Fundamental Safety Testing and Analysis of Hydrogen Storage Materials and Systems

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We Put Science To Work

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Savannah River National Laboratory
May 16, 2007

Project ID #: ST 22

This presentation does not contain proprietary or confidential information

Overview

Timeline

- Start: 10/1/05
- End: 9/30/10
- Percent complete: 10%

Budget

- Funding received in FY06
  - $100,000
- Funding for FY07
  - $300,000

Barriers Addressed

- **Environmental, Health & Safety**
- Gravimetric Density
- Volumetric Density
- System Cost

Partners

- **M. Fichtner,** Forschungszentrum Karlsruhe, Germany
- **N. Kuriyama,** National Institute for Advanced Industrial Science and Technology, Japan
- **R. Chahine,** Université du Québec à Trois-Rivières, Canada
- **D. Mosher,** United Tech. Res. Ctr., USA
- **D. Dedrick,** Sandia NL, USA

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DoE Technical Targets

Target	2007	2010	2015
Wt % H_2 (Useable)	4.5	6	9
Vol. Cap. (kg H_2/L)	0.036	0.045	.081
Cycles	500	1000	1500
Minimum rate (g/s)/kW	.02	.02	.02
Minimum/Maximum pressure (atm) [FC]	8/100	4/100	3/100
Minimum/Maximum ambient temperature (°C)	-20/50	-30/50	-40/60
Start time to full flow (s)	4	4	0.5
System fill time (min)	10	3	2.5
Safety	Meet or exceed applicable standards		

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Objective

The objective of this study are to fundamentally understand the safety issues regarding solid state hydrogen storage systems through:

- Development of standard testing techniques to quantitatively evaluate both materials and systems.
- Determine the fundamental thermodynamics & chemical kinetics of environmental reactivity of hydrides.
- Develop amelioration methods and systems to mitigate the risks of using these systems to acceptable levels.

Task Plan

- ***Task 1: Risk Assessment***
  - Assess the potential risks of using solid state hydrides
  - Test six compounds in three discharge states using standardized semi-quantitative test methods
- ***Task 2: Thermodynamics & Chemical Kinetics***
  - Quantitatively assess chemical reactions of compounds with air, water & other engineering materials
- ***Task 3: Risk Mitigation***
  - Quantitatively assess chemical reactions of compounds with potential inhibitors
  - Evaluate efficacy of inhibitors in laboratory scale tests
- ***Task 4: Prototype System Testing***
  - Design assemble and test prototype storage systems to evaluate effectiveness of inhibitor systems.

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Materials Test Plan

1. Three major classes of solid state hydrogen storage materials are being studied: metal hydrides, complex hydrides & activated carbon.
2. The three major classes of complex hydrides are being evaluated: Alanates, Amides & Boronates

Some Known

Complete Analysis

- $NaAlH_4$ + 2%$TiCl_3$
- 2LiH + $Mg(NH_2)_2$
- Mg_2NiH_4
- $LaNi_5H_6$

Little Known

Investigations Initiated

- AlH_3
- NH_3BH_3
- Activated Carbon
- $LiBH_4$ + MgH_2

Little Known

Start if Required

- Li_3AlH_6
- Organic Hydrides
- …

Materials Prep Plan

- **Mill to Use Particle Size**
  - **Fully Charged**
  - Partially Discharged
  - Fully Discharged

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Task 1: Standard Tests

DOT/UN Doc., *Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria*, 3rd Revised Ed., ISBN 92-1-139068-0, (1999).

- **Flammability**
  - *Flammability Test*
  - *Spontaneous Ignition*
  - *Burn Rate*
- **Water Contact**
  - *Immersion*
  - *Surface Exposure*
  - *Water Drop*
  - *Water Injection*
- **Impact Sensitivity**

- *Standard Test Method for Pressure and Rate of Pressure Rise for Combustible Dusts* (ASTM E1226)
  - P_{max} & $(dP/Dt)_{max}$
  - *Min. Exp. Conc.*
  - *Min. Ignition Energy*
  - *Min. Ignition Temp.*
  - *Min. Dust Layer Ignition Temp.*

Task 1: Impact Sensitivity

- Purpose
  - To measure the sensitivity of solids to drop weight impact.
- Procedure
  - A ~100 mg sample is placed in the anvil cell
  - A 10 kg steel striker dropped from 50mm impacts the sample in a closed chamber.
  - If detonation does not occur, the mass is raised by 25mm to a maximum of 500mm and retested un till detonation is detected.
- Needs quantification to measure energy released.

