IV.E.3 Fundamental Environmental Reactivity Analysis of Hydrogen Storage Materials

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Objectives

- Develop internationally recognized standard testing techniques to quantitatively evaluate both materials and systems risks.
- Determine the fundamental thermodynamics and chemical kinetics of the environmental reactivity of hydrogen storage materials.
- Build a predictive capability to determine probable outcomes of hypothetical accident events.
- Develop amelioration methods and systems to mitigate the risks of using these systems to acceptable levels.

Technical Barriers

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

(F) Codes and Standards

(P) Understanding of Hydrogen Physisorption and Chemisorption

(Q) Reproducibility of Performance

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

- Standardized United Nations (U.N.) hazard analysis tests completed for all promised hydrides except alane.
- Modeling has been used to determine a critical radius for pelletization of $2LiBH_4$-MgH_2.
- Calorimetric characterization of NH_3BH_3 is completed and the accompanying modeling work is nearly completed.
- A modified burn rate test has been developed and verified using less than one-half the material required for the standard U.N. burn rate test.
- The U.N. self-heating test has been modified to a cylindrical geometry to more thoroughly support the modeling effort.
- Environmental exposure risk mitigation strategy invention disclosure filed.
- Four mitigation strategies have been evaluated preliminarily and several have been promising enough to be evaluated under cyclic sorption conditions.
- Initial thermal and chemical kinetic model completed having predictive capabilities for environmental exposure and reactivity scenarios.

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Introduction

This report gives a summary of standardized U.N. tests for material packing and shipping, along with calorimetric experiments performed in order to quantify both the rate and the amount of the energy released for hydrogen storage materials. A mathematical modeling effort has been started to predict hydride behavior for hypothesized accidental exposure of the storage materials to an ambient environment, which facilitates an assessment of the risk associated with the utilization of a particular hydrogen storage material. An idealized finite volume model was developed to represent the behavior of dispersed hydride from a breached storage tank or container. Thermodynamic calculations and substantiating calorimetric experiments were performed in order to quantify the energy released, the energy release rates and the reaction products resulting from

water and air exposure of ammonia borane. This thermodynamic data will be used in the computational fluid dynamics model to predict both the hydrogen generation rates and concentration profiles along with localized temperature distributions. The results of these numerical simulations will be used in future work to predict safety windows and to assist in the design of environmental exposure mitigation strategies.

Approach

In order for the information generated by this project to be widely accepted and globally distributed, an international program 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 has been defined. These tests include exposure to air, humidity, water, and could be modified to include proposed cooling fluids. Numerous potential hydrogen storage materials such as activated carbon, $NaAlH_4$, NH_3BH_3, $Mg(NH_2+LiH$, AlH_3, and $2LiBH_4+MgH_2$ have been tested identically under these conditions to quantitatively determine their reactivity under normally occurring environmental conditions. Independent studies have been 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 are continuing to investigate the time-dependent reaction rates of the

materials. Mathematical simulations are being developed to predict the behavior of these hydrogen storage materials upon accidental environmental exposure.

Results

U.N. Tests

The standard materials testing procedures employed are based on existing U.N. testing protocols that are used to determine 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. 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. Table 1 shows the U.N. test results for ammonia borane, alane, lithium borohydride-magnesium hydride (2:1 ratio), and the lithium hydride and magnesium hydride (8:3 ratio) hydrogen storage systems. The $8LiH·3MgH_2$ system is the only material that failed the pyrophoricity test. All materials, with the exception of ammonia borane, showed reactivity towards water.

