

IV.E.4 Fundamental Environmental Reactivity Analysis of Hydrogen Storage Materials

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Objectives

- Quantify the risks associated with using solid state hydrogen storage compounds.
- Ameliorate these risks to acceptable levels through the development of mitigation strategies.
- Demonstrate the efficacy of these mitigations strategies in sub scale component demonstrations.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan in descending order of impact:

- (F) Codes and Standards
- (A) System Weight and Volume
- (B) System Cost

Technical Targets

This project is conducting fundamental studies of the air and water exposure of numerous solid state hydride materials in order to assess their risks. Insights gained from these studies will be applied toward the design of risk mitigation methodologies that meet the following DOE 2010 and 2015 hydrogen storage target:

- Environmental Health and Safety: Meets or Exceeds Applicable Standards

Accomplishments

- An international team has been organized including the National Institute for Advanced Industrial Science and Technology in Japan, Forschungszentrum Karlsruhe in Germany, Université du Québec à Trois-Rivières in Canada, and United Technologies and Sandia National Laboratories (SNL) in the U.S., with International Partnership for the Hydrogen Economy (IPHE) sanctioning granted.
- An intranet Web site has been established utilizing the SNL QuickPlace site.
- Thermodynamic assessment of air and water contact performed at operating temperatures was performed for NH_3BH_3 , AlH_3 , $8\text{LiH}+3\text{Mg}(\text{NH}_2)_2$ and $2\text{LiBH}_4+\text{MgH}_2$, resulting in predicted products and thermodynamically expected thermal releases.
- Calorimetric experimental procedures completed and initial water and air exposure and tests conducted on $2\text{LiBH}_4+\text{MgH}_2$ and initial testing begun on $8\text{LiH}+3\text{Mg}(\text{NH}_2)_2$ and NH_3BH_3 to validate the thermodynamic predictions performed showing partial reaction to thermodynamically predicted products and only partial exothermic discharge.
- Standardized United Nations (U.N.) test procedures identified and completed for $2\text{LiBH}_4+\text{MgH}_2$ and initial testing begun on NH_3BH_3 .



Introduction

In searching for ever higher gravimetric and volumetric density hydrogen storage materials and systems, it is inevitable that higher energy materials will be studied and used. To make safe and commercially acceptable systems, it is important to understand, quantitatively, the risks involved in using and handling these materials and to develop appropriate safety systems to handle unforeseen accidental events. Reported here is a summary of thermodynamic calculations and calorimetric experiments performed to identify the theoretical and actual reaction products and kinetics of air and water reactions of selected candidate hydrogen storage materials. In addition, standardized tests are outlined based on internationally accepted hazards analyses which will be performed in the coming year.

Approach

In order for the information generated by this project to be widely accepted and globally distributed, an international activity was established linking laboratories in North America, Europe and Asia to perform specialized tasks specific to their organizations capabilities. A set of materials testing procedures, based on internationally accepted standards drawn from U.N. testing procedures will be defined. These tests will include exposure to air, humidity, water, and proposed cooling fluids. Numerous potential hydrogen storage materials such as activated carbon, NaAlH_4 , NH_3BH_3 , $\text{LiNH}_2+\text{MgH}_2$, AlH_3 and $2\text{LiBH}_4+\text{MgH}_2$ will be tested identically under these conditions to quantitatively determine their reactivity under normally occurring environmental and operating conditions. Independent studies will be performed to understand the chemical kinetics of these reactions with air, oxygen and water as both liquid and vapor as a function of temperature. Calorimetric studies will be performed to investigate the time-dependent reaction rates of the materials. Time resolved X-ray diffraction facilities will be used to quantify chemical kinetics and reaction products. Dynamic models will be developed to predict the behavior of leaking storage systems.

