IV.F.5 Safety Analysis of Solid State Hydride 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 including 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. was established; International Partnership for the Hydrogen Economy (IPHE) sanctioning was granted.
- Materials to be studied were selected initially including activated carbon, $NaAlH_4$, NH_3BH_3, $2LiNH_2+MgH_2$, AlH_3 and $2LiBH_4+MgH_2$ and priorities set for their evaluation.
- Thermodynamic assessment of air and water contact performed at operating temperatures were performed for NH_3BH_3, AlH_3 and $2LiBH_4+MgH_2$, resulting in predicted products and thermodynamically expected thermal releases.
- Calorimetric experimental procedures completed and initial water and air exposure and tests conducted on $2LiBH_4+MgH_2$ to validate the thermodynamic predictions performed showing partial reaction to thermodynamically predicted products and only partial exothermic discharge.
- Standardized test procedures identified, laboratory hazards analysis completed and laboratory equipped to perform United Nations [1] designated tests.

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 project was established linking laboratories in North America, Europe and Asia to perform specialized tasks specific to their organizations capabilities. This project will furthermore organize these international efforts and institute meetings of the partners and establish appropriate web sites for both inter-team communications and intra-team distribution of findings. A set of materials testing procedures, based on internationally accepted standards drawn from American Society for Testing Materials (ASTM) and United Nations 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, $LiNH_2+MgH_2$, AlH_3 and $2LiBH_4+MgH_2$ will be tested identically under these conditions to quantitatively determine their reactivity under normally occurring environmental and operating conditions and various metal organic framework and related materials as well as nano-carbons used in physisorption storage of hydrogen will also be considered. The materials will be tested in the fully charged, partially discharged and fully discharged conditions in both packed and finely dispersed forms with and without an ignition source. A baseline set of tests will also be conducted utilizing both MgH_2 and $LaNi_5$ materials for comparison of reactivity.

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. Chemical reactivity with organic and inorganic solutions will also be studied to determine those fluids which are safe to use as heat transfer, processing and inhibitor liquids. 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. Depth-resolved surface analysis will be performed to investigate reaction progress and/or properties of inhibiting layers. Cycling studies will be performed to study the stability of the materials. Dynamic models will be developed to predict the behavior of leaking storage systems.

Methods of mitigating the risk of exposure to air and humidity will be investigated. These mitigation methods may take the form of either materials modifications or system level methods which would lessen the probability or effects of environmental exposure. Proposed methods for inhibiting reactions include the application of thin film coatings or the use of liquid film inhibitors. Fluid dynamic simulations will be performed to study dispersion properties of leaks from sorption-based storage systems.

Results

Partnering

The international team was established, with each partner agreeing to share information and combine efforts to determine the risks associated with using solid and liquid hydrogen storage materials. Partners in the project 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. Materials selection, test identification and test methodology will be agreed to within this team with data distributed through both the IPHE and International Energy Agency (IEA) organizations. A proposal was written and submitted to the IPHE for sanctioning in an effort to facilitate funding for the partners. IPHE sanctioning was subsequently granted, greatly enhancing the visibility of the project and allowing for wide dissemination if its results and conclusions.

Standard Tests

The standard materials testing procedures employed are based on existing United Nations testing protocols in order to confirm the material classification and ensure safe transport and handling [1]. There are eight standardized tests that will be performed at the SRNL in order to examine the materials sensitivity to air and water exposure, as well as mechanical impact. These tests will include (i) pyrophoricity, (ii) dangerous self heating, (iii) impact, (iv) water immersion, (v) burn rate (vi) thermal stability, (vii) water surface contact and (viii) water drop testing. The materials to be tested may be modified as necessary through discussions with DOE, the Centers of Excellence and the safety team partners.

The Hazard Analysis Protocols (HAP) for the experimental work on the air, water and mechanical impact sensitivity tests have been submitted and are currently under review. The test equipment for the air and water sensitivity tests has been procured and the testing facilities are under construction. Vendor estimates and specifications for the mechanical impact sensitivity test apparatus are currently being sought. Experiments are expected to begin in August once approval of HAP and lab installations are completed. Due to the requirement of large quantities of custom synthesized materials for these tests, Center of Excellence partners have been approached and informed of the required quantity, in order to facilitate materials testing. In addition, shipping and handling protocols for materials are under review with safety team members and a universal standard will be applied when packing/unpacking materials [2].

Thermodynamics Assessment

In the absence of kinetic limitations the reaction with the lowest ΔG_r will be the favored reaction product. The actual reaction products can be experimentally verified using X-ray analysis to determine the products structure and semi-quantitative compositions. The final product compositions can lead to determination of actual reaction enthalpies given thermodynamic data is available for all of the phases. Multicomponent reaction equilibrium including equilibrium compositions as a function of temperature (T) and pressure (P) and initial starting compositions may also be analyzed using thermodynamic tables. Results of this analysis have been performed on the material systems MgH_2, $LiBH_4$, $2LiBH_4*MgH_2$, AlH_3, and NH_3BH_3 for air exposure and water exposure (hydrolysis) as a function of temperature.

