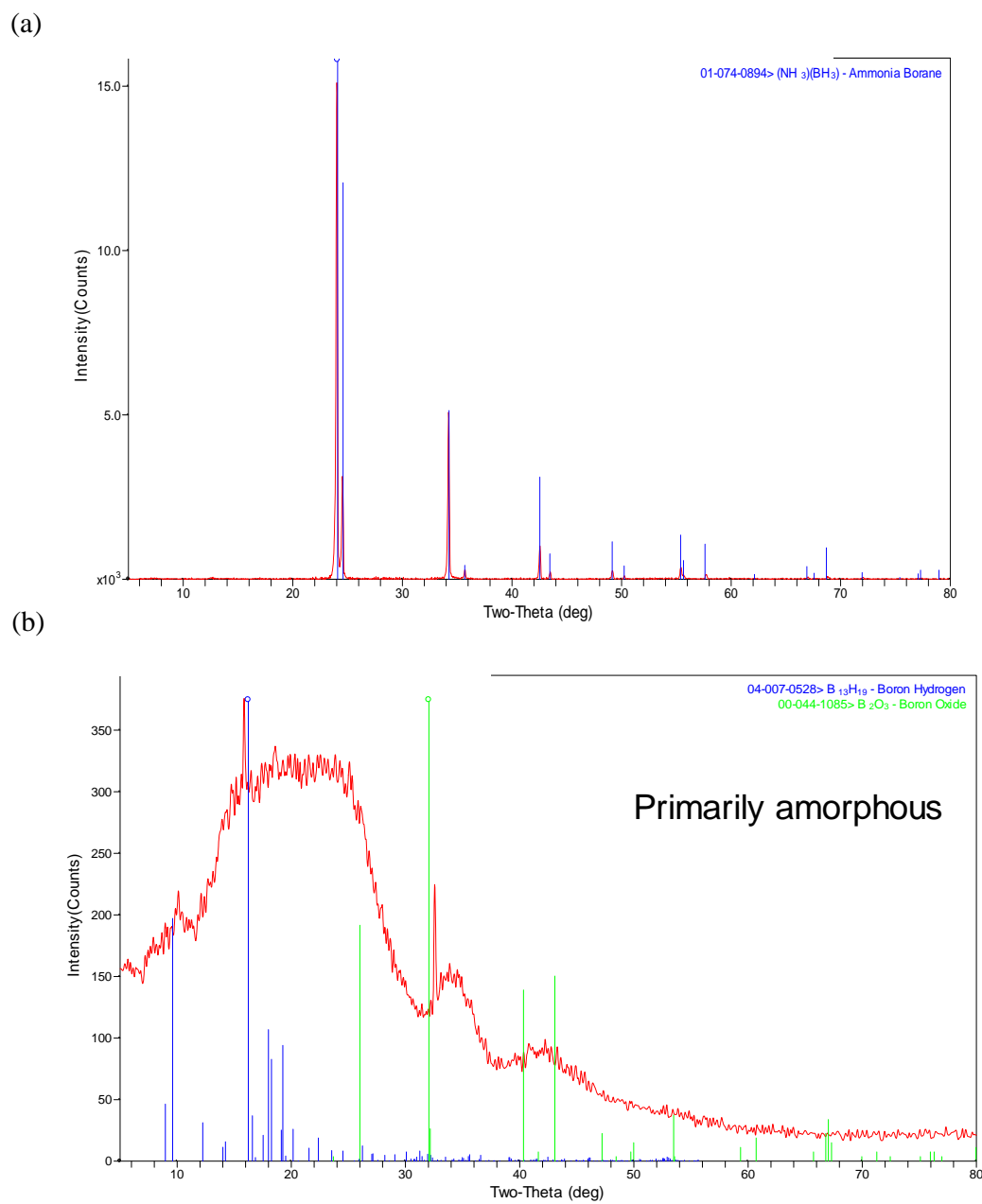


Figure 5: (a) XRD pattern of charged Ammonia Borane (b) XRD pattern of discharged Ammonia Borane

Conclusions

As the use of solid-state hydrogen storage materials become more prevalent, the understanding of the environmental reactivity is imperative. This includes the risks and hazards associated with each material. These risks are unique for each material and thus significant experimental data needs to be generated to understand the reactivity of these materials with potential environmental scenarios. This study has shown the calorimetric results of dry and humid air exposure of both charged and discharged $2\text{LiBH}_4\cdot\text{MgH}_2$ and NH_3BH_3 . The $2\text{LiBH}_4\cdot\text{MgH}_2$ material was much more reactive than the NH_3BH_3 , releasing nearly an order of magnitude more heat per mole, but still somewhat less reactive than NaAlH_4 . NH_3BH_3 , reacted endothermically upon exposure to both dry and humid environments with the discharged state somewhat more reactive.

A finite element modeling approach was developed to describe behavior for a breach-of-tank scenario when pelletized material is ejected. This model took into account the simultaneous generation and loss of heat and hydrogen through radiative, convective means. The $2\text{LiBH}_4\cdot\text{MgH}_2$ system was modeled using a 2-D axi-symmetric sphere to determine a critical radius ($0.25\text{ in} < r < 0.5\text{ in}$) for the auto-ignition of hydrogen to occur. These models incorporate thermal data from the self-heating test (UN testing) and calorimetry for water and air exposure to quantify the energy and hydrogen release rates. It was concluded that FEM approaches to predicting potential ignition events are promising. Both minimum ignition temperatures and minimum ignition concentrations were identified and potential ignition circumstances predicted. Further work in modeling and validation of the models for potential accident scenarios is warranted in order to reduce the time and expense of performing physical experiments.

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