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Task 1 Plans

- Synthesize/acquire bulk quantities of fine grained (>10μm) NH_3BH_3, $2LiBH_4$+MgH_2 & AlH_3 for use and distribution to IPHE team.
- Perform water contact & flammability experiments
- Identify both solid and gaseous reaction products
- Design/develop instrumented impact test based on BAM Fallhammer Test
- Assess impact sensitivity of all materials after humid air exposure.

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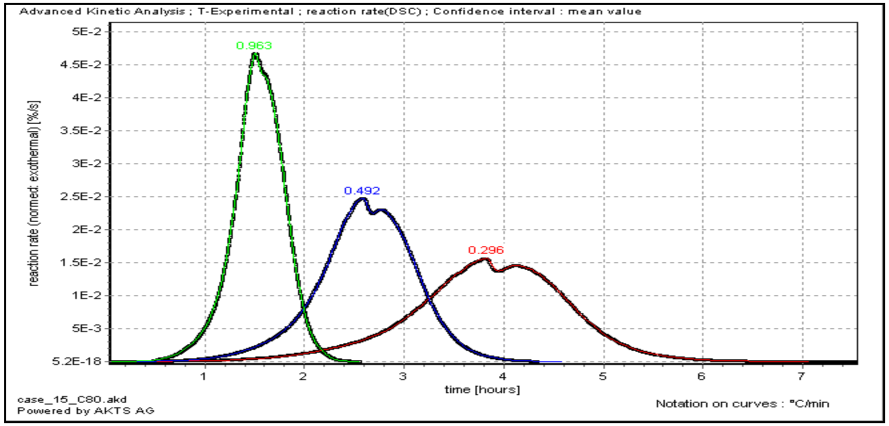
Task 2: Thermodynamics & Chemical Kinetics

Quantitative studies will be performed to understand the **chemical kinetics** and **thermo-chemical release** 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 may also be studied to determine those fluids which are safe to use as heat transfer and synthesis 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, mechanisms and/or properties of inhibiting layers.



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Calorimetric Experimental Procedures Established

- Thermodynamic assessment has been initiated on the $2LiBH_4+MgH_2$ system for:
  - Water reaction at 30^{o}C
  - Air reactions at 30^{o}C 0<RH<100%
- Laboratory *Hazards Analysis Process* Completed
- Initial water contact experiments
- Initial humid air experiments
- Identification of reaction products

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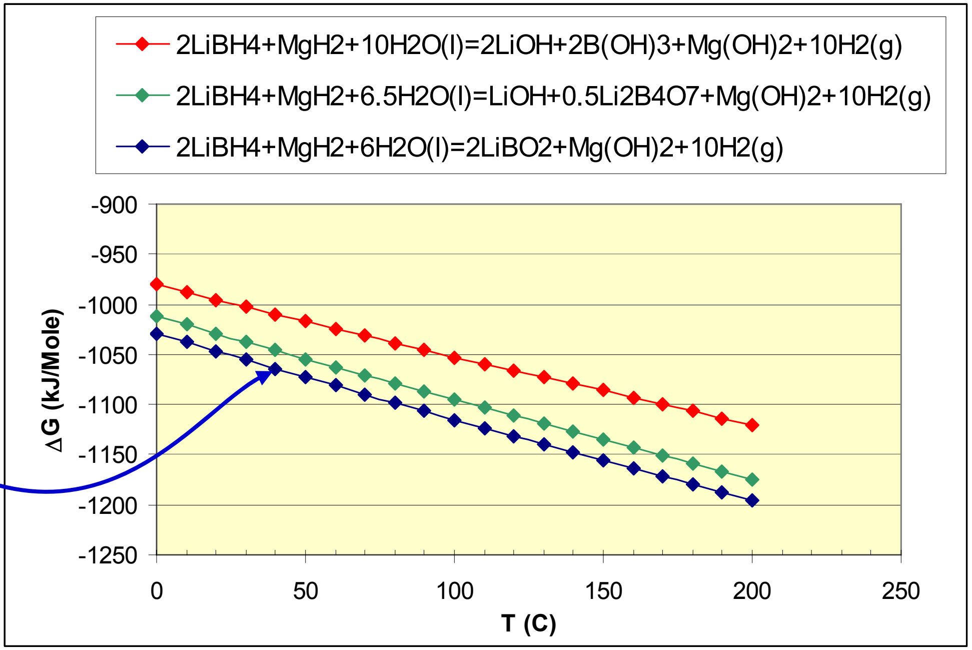
Thermodynamics of Water Contact