It is seen that, in general, the reaction with oxygen has a lower free energy and is thus favored over the reaction with water vapor. The lowest energy products from the air reactions are predicted to be LiOH, $Mg(OH)_2$ and H_3BO_2 or $B(OH)_3$ (these products give similar energy). The reaction with water gives similar predictions for LiOH and $Mg(OH)_2$ compounds, however the H_3BO_2 product is the energetically favored boron containing reaction product.

Table 1 presents the reaction with lowest ΔG_r value and its corresponding ΔG_r for a range of materials to be examined in this project. An examination of the reactions occurring with liquid water as compared to water vapor showed that the ΔG_r and predicted reaction products were the same. However, the enthalpy of reaction, ΔH_r, was greater with water vapor at temperatures above 100°C due to endothermic vaporization, reducing the overall reaction enthalpy by the 41 kJ/mol H_2O (the ΔH_{tr} for $H_2O(l) \Rightarrow H_2O(g)$ at 100°C). Thus the water vapor calculations were eliminated from the table, but can be easily calculated.

The reactions presented in Table 1 have been normalized to the formula unit of the principal component for ease of comparison ($LiBH_4*1/2MgH_2$ instead of $2LiBH_4*MgH_2$). The ΔG and ΔH energies versus material system are graphically depicted in Figure 1 in order of increasing ΔH. It is seen that for all of the materials investigated thus far, with the exception of NH_3BH_3, environmental exposure to oxygen should dominate the material response. This interaction would result in a very significant exothermic release if carried to conclusion. This thermodynamic prediction contradicts the common observation that some of these materials can be exposed to air for long durations with no apparent reaction. They have been observed, however, to react violently when exposed to water. This can be attributed to the formation of an oxide or hydroxide layer on the material surface (i.e. Al_2O_3 or $Al(OH)_3$ in AlH_3) reducing its reactivity with air [5].

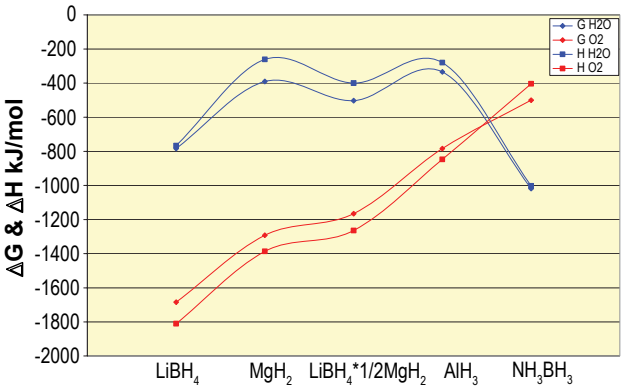

FIGURE 1. Gibbs Free Energy of Lowest Energy Reaction ΔG (kJ/mole) and Reaction Enthalpy ΔH at 373 K for the Materials to be Studied Initially in This Project

TABLE 1. Thermodynamic Calculations for Environmental Air and Water Exposure

Material System	Environmental Exposure	Lowest Energy Reaction	*ΔG (kJ/mole)*, ΔH (kJ/mole) at 373 K
$LiBH_4$	H_2O (liquid)	$LiBH_4 + 2H_2O(l) = 4H_2(g) + LiBO_2$	***-390,*** -261
	O_2	$LiBH_4 + 1.5O_2(g) = LiOH + H_3BO_2$	***-1292,*** -1386
MgH_2	H_2O (liquid)	$MgH_2 + 2H_2O(l) = Mg(OH)_2 + 2H_2(g)$	***-334,*** -280
	O_2	$MgH_2 + O_2(g) = Mg(OH)_2$	***-784,*** -847
$LiBH_4*1/2MgH_2$	H_2O (liquid)	$LiBH_4 + 1/2MgH_2 + 4H_2O(l) = LiOH + 1/2\ Mg(OH)_2 + H_3BO_2 + 4H_2(g)$	***-784,*** -766
	O_2	$LiBH_4 + 1/2MgH_2 + 2O_2(g) = LiOH + 1/2Mg(OH)_2 + H_3BO_2$	***-1684,*** -1810
AlH_3	H_2O (liquid)	$AlH_3 + 3/2H_2O(l) = 1/2Al_2O_3 + 3H_2(g)$	***-503,*** -400
	O_2	$AlH_3 + 3/2O_2(g) = Al(OH)_3$	***-1165,*** -1264
NH_3BH_3	H_2O (liquid)	$BNH_6 + 2H_2O(l) = 1/2N_2(g) + 7/2H_2(g) + H_3BO_2$	***-500,*** -404
	O_2	$BNH_6 + 1.75O_2(g) = 1/2N_2(g) + 2H_2O(g) + 1/2B_2O_3 + H_2(g)$	***-1018,*** -1003