Risk Mitigation

Four risk mitigation strategies have been identify to mitigate the risks associates with air and water reactivity in this type of materials. Currently, invention disclosures

TABLE 1. Results of the U.N. Standardized Tests

Material / UN Test	Pyrophoricity	Self-Heat	Burn Rate	Water Drop	Surface Contact	Water Immersion
NH_3BH_3 SRNL	No ignition event. Hygroscopic material absorbed H_2O from air.	Self-heated ~300°C within 10 min, 5 min at T_{oven} = 150°C	Flame propagated in 6 sec with burn rate of 33 mm/sec	No reactivity detected	No ignition event recorded. Gas evolved for about 5 min	No reactivity detected
AlH_3 SRNL (chemically synthesized)	No ignition event.	Not Tested	Flame Propagates at 250 mm/sec	Material ignited	Material sparked upon contact with wet surface.	Material sparked upon contact with water. Gas evolved for about 15 min.
$2LiBH_4·MgH_2$ SRNL	No ignition event. Hygroscopic material absorbed H_2O from air.	Self-heated ~300°C within 5 min at as T_{oven} = 150°C is approached.	Flame propagated in 5 sec with burn rate of 52 mm/sec.	2 drops required for near-instant ignition.	Material ignited	No ignition event recorded. Gas evolved for about 5 min
$8LiH·3Mg(NH_2)_2$ AIST	Ignition event recorded in room temp experiment[*]	Not Tested	Flame Propagates at 463 mm/sec[*]	Material ignited	Material ignited	No Ignition detected.
NaAlH4 (UTRC)	No ignition event	Not Tested	Flame propagated with burn rate of 51 mm/sec.	Material ignited	Not Tested	Not Tested

* Reported values from the Japanese National Institute of Advanced Industrial Science and Technology (JNAIST) (Kuriyama).
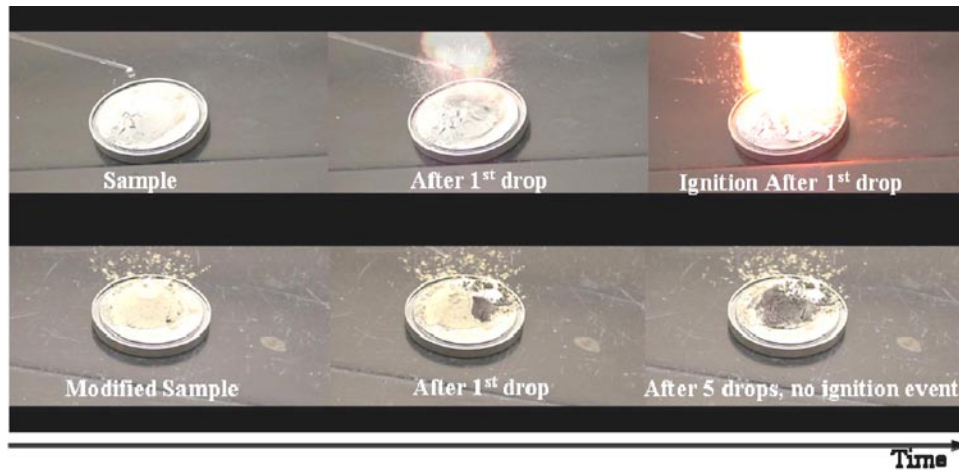
FIGURE 1. Water Drop Test for 8LiH 3Mg(NH$_2$)$_2$ (top) and Modified Sample (bottom)

are being prepared addressing the use of these strategies for these purposes. The 8LiH·3Mg(NH$_2$)$_2$ system, supplied by JNAIST was used for testing these strategies. Experiments performed at JNAIST and SRNL show that the systems exhibits high reactivity to both air and water. Figure 1 shows the water drop test for this system as well as a modified sample utilizing one of the strategies pursued. As it can be observed, the original sample ignites upon in contact with the first drop of water. In contrast, the modified sample shows significant charring but did not undergo an ignition event even after being in contact with five drops of water.