Water Hydrolysis Possibilities

- $2LiBH_4 + MgH_2 + 10H_2O_{(\ell)} \Rightarrow LiOH + 2B(OH)_3 + 2Mg(OH)_2 + 10H_{2(g)}$
- $2LiBH_4 + MgH_2 + 6.5H_2O_{(\ell)} \Rightarrow LiOH + 0.5Li_2B_4O_7 + Mg(OH)_2 + 10H_{2(g)}$
- $2LiBH_4 + MgH_2 + 6H_2O_{(\ell)} \Rightarrow 2LiBO_2 + Mg(OH)_2 + 10H_{2(g)}$

ΔH^{373} = -804 kJ/mole formula unit



Based on available thermodynamic data in JANAF database

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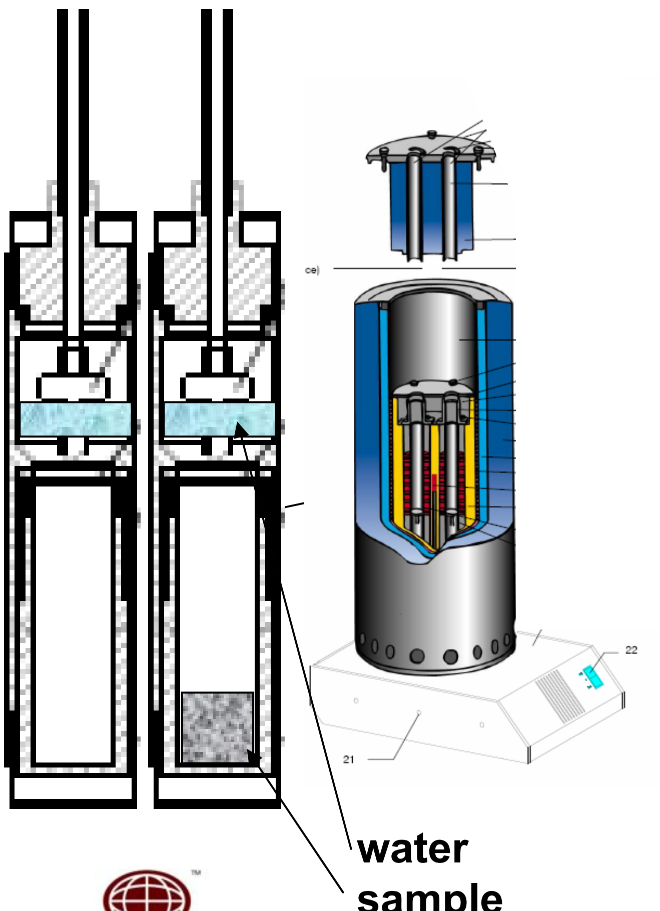
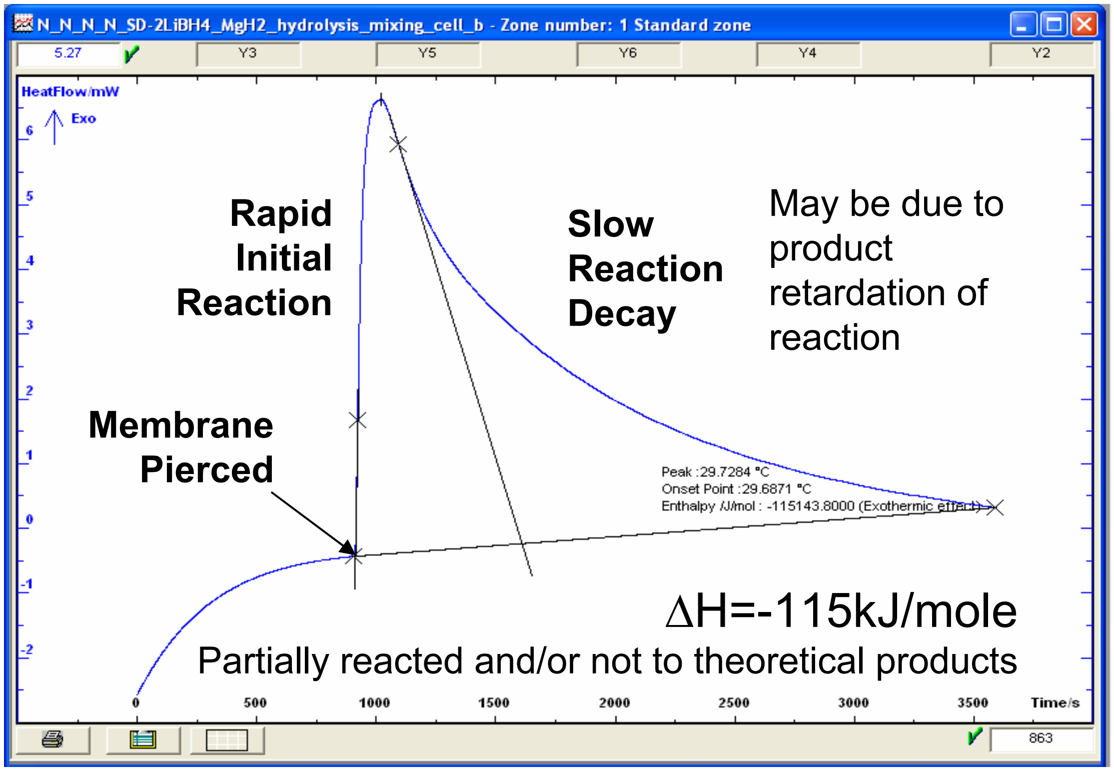
Thermo-chemical Analysis of Water Contact