$LiBH_4$*MgH_2

Thermodynamic calculations have been performed for ΔG_r for possible reactions involving $LiBH_4$*MgH_2 with water (hydrolysis). Lithium hydroxide (LiOH), magnesium hydroxide ($Mg(OH)_2$), boronic acid (H_3BO_2) and gaseous hydrogen are the predicted lowest energy products. The calculations have been also been performed for exposure to dry air (essentially reaction with oxygen) and humid air (water vapor) as a function of temperature resulting in the following possible reactions. The reactions in bold face are those which have the lowest ΔG_r.

$2LiBH_4 + MgH_2 + 10H_2O_{(g)} \Rightarrow LiOH + 2B(OH)_3 + 2Mg(OH)_2 + 10H_{2(g)}$
$2LiBH_4 + MgH_2 + 5O_{2(g)} \Rightarrow 2LiOH + 2B(OH)_3 + Mg(OH)_2$

$2LiBH_4 + MgH_2 + 6.5H_2O_{(g)} \Rightarrow LiOH + 0.5Li_2B_4O_7 + Mg(OH)_2 + 10H_{2(g)}$
$2LiBH_4 + MgH_2 + 3.25O_{2(g)} \Rightarrow LiOH + 0.5Li_2B_4O_7 + Mg(OH)_2 + 3.5H_{2(g)}$

$2LiBH_4 + MgH_2 + 6H_2O_{(g)} \Rightarrow 2LiBO_2 + Mg(OH)_2 + 10H_{2(g)}$
$2LiBH_4 + MgH_2 + 3O_{2(g)} \Rightarrow 2LiBO_2 + Mg(OH)_2 + 4H_{2(g)}$

$2LiBH_4 + MgH_2 + 8H_2O_{(g)} \Rightarrow 2LiOH + Mg(OH)_2 + 2H_3BO_2 + 8H_{2(g)}$
$2LiBH_4 + MgH_2 + 4O_{2(g)} \Rightarrow 2LiOH + Mg(OH)_2 + 2H_3BO_2$

AlH_3

The environmental reactions of AlH_3 are given in Table 1 where it is shown that water exposure leads to an Al_2O_3 product and a reaction with oxygen leads to $Al(OH)_3$. However, it is known that AlH_3 is thermodynamically unstable (ΔG dehydrogenation -61 kJ/mole at 100°C) and therefore a two step reaction for environmental exposure may also be envisioned such as:

$AlH_3 \Rightarrow Al + 3/2H_2(g)$ Step 1

$2Al + 1.5\ O_2(g) \Rightarrow Al_2O_3$ Step 2
$2Al + 6H_2O \Rightarrow 2Al(OH)_3 + 3H_2(g)$

Furthermore it was seen that any $Al(OH)_3$ formed will decompose to form a hydrated Al_2O_3 at low temperatures and Al_2O_3 plus water vapor at higher temperatures. The free hydrogen from the dehydrogenation step would undergo a combustion reaction producing heat and water vapor.

Calorimeter Experiments

Water Reactions in Mixing Cell

Measuring the heat given off during the reaction of a hydride compound with exposure to air or water in a calorimeter provides a way of checking if the thermodynamically predicted reactions actually occur. The experiments in this section were performed on a SETRAM C-80 calorimeter equipped with gas flow cells, and membrane mixing cells in order to replicate environmental exposure conditions from ambient temperature to 300°C.

Figure 2 displays the heat of reaction between a $2LiBH_4$*MgH_2 starting material and liquid water at 30°C. An immediate exotherm was observed at the initiation of material/water contact followed by a slow decay giving an experimentally determined heat of reaction ΔH of -115 kJ/mole as compared to the experimentally predicted -843 kJ/mole. Figure 3 displays the X-ray diffraction analysis of the reaction products indicating un-reacted MgH_2 remains along with $Mg(OH)_2$, hydrated $LiBO_2$, and $LiBO_2$. In this case the thermodynamically predicted ΔH did not correspond with the experimentally determined ΔH because the reaction did not proceed as expected. The theoretical