Calorimeter Experiments

Alane calorimetric measurements (refer to Figure 2) were conducted under dry air as well as 30% relative humidity and 40°C. While the dry air environmental displayed a typical exothermic behavior, the presence of 30% water vapor caused a distinct behavior change in the alane. An exothermic peak is initially observed upon
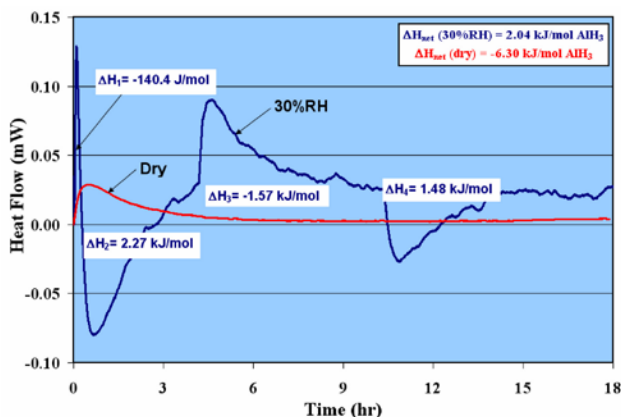

FIGURE 2. Isothermal Calorimetric Measurements for Alane at 40°C for Dry and 30% Relative Humidity Conditions

exposure humid air attributed the interaction of moisture with the material. Subsequently, a competing effect is then observed between the dehydrogenation of alane (endothermic peaks) and the oxidation of aluminum metal (exothermic peak). In situ X-ray diffraction studies are underway to further understand changes in crystal structure upon exposure to humid air condition.

Numerical Simulations

The numerical simulation examined an environmental exposure of storage material, where the hydride has been released from its containment vessel and is falling through the ambient air. The governing equations solved for each analysis include mass, momentum, and energy balances, plus additional kinetics equations based on isothermal calorimetry data at 70°C for porous 2LiBH$_4$:MgH$_2$ exposed to water. FLUENT, a general purpose computational fluid dynamics package, was used to solve the equations using the finite volume approximation method [2]. Further details of the mathematical model are availabe in the publications list below.

Two sets of initial conditions were used to evaluate the different release scenarios. For the first set of scenarios, the hydride is initialized with ambient air filling the porous media. This assumes the hydride has been out of the container for a short amount of time prior to a reaction occuring, which allows all of the hydrogen gas within the hydride to dissipate (replaced by ambient air) prior to the reaction. Typical results from these simulations are shown in Figure 3 and summarized in Table 2. The smallest diameter hydride spheres (0.05 inch and 0.25 inch radius models) never reach the lower flammability limit (LFL = 0.04) for hydrogen concentration, which means no ignition event occurs. For the larger spheres (0.50 inch and higher radius models), the LFL and/or the auto-ignition temperature (500°C or 571°C depending on the H$_2$ concentration)
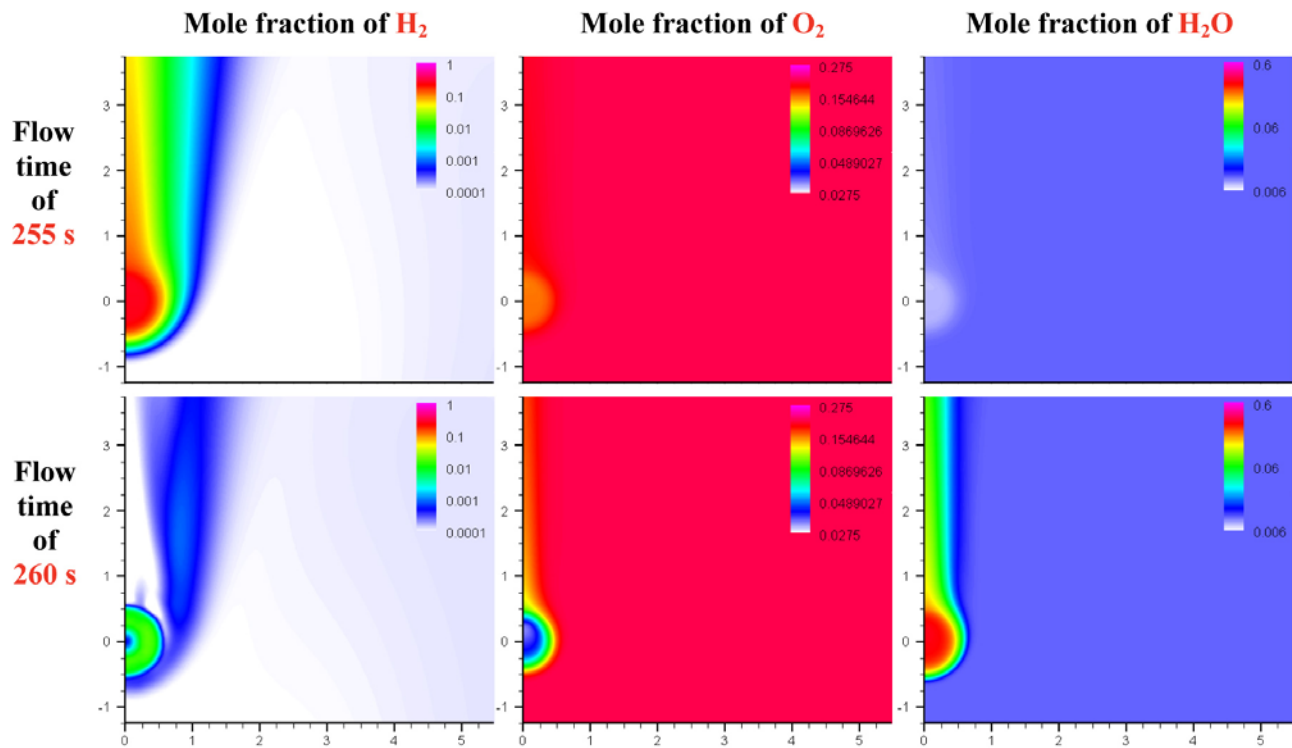
FIGURE 3. Mole Fractions of H_2, O_2, and H_2O Before and After Hydrogen Ignition (255 s and 260 s, respectively) for the Axisymmetric Sphere with a 0.5 Inch Radius

TABLE 2. 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 = 160 s	Maximum temperature of 164.2°C at t = 300 s
¼ in	None	LFL reached between t = 55 s and 60 s Max of 0.135 at t = 230 s	Maximum temperature of 752.4°C at t = 370 s
½ in	Between t = 255 s and 260 s: H_2 mf = 0.266 and 0.015 Temp = 569°C and 571°C	LFL reached between t = 30 s and 35 s Max of 0.266 at t = 255 s	Maximum temperature of 1,422°C at t = 540 s

of hydrogen is reached and an ignition event occurs. Figure 3 highlights the species concentrations before and after the hydrogen ignition event occurs for the 0.50 inch hydride sphere model. The H_2 concentration (26.6% mole fraction, mf) is well above the LFL prior to the ignition event and then drops off rapidly after the event (~1.5% mf). Note that as the H_2 and O_2 burn away, water vapor (H_2O) increases in their place. Similar results are seen for the larger spheres (1 inch and greater models), but are not shown for brevity.

For the second set of scenarios, the hydride is initialized with hydrogen gas filling the porous media. These scenarios assume that the 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. However, due to the high dissipation rate of H_2 into the ambient, most or all 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 have similar results to the air-initialized hydride models and are not shown for brevity. As is shown from the preceding results, small amounts of hydride have a lower chance of ignition compared to the larger amounts of hydride.

Conclusions and Future Directions

Conclusions

- Calorimetric measurements for alane show a competing effect between the dehydrogenation of alane and the oxidation of aluminum.
- NH_3BH_3 poses significantly less risk of ignition than the other materials tested for environmental exposure.
- Four risk mitigation strategies have been identified. Preliminary results on the 8LiH 3Mg(NH_2)_2 showed significantly reduced reactivity upon exposure to water.
- The mathematical modeling is an effective method of determining heat and hydrogen concentrations developed during simulated accident scenarios.

Future Directions

- Conclude standardized testing of AlH_3 as decided in consultation with the centers of excellence.
- Continue the thermodynamic and kinetic testing with AlH_3 and 8LiH:3Mg(NH_2)_2 to feed information into the numerical simulations.
- Continue modeling effort to include actual chemical kinetics to render predictive capabilities
- Evaluate proposed mitigation strategies utilizing calorimetry and modified U.N. tests.

Special Recognitions, Awards/Patents Issued

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

This project has been recognized by the International Energy Agency-Hydrogen Implementation Agreement with award of the *Annual Project Prize for 2010* for "Fundamental research characterized by technical excellence and harmony in international cooperation that contributes to the understanding and advancement of basic and applied hydrogen science."

FY 2010 Presentations/Publications

Presentations

1. Environmental Reactivity of Solid State Hydride Materials: Modeling and Testing for Air and Water Exposure, D.L. Anton, C.W. James, D.A. Tamburello, J.A. Cortes-Concepcion, J.R. Gray, and K.S. Brinkman, Proceedings of CIMTEC 2010: 5th Forum on New Materials, June 13–18, 2010, Montecatini Terme, Italy.

2. Fundamental Testing and Modeling of Hydrogen Storage Materials for Potential Accident Scenarios, D. Anton, D. Tamburello, W. James, and J. Cortes. International Energy Agency (IEA) Meeting, Death Valley, USA, May 2010.

3. Fundamental Testing and Modeling of Hydrogen Storage Materials for Potential Accident Scenarios, D. Anton, D. Tamburello, W. James, and J. Cortes. International Energy Agency (IEA) Meeting, Paris, France, October 2009.

4. Modeling of 2LiBH_4+MgH_2 Hydrogen Storage System Accident Scenarios Using Empirical and Theoretical Thermodynamics, C.W. James, D. Tamburello, K. Brinkman, J.R. Gray, B. Hardy, and D. Anton. International Conference on Hydrogen Safety, Corsica, France, September 2009.

5. Environmental Reactivity of Solid State Hydride Systems, J.R. Gray and D.L. Anton. International Conference on Hydrogen Safety, Corsica, France, September 2009.

Publications

1. Environmental Reactivity of Solid State Hydride Materials: Modeling and Testing for Air and Water Exposure, D.L. Anton, C.W. James, D.A. Tamburello, J.A. Cortes-Concepcion, J.R. Gray, and K.S. Brinkman, Proceedings of CIMTEC 2010: 5th Forum on New Materials, June 13–18, 2010, Montecatini Terme, Italy.

2. Modeling of 2LiBH4+MgH2 Hydrogen Storage System Accident Scenarios Using Empirical and Theoretical Thermodynamics, C. James, D. Tamburello, K. Brinkman, J. Gray, B. Hardy, and D. Anton, International Journal of Hydrogen Energy: Proceedings of the International Conference on Hydrogen Safety, 2010.

3. Modeling of 2LiBH4+MgH2 Hydrogen Storage System Accident Scenarios Using Empirical and Theoretical Thermodynamics, C. James, D. Tamburello, K. Brinkman, J. Gray, B. Hardy, and D. Anton, Proceedings of the International Conference on Hydrogen Safety, September 16–18, 2009, Corsica, France.

4. Environmental Reactivity of Solid State Hydride Materials, J. Gray and D. Anton, Proceedings of the International Conference on Hydrogen Safety, September 16–18, 2009, Corsica, France.

5. Hierarchical methodology for modeling hydrogen storage systems. Part II: Detailed models, B. Hardy and D. Anton, IJHE, 34 (7) 2009, pp. 2992-3004.

6. Hierarchical methodology for modeling hydrogen storage systems. Part I: Scoping models, B. Hardy and D. Anton, IJHE, 34 (5) 2009, pp. 2269-2277.

Endnotes

1. United Nations: Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria, 4th Revised Ed., ISBN 92113906800, (2000).

2. User's Manual for FLUENT 6.