$$2LiBH_4 + MgH_2 + 6H_2O_{(\ell)} \xrightarrow[Ar]{30^oC} 2LiBO_2 + Mg(OH)_2 + 10H_2(g)$$

Theoretical: ΔH^{303} = -792 kJ/mole formula unit





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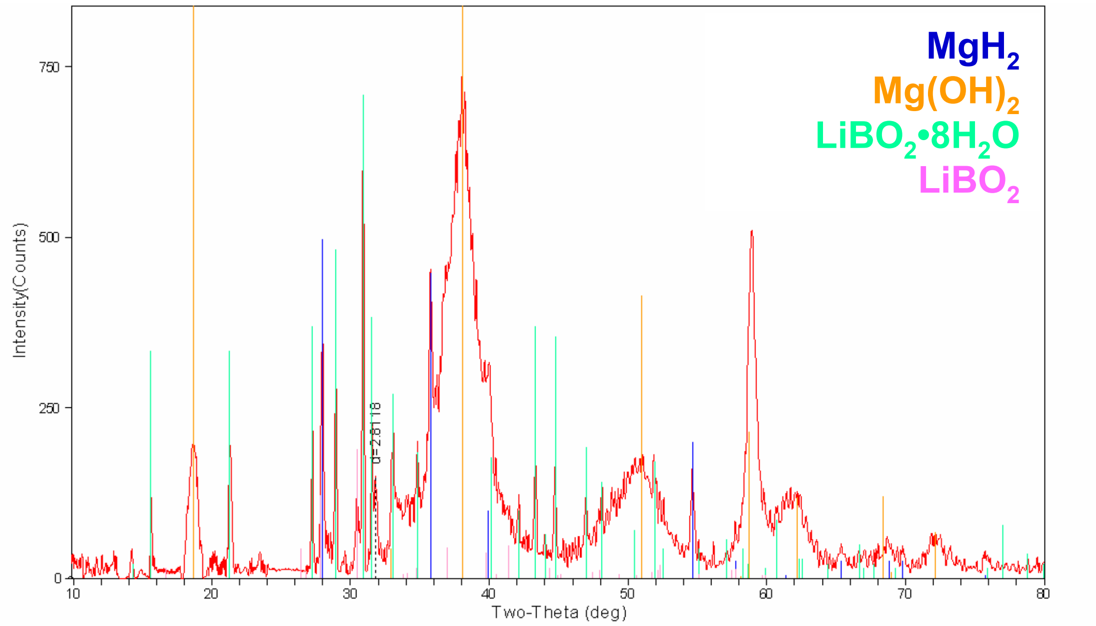
XRD Results of Water Contact

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

Thermodynamic data to be identified



- Products yield fully hydrated $LiBO_2 \bullet H_2O$
- Approximately one half of the MgH_2 hydrated
- **Difficult to predict thermal release when actual products do not match predicted**