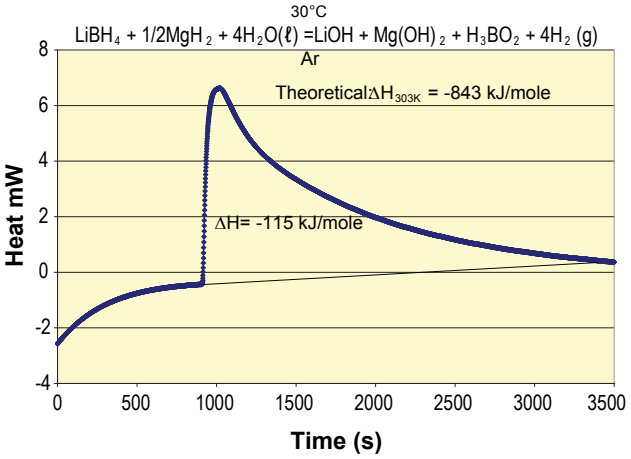

FIGURE 2. Calorimeter determined heat of reaction between $LiBH_4$*1/2MgH_2 and water at 30°C. A membrane mixing cell was used to react 20 mg of metal hydride with 1 ml of water.

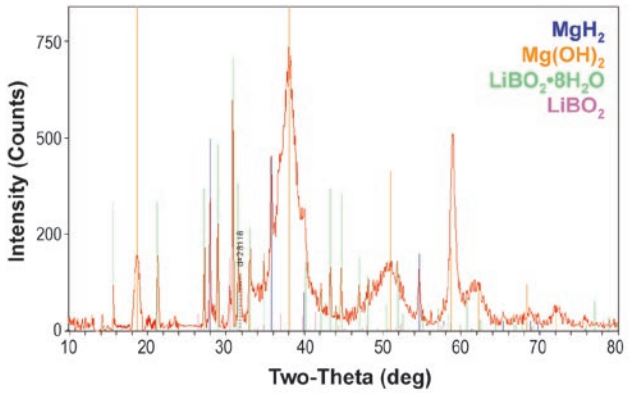

FIGURE 3. X-ray analysis of water hydrolysis products from calorimeter experiment in Figure 2. Water exposure in mixing cell.

thermodynamic value for ΔH of the experimentally observed reaction cannot currently be estimated due to lack of c_p data for hydrated $LiBO_2$ products observed.

- Predicted Reaction:

$$2LiBH_4 + MgH_2 + 8H_2O_{(g)} \Rightarrow 2LiOH + Mg(OH)_2 + 2H_3BO_2 + 8H_{2(g)}$$

- Observed Reaction:

$$2LiBH_4 + MgH_2 + 21H_2O_{(g)} \Rightarrow 2LiBO_2 \bullet 8H_2O + 1/2Mg(OH)_2 + 1/2MgH_2 + 9H_{2(g)}$$

Dry Air Exposure in Flow Cell

Experiments were performed to measure the heat of reaction measured in a gas flow cell where $LiBH_4$*MgH_2 was reacted at 30°C with dry air. An exotherm was observed when gas flow was initiated, however the reaction was slow and gave off much less heat than predicted (-0.63 kJ/mole compared to the predicted value of -2810 kJ/mole).

- Predicted Reaction:

$$LiBH_4 + 1/2MgH_2 + 2O_{2(g)} \Rightarrow LiOH + 1/2Mg(OH)_2 + H_3BO_2$$

- Observed Reaction:

$$2LiBH_4 + MgH_2 + 5O_{2(g)} \Rightarrow XLi_2(B_{12}H_{12}) \bullet 7(H_2O) + MgH_2 + LiBH_4 + YLi_iB_jO_kH_l$$

The theoretical thermodynamic value for ΔH of the experimentally observed reaction cannot currently be estimated due to lack of c_p data for the lithium borate products.

Conclusions and Future Directions

Conclusions

1. A theoretical background has been laid for assessing the thermodynamic energy release rates of candidate hydrogen storage materials.
2. A calorimetric experimental test methodology has been developed and is being refined which will yield quantitative chemical kinetics and resultant thermal releases for these reactions. Initial experiments with $2LiBH_4$+MgH_2 have shown that the thermodynamically products of water and air exposure are not the experimentally determined products. This is due to both a significant lack of thermodynamic data for many compounds and also to incomplete reactions. The later will be very useful in that the total energy releases will be somewhat mitigated due to kinetic limitations.

Future Directions

1. Thermodynamic assessments of air and water exposure of candidate materials $NaAlH_4$, $LaNi_5H_6$, $8LiH+3Mg(NH_2)_2$ and Mg_2NiH_4 will continue.
2. Calorimetric experiments will continue at various temperature and humidity levels on the initial set of compounds.
3. Standardized testing will initiate shortly on the initial set of compounds to include pyrophoricity, burn rate, dangerous self heating and water exposure testing to include analysis of flame and heat propagation as well as identification of products and assessment with predicted thermodynamic results.
4. Risk mitigation strategies will be outlined and preliminary thermodynamic calculations performed to evaluate their efficacy.

Special Recognitions & Awards/Patents Issued

This project has been recognized by the International Partnership for the Hydrogen Economy, IPHE. Partners in the project 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.

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