IV.E.5 Quantifying and Addressing the DOE Material Reactivity Requirements with Analysis and Testing of Hydrogen Storage Materials and Systems

Daniel A. Mosher (Primary Contact),
Yehia F. Khalil and Bruce L. Laube
United Technologies Research Center (UTRC)
411 Silver Lane
E. Hartford, CT 06108
Phone: (860) 610-7011; Fax: (860) 660-1284
E-mail: mosherda@utrc.utc.com

DOE Technology Development Manager:
Ned Stetson
Phone: (202) 586-9995; Fax: (202) 586-9811
E-mail: Ned.Stetson@ee.doe.gov

DOE Project Officer: Jesse Adams
Phone: (303) 275-4954; Fax: (303) 275-4753
E-mail: Jesse.Adams@go.doe.gov

Contract Number: DE-FC36-07GO17032

Subcontractor:
Kidde-Fenwal, Combustion Research Center,
Holliston, MA

Project Start Date: June 1, 2007
Project End Date: June 1, 2010

Objectives

Provide improved definition of the DOE Environmental Health and Safety (EH&S) Target and its link to material reactivity to guide research of storage materials. More detailed objectives include:

- Develop qualitative and quantitative analysis tools to evaluate risks for materials-based hydrogen storage systems before and after mitigation methods.
- Perform dust explosion tests for metal hydride, chemical hydride and adsorbent materials.
- Characterize chemical reactions for material exposures associated with both risk events and mitigation approaches using time resolved X-ray diffraction (XRD).
- Assess the trade-offs between residual risk after mitigation and the system weight and volume as well as reaction rates.

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:

(F) Codes and Standards
(A) System Weight and Volume
(E) Charging/Discharging Rates

Technical Targets

The key technical target of this project is EH&S, having a focus on the Safety sub-target with some consideration for toxicity. The technical target for safety is currently specified generally as "Meets or exceeds applicable standards." For metal hydride, chemical hydride and adsorbent materials and systems, however, no such standards exist today. Furthermore, standards currently under development will be high-level in scope, being primarily focused on systems and will not provide adequate guidance to help evaluate new materials and assist in selecting viable candidates. As part of this effort, trade-offs will be evaluated between the residual risk after mitigation of the two technical barriers: System Weight and Volume, and Charging/Discharging Rates.

Accomplishments

- Developed customized design failure modes and effects analysis (dFMEA) framework and set of failure modes for on-board reversible systems using prior $NaAlH_4$ material and system experience as guidance.
- Initiated Event Tree Analysis/Fault Tree Analysis (ETA/FTA) for key dFMEA risks.
- Performed dust explosion testing for the material $2LiBH_4 + MgH_2$ in the hydrided and partially dehydrided states, evaluating the effect of particle size for the latter state.
- Conducted time resolved XRD on $2LiBH_4 + MgH_2$ during exposure to humid air and analyzed the XRD patterns to determine crystalline product evolution which will support reactivity modeling.

◆ ◆ ◆ ◆ ◆

Introduction

EH&S is one of the highest criteria for consumer selection of vehicle fuel based on recent DOE surveying associated with measuring H2IQ. The current EH&S target is "Meets or exceeds applicable standards," although none currently exist. The current project, in close coordination with efforts at Savannah River National Laboratory (SRNL) and Sandia National Laboratories (SNL), will provide meaning to this target and support the development of such codes and standards (C&S). The ultimate adoption of these C&S can be a lengthy process; however, the results from these efforts will also have nearer term impact in guiding storage materials research and the development of materials/systems risk mitigation methods.