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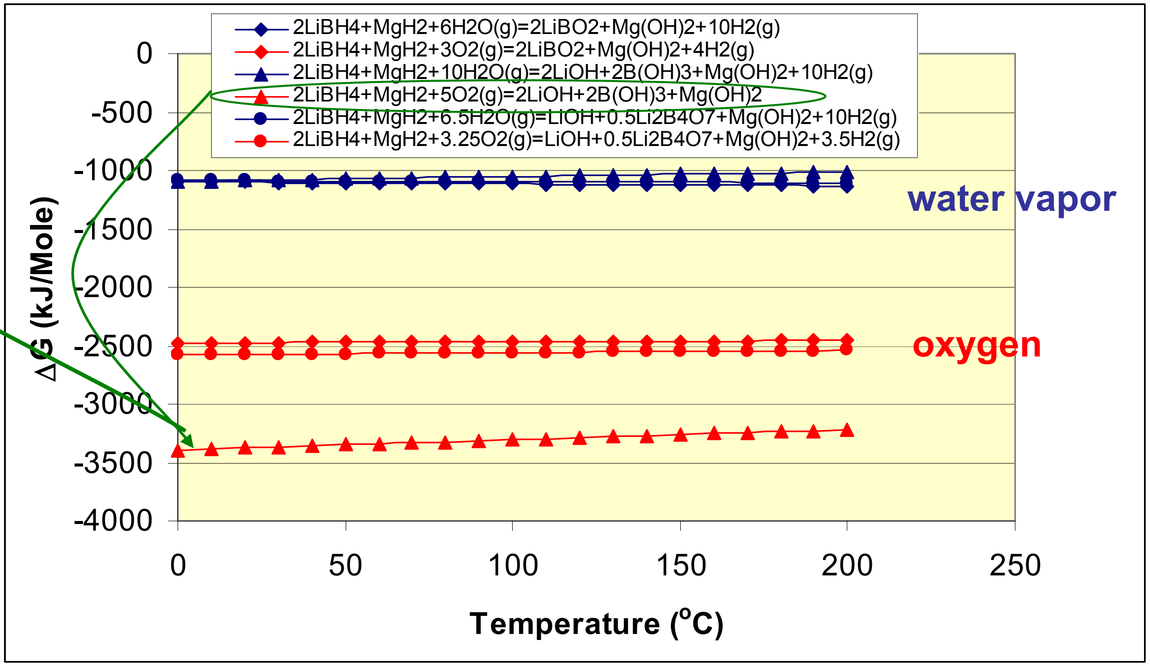
Thermodynamics of Air Exposure

Air Exposure Possibilities *(oxygen & water vapor only)*

- $2LiBH_4 + MgH_2 + 10H_2O_{(g)} \Rightarrow LiOH + 2B(OH)_3 + 2Mg(OH)_2 + 10H_{2(g)}$
- $2LiBH_4 + MgH_2 + 5O_{2(g)} \Rightarrow 2LiOH + 2B(OH)_3 + Mg(OH)_2$ **ΔH^{373} = -3,304 kJ/mole formula unit**

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

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



Based on available thermodynamic data in JANAF database

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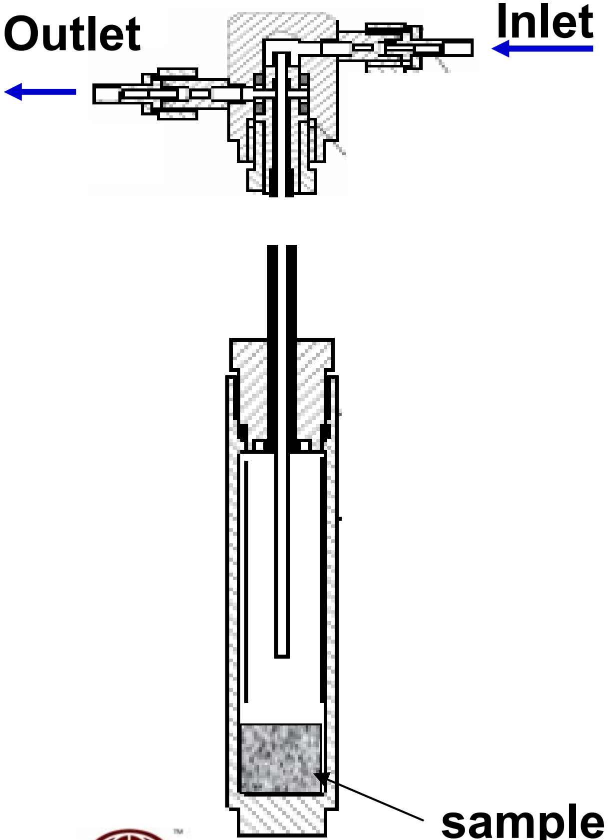