Results

United Nations Tests

The standard materials testing procedures employed are based on existing U.N. testing protocols in order to confirm the material classification and ensure safe transport and handling [1]. Six standardized tests were performed including (1) water immersion, (2) water surface contact, (3) water drop testing, (4) pyrophoricity, (5) burn rate, and (6) dangerous self heating. Large amounts of materials were required for some of the tests, in particular the burn-rate and self-heating tests, which presented a challenge in terms of procuring and preparing the material in a standardized state using ball-milling techniques. In addition, shipping and handling protocols for materials are under review with safety team members and a universal standard was applied when packing/unpacking materials.

The first material that was selected for testing was $2\text{LiBH}_4\cdot\text{MgH}_2$, previously identified as a material of interest within the Metal Hydride Center of Excellence. The U.N. tests were modified to include visual recording of the testing event, and the addition of thermocouples in those experiments where this was possible. The results for the various tests are given in the following. Although not explicitly reported here, many of these tests are also first performed on the pure constituent materials, LiBH_4 and MgH_2 , in order to put the test of the combined material into perspective.

Water Reactivity

Material behavior upon contact with H_2O under differing scenarios is obviously of great concern for many materials associated with solid state hydrogen storage. Water is environmentally ubiquitous and many materials of interest for hydrogen storage undergo rapid exothermic hydrolysis and oxidation reactions which are associated with the release of H_2 , NH_3 , B_2H_6 , or other flammable or explosive gases. Water contact is assessed in three different scenarios: 1) a small amount of material with an excess of H_2O , 2) a small amount of material with restricted contact to an excess of water, and 3) an excess of material with a small amount of water.

The first scenario is the small amount of material with an excess of water. The test is performed inside a standard laboratory fume hood using approximately 20 mg of material, which is dropped into 250 ml of de-ionized H_2O (Figure 1). Any notable chemical reaction involving combustion/conflagration or the release of gas is noted, and the material is considered to have failed the test. When the material is dropped into the beaker of water, there may be a very small spark event, but typically there is no actual combustion event. Some of the material (presumably the LiBH_4) became solvated in the water, while some of the material (presumably MgH_2) formed a coalescent film on the surface of the water. After 2 minutes, gas evolution is observed, which is presumed to be H_2 from hydrolysis. Upon this basis, the material fails the water immersion test.

The second water contact scenario tested is the small amount of material in limited contact with an excess of water. The experimental setup for this test is very similar to that used in the water immersion test, with the difference being that an appropriately sized filter paper is placed on the surface of the water. Initially, the sample evolved hydrogen gas within seconds. After 10 seconds, a combustion event is recorded which seems to be limited to burning the hydrogen gas and any dry material that may be present. Afterwards, the material gave off trace amounts of hydrogen gas, but no further combustion-type events are recorded over a 15 minute period. Material, which is presumably predominantly MgH_2 and oxidized Li- and Mg- species may begin to slowly settle into the beaker around the filter paper if there are any gaps, such as that presented by the pour spout. However, there is no indication that any material permeates or otherwise transports across the material, as the plume of material

The third scenario tested for water contact is the scenario where an excess of material is brought into contact with a small amount of water. This is accomplished by putting an appropriate amount of material (typically 1-2 grams, depending on material density) inside a truncated conical mold with a flat portion at the cone tip in order to present a standardized

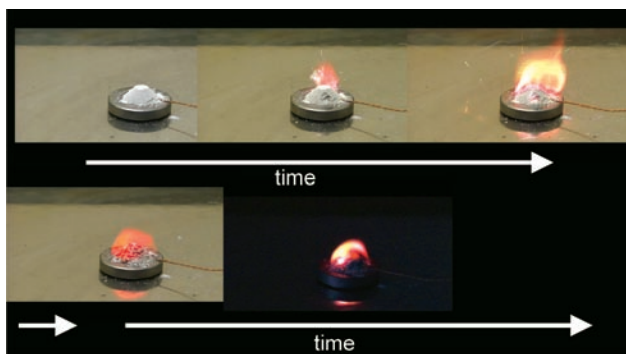


FIGURE 1. Water Drop Tests of $2\text{LiBH}_4\cdot\text{MgH}_2$

form for the material prior to water contact. Both the pure LiBH_4 and $2\text{LiBH}_4\cdot\text{MgH}_2$ mixtures, the highly hydrophilic and reactive nature of LiBH_4 resulted in near instantaneous reaction with the water drop (Figure 1). After approximately 2 seconds, a combustion event is recorded that is the most powerful of the three water contact scenarios. The initial combustion is due to the ignition of H_2 gas, while at longer times the hydride itself seems to be undergoing direct pyrolysis in addition to the burning of the hydrogen released. The small ball-like formations observed in during the burning process, which are also observed in the burn rate test (see Burn Rate section), are most likely caused by the interaction of the hydrophobic MgH_2 phase with the H_2O that is generated by the burning of H_2 . The material will burn for an extended time, but will generally be burned out within 10 minutes.

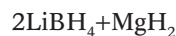
Air Reactivity

The first of the air reactivity scenarios investigated is the standard test for pyrophoricity, which involves dropping the material from a height of 40 inches and observing whether any type of spontaneous or other reaction during the fall, or within 5 minutes of the material making contact with the ground. It was observed that at no time during the test is any combustion event recorded, although at longer times some gas is likely given off as the material begins to absorb water from the atmosphere and undergo hydrolysis. Therefore, this material is not found to be pyrophoric as per the standardized U.N. tests, which is consistent with the rating of the pure components.

The burn rate test was conducted by arranging the material into a line of a predetermined length. A propane torch is then used to ignite one end of the material, and a combination of visual and thermocouple measurements are used to calculate the burnrate. It was observed that the material easily ignites under the temperatures produced by the propane torch ($T_{\text{flame}} \approx 2,000^\circ\text{C}$) and rapidly propagates down the line of material. The flame propagates down the entire 250 mm within approximately 5 seconds, and continues to burn

for slightly longer than 10 minutes. The calculated burn rate is 52 mm/sec [1].

The final air-reactivity scenario considered in this work is the standardized test for dangerous self-heating. A 25 mm cube of material is suspended within an oven at 150°C , and the temperature of the sample is monitored. For this testing, multiple thermocouples were placed inside the sample at the center corner and edge of the cube. Within the first 5 minute period, all three interior thermocouple locations experienced sufficient heat to fail or nearly fail (in the case of the center measurement) the self-heating criterion; furthermore, enough heat was generated that the exterior couple measuring the ambient oven temperature experienced measureable heating. The trends observed in the temperature rises can be explained by consideration of the reaction front for local hydrolysis reactions and/or combustion from the evolved hydrogen and heat release as water is absorbed and reacts with the materials. The maximum temperature of $\sim 450^\circ\text{C}$ was experienced at the central location after about 30 minutes.



Calorimeter Experiments

Hydrolysis and oxidation studies were performed in a Calvet calorimeter (Setaram C-80) equipped with a mixing cell using neutral water to react nominally 5-10 mg of solid with 1 ml of liquid. Gas phase reactivity examining oxidation and gas phase hydrolysis was performed at varying relative humidity levels and temperatures using the calorimeter equipped with a flow cell using argon or air as the carrier gas with a flow rate of 10 ml/min reacting with nominally 5-10 mg of solid.

Effect of Temperature on Neutral Water Hydrolysis

As shown in Figure 2, a temperature increase of 30°C (from 40 to 70°C) resulted in a modified calorimetric signal. Both the total heat released for the hydrolysis reaction was different at the two temperatures as well as the final crystalline phase composition suggesting different reaction pathways occurred. Amorphous lithium products were observed at the lower 40°C temperature along with $\text{Mg}(\text{OH})_2$, while crystalline lithium compounds such as $\text{Li}(\text{H}_2\text{O})_4\text{B}(\text{OH})_4(\text{H}_2\text{O})_2$ were observed in the higher temperature hydrolysis reaction at 70°C . The result allows us to quantify the increase in reaction rate: a temperature increase of 30°C (from 40 to 70°C) resulted in an increase of the reaction progress from 40 to 70% after 1 hour.

Relative Humidity Effects in Gas Phase Hydrolysis

The heat flow signal was measured during humid air exposure for the mixture $2\text{LiBH}_4\cdot\text{MgH}_2$ at 40°C with

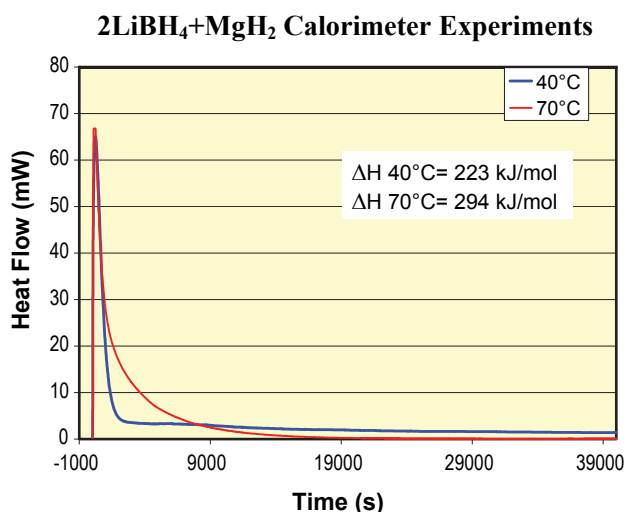


FIGURE 2. Heat Flow Signal from Neutral Water Hydrolysis of 2LiBH₄:MgH₂ at 40°C and 70°C

both 30% relative humidity (RH) and 60% RH. The total amount of heat released was approximately the same at different RH levels with a value of 268 kJ/mol at 40°C 30% RH and 251 kJ/mol at 40°C 60% RH. The resulting crystalline products were identified as LiB(OH)₄ and residual MgH₂ crystalline products for both levels of RH. In gas phase hydrolysis, the amount of water vapor seems only to impact the reaction time and not the pathway or final products. An increase in water vapor available for hydrolysis decreases the time required to complete the reaction. The effect of temperature on gas phase hydrolysis was investigated comparing the reaction of 2LiBH₄:MgH₂ with air at 70°C and 40°C with 30% RH. The tests showed approximately the same crystalline products (LiB(OH)₄ and MgH₂) and total heat release (242 kJ/mol) at both temperatures. The only impact of increased temperature seems to be an increase in the amount of water vapor in the air thus speeding up the hydrolysis reaction.

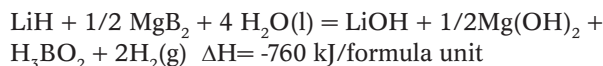
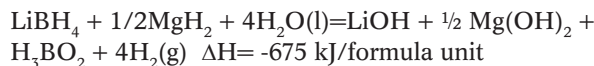
Gas Product Characterization

Gas chromatography was used in order to quantify the hydrogen concentration in the hydrolysis products gas stream as a function of time. It was seen that the hydrogen gas concentration tracks the heat flow signal, reaching the lower flammability limit of H₂ in air at 50 mW for this sample with a mass of 22 mg; or a normalized heat flow signal of 2.3 mW/mg for the given experimental setup and flow rate of 10 ml/min.

Material Charged State

The maximum heat flow for the component LiBH₄, MgH₂ and 2:1 destabilized mix was observed under liquid hydrolysis conditions. The maximum heat

flow for liquid phase hydrolysis at 40°C and 70°C as a function of the materials hydrogen charged state. The maximum heat flow increases as the material desorbs hydrogen and converts into more reactive LiH, Mg, and MgB₂ chemical compounds as is seen predicted by the following chemical reactions:



This data shows that the discharged material states are more reactive to air and water exposure than the fully charged material states in the 2LiBH₄:MgH₂ system. Engineering design for storage tanks containing the 2LiBH₄:MgH₂ material should be based on the discharged material states as a worst case estimate for environmental exposure scenarios.

Conclusions and Future Directions

Conclusions

- The environmental reactivity of the destabilized 2LiBH₄:MgH₂ system was most sensitive to water hydrolysis reactions.
- The 2LiBH₄:MgH₂ destabilized mix followed the behavior of the LiBH₄ component due to the relative lack of MgH₂ hydrolysis reactivity.
- The experimentally observed products often contained significant amorphous content which is not reflected in the thermodynamic predictions.
- Discharged material states for 2LiBH₄:MgH₂ were significantly more reactive (factor of 2 for fully discharged material under liquid hydrolysis) than the fully charged materials and should be the basis of engineering design for mitigation strategies in solid state hydrogen storage tank containing this material system.
- The maximum normalized heat flow for the fully charged material was 6 mW/mg under liquid phase hydrolysis; and 14 mW/mg for the fully discharged material also occurring under liquid phase hydrolysis conditions.

Future Directions

- Calorimetric experiments will continue at various temperature and humidity levels on the NH₃BH₃, LiH:Mg(NH₂)₂ and additional compounds of interest.
- Standardized testing will continue for NH₃BH₃ and AlH₃.
- Models will be completed for various accident scenarios based on tank rupture type, temperature, humidity

and presence of water and wind to determine ultimate conclusion and time to critical events.

- Risk mitigation strategies will be outlined and preliminary thermodynamic calculations performed to evaluate their efficacy.

Special Recognitions & Awards/Patents Issued

1. This program has been recognized by the International Partnership for the Hydrogen Economy, IPHE. Partners include the National Institute for Advanced Industrial Science and Technology in Japan, Forschungszentrum Karlsruhe in Germany, Université du Québec à Trois-Rivières in Canada, United Technologies and Sandia National Laboratories in the U.S.

FY 2008 Presentations

1. Fundamental Safety Testing and Analysis of Solid State Hydrogen Storage Materials and Systems, D. Anton, D. Mosher, M. Fichtner, N. Kuriyama, R. Chahine & D. Dedrick, 2nd International Conference on Hydrogen Safety, San Sebastian, Spain, 2008.
2. Solid-State Hydrogen Storage System Development and Engineering Analysis, T. Motyka, D.L. Anton, 2008 ACS/ASM National Meeting on Hydrogen Energy, Cocoa Beach, FL, 2008.
3. The Hydrolysis and Oxidation Behavior of Lithium Borohydride and Magnesium Hydride Determined by Calorimetry, K. Brinkman, J. Gray, B. Hardy, and D. Anton, Materials Research Society (MRS), March 24-28, 2008, San Francisco, California.

4. Environmental Reactivity of Solid State Hydride Materials: Standardized Testing of $2\text{LiBH}_4\text{:MgH}_2$ for Air and Water Exposure, J. Gray, K. Brinkman, B. Hardy, and D. Anton, Materials Research Society (MRS), March 24-28, 2008, San Francisco, California.
5. Environmental Reactivity of the $2\text{LiBH}_4\text{+MgH}_2$ System, D.L. Anton, K. Brinkman & J. Gray, MH2008, Reykjavik, Iceland, June 23-28, 2008.

FY 2008 Publications

1. The Hydrolysis and Oxidation Behavior of Lithium Borohydride and Magnesium Hydride Determined by Calorimetry, K. Brinkman, J. Gray, B. Hardy, and D. Anton, Proceedings of the Materials Research Society (MRS), March 24-28, 2008, San Francisco, California.
2. Fundamental Safety Testing and Analysis of Solid State Hydrogen Storage Materials and Systems, D. Anton, D. Mosher, M. Fichtner, N. Kuriyama, R. Chahine and D. Dedrick, International Journal of Hydrogen Energy, J. Hydrogen Energy, (in press).
3. Design, Fabrication and Testing of NaAlH_4 Based Hydrogen Storage Systems, J. Alloys and Compounds (in press).
4. Hydrogen Storage Properties of Na-Li-Mg-Al-H Complex Hydrides, J. Alloys and Compounds (in press).

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1. United Nations: Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria, 3rd Revised Ed., ISBN 92-1-139068-0, (1999).