Approach

The project has five distinct elements, described below, to perform the range of studies required:

- **Risk Analysis:** Formal analysis methods are developed and employed to produce tools which provide increasingly quantitative descriptions of the risks-associated primarily with on-board automotive hydrogen storage before and after the use of mitigation methods.
- **Standardized Materials Testing:** A set of standard materials tests, focusing on dust explosion, are performed on storage materials to quantify their reactivity under conditions of potential risk scenarios.
- **Chemical Reaction Kinetics Testing and Modeling:** Fundamental studies are performed to evaluate the chemical kinetics of material reactions with oxygen, water and various fluids (primarily gases) using time resolved XRD and other techniques to support risk mitigation development.
- **Risk Mitigation:** Concepts to reduce the dominant risks will be devised and investigated both at the material and system levels. The impact on system performance targets will also be determined.
- **Prototype System Testing:** Pending a go/no-go decision, sub-scale prototype tests will be performed to evaluate the response for larger quantities of storage material and the effectiveness of the risk mitigation methods.

A sketch illustrating the central role of risk analysis, linking the more detailed material measurements and modeling with the higher level DOE target and C&S, is shown in Figure 1. Additional data from the SRNL and SNL coordinated projects as well as from international partners in an associated International Partnership for the Hydrogen Economy (IPHE) project are being incorporated into the reaction kinetics modeling and risk analyses.

Results

During this first year of the project (Q4 Fiscal Year 2007 to Q3 FY 2008), a dFMEA risk analysis framework was developed for on-board reversible hydrides with a focus on $NaAlH_4$ class systems due to prior safety test data and prototype development experience available for this material. The dFMEA framework was constructed based on accepted standards [1,2], but customized regarding the scoring details for probability, consequence and detectability as well as data fields to track the impact on performance targets, technology readiness levels for mitigation approaches and the connection to DOE multi-project plans. The dFMEA is in the process of being reviewed by a diverse expert panel for hazard descriptions and risk scoring. As detailed data are developed through testing and analysis, the expert panel assessment will be updated and analyzed for confidence levels.

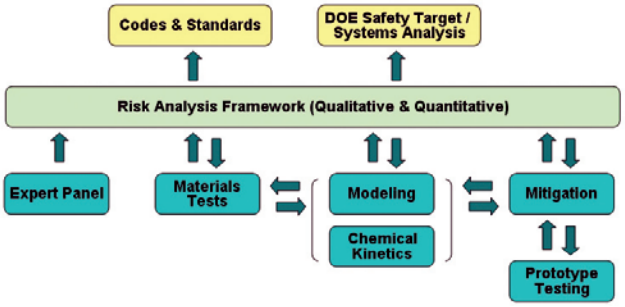

FIGURE 1. Relationships between Detailed Studies, Risk Analyses and High Level Objectives

Quantitative ETA/FTA has been structured for key risks determined from preliminary dFMEA scoring. In ETA, a sequence of events is defined with dependencies and probabilities of occurrence. A set of end state results from the event tree and severity or consequence levels are determined for each end state. An example is an automobile subjected to the initiating event of an accident. Subsequent accident progression events then involve whether or not 1) the vessel ruptures, 2) a critical amount of hydride is released, 3) the environment is wet (ex. rain), and other potential events. These analyses will be continually refined as information is gained from the testing and modeling from UTRC, SRNL, SNL and the IPHE collaborators.

Dust explosion testing was performed for the material $2LiBH_4 + MgH_2$ in the hydrided and partially dehydrided states. The following ASTM tests were conducted to measure the given quantities:

- E1226: P_{max}, $(dP/dt)_{max}$, K_{ST}
- E1491: Minimum Ignition Temperature (T_C)
- E1515: Minimum Explosive Concentration (MEC)
- E2019: Minimum Ignition Energy (MIE)

The results are given for the hydrided material in Table 1 along with data for $NaAlH_4$ from a prior DOE contract [3] and Lycopodium spores which is a well defined dust used to calibrate dust explosion test devices.

The characteristics of the $2LiBH_4 + MgH_2$ and $NaAlH_4$ powder samples are similar except for the MEC. The parameter K_{ST} is a volume normalized pressure rise rate,

$$K_{ST} = \left(\frac{dP}{dt}\right)_{\max} * V^{1/3}$$

which properly would reach a maximum at some dust concentration. However, the measured value continued to increase to the highest levels of dust concentration tested and therefore the number reported in Table 1 represents a lower bound for the true K_{ST}. A value of K_{ST} >300 bar-m/s results in the highest dust classification of St-3.

The $2LiBH_4 + MgH_2$ powder was partially desorbed at 330°C for 2 hours under vacuum. The resulting material had a coarse, sintered consistency, and dust explosion testing in this state would not be meaningful. If one considers the breach of a storage system vessel under moderately high pressures (100 bar, shortly after charging), the sudden drop of pressure and/or rapid velocity of the released hydrogen jet could break up the material into finer particles. To mimic this, the material was ball milled for 2.5 minutes and sieved to separate the powder into three particle size ranges:

- 40 to 100 mesh (420 µm to 150 µm)
- 100 to 200 mesh (150 µm to 75 µm)
- <200 mesh (<75 µm)

and tested separately to examine the influence of particle size. In general, as expected, the reactivity was decreased for the larger particle sizes. The most significant influence was on the important $(dP/dt)_{max}$ and associated K_{ST} parameter which is plotted in Figure 2. Increasing the particle size reduces the material to the lowest dust classification for which K_{ST} <200 bar-m/s. These results motivate additional work within the IPHE team to measure particle size distributions resulting from dispersion events after absorption/desorption cycling.

TABLE 1. Dust Explosion Test Results for $2LiBH_4 + MgH_2$ in the Hydrided State

	$2LiBH_4$+ MgH_2	$NaAlH_4$	Lyco. Spores
P_{max}, bar-g	10.7	11.9	7.4
$(dP/dt)_{max}$, bar/s	2036	3202	511
K_{ST}, bar-m/s	553	869	139
Dust Class	St-3	St-3	St-1
MEC, g/m^3	30	140	30
T_C, °C	150	137	430
MIE, mJ	<9	<9	17

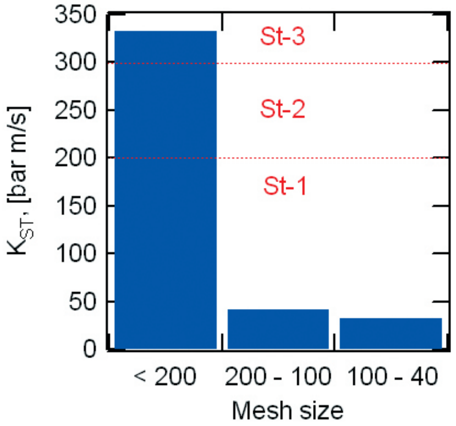

FIGURE 2. Dust Explosion Parameter for Different Particle Sizes of Partially Discharged $2LiBH_4 + MgH_2$

The reaction kinetics during humid air exposure were evaluated using time resolve XRD on the $2LiBH_4 + MgH_2$ mixture in the hydrided and partially dehydrided states and also on the individual hydrides. This material undergoes a complex sequence of steps during hydrolysis/oxidation starting with adsorption of water, formation of a deliquescent paste, release of hydrogen that produces bubbles (and spatters material), followed by longer term drying and recrystallization of the products. The XRD patterns were analyzed using whole pattern fitting with the JADE software package to determine the crystalline compounds. In general, the $LiBH_4$ material reacts much more rapidly than MgH_2 both when tested separately and in the 2:1 mixture. A graph of the short time frame evolution of the crystalline material is shown in Figure 3. Some Li_3BH_6 and other crystalline products are formed before disappearing (becoming amorphous) with the exception of MgH_2. The left hand axis gives the mass fraction or relative amount of material, while the right hand axis estimates the absolute mount of material through the primary XRD peak area. From this, we see the amount of MgH_2 is nearly constant and decreases slightly. This data will be combined with information from SRNL and SNL to develop reaction kinetics models that can be used in evaluating larger scale hazard scenarios of the risk analyses.

Conclusions and Future Directions

Broad qualitative and more specific quantitative risk analyses methods have been developed, which will continue to be updated as information is gathered and generated through this project and the efforts of other DOE and IPHE collaborators. The detailed information generated to date includes dust explosion testing and

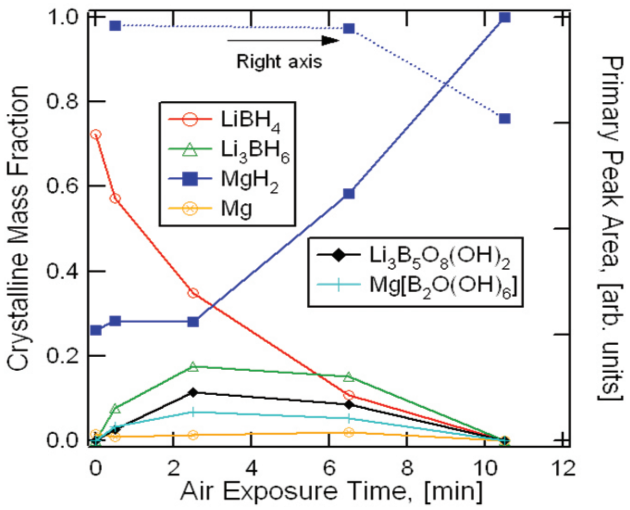

FIGURE 3. Exposure of 2LiBH$_4$ + MgH$_2$ to Humid Air at 24°C and 48% Relative Humidity

humid air exposure experiments for 2LiBH$_4$ + MgH$_2$. For the dust explosion testing, the material behaves similarly to NaAlH$_4$, and the influence of particle size on the primary parameter characterizing severity, K$_{ST}$, has been quantified.

In future work, input from the expert panel will be used to assess the dominant risks and the techniques discussed in the first publication listed below will be applied to estimate uncertainties associated with expert judgment. Additional test data, modeling results and surrogate field information associated with dust explosion, water exposure, reaction kinetics, component reliability and hazard characteristics will be produced or acquired to support the quantitative risk analysis. The assessments and experimentation will be extended to other material systems such as alane and activated carbon, including the dust explosion and humid air exposure tests.

FY 2008 Publications/Presentations

1. Y. Khalil and D. Mosher, "Probabilistic Treatment of Expert Judgment on Aleatory and Epistemic Uncertainties Associated with On-board Vehicle Hydrogen Storage Systems," International Topical Meeting on Probabilistic Safety Assessment & Analysis, PSA08, Knoxville, TN, September 7-11, 2008. (in preparation)

2. D. Mosher, Y. Khalil, X. Tang, B. Laube, R. Brown, J. Senecal and K. Sorinmade "Fundamental Safety Testing & Analysis of Solid State Hydrogen Storage Materials & Systems," IEA Task 22 Meeting, Quebec, Canada, March 2-5, 2008.

3. D. Mosher, Y. Khalil, X. Tang, B. Laube and R. Brown, "Fundamental Safety Testing & Analysis of Solid State Hydrogen Storage Materials & Systems," IEA Task 22 Meeting, Petten, Netherlands, September 3-7, 2007.

References

1. "Potential Failure Mode and Effects Analysis in Design (Design FMEA) and Potential Failure Mode and Effects Analysis in Manufacturing and Assembly Processes (Process FMEA) and Effects Analysis for Machinery (Machinery FMEA)," SAE document J1739, August 2002.

2. "Recommended Failure Mode and Effects Analysis (FMEA) Practices for Non-Automobile Applications," SAE document ARP5580, July 2001. (replaces military standard MIL-STD-1629)

3. D. Mosher, X. Tang, R. Brown, S. Arsenault, S. Saitta, B. Laube, R. Dold and D. Anton, "High Density Hydrogen Storage System Demonstration Using NaAlH$_4$ Based Complex Compound Hydrides," Final report for DOE contract DE-FC36-02AL67610, OSTI document, July 27, 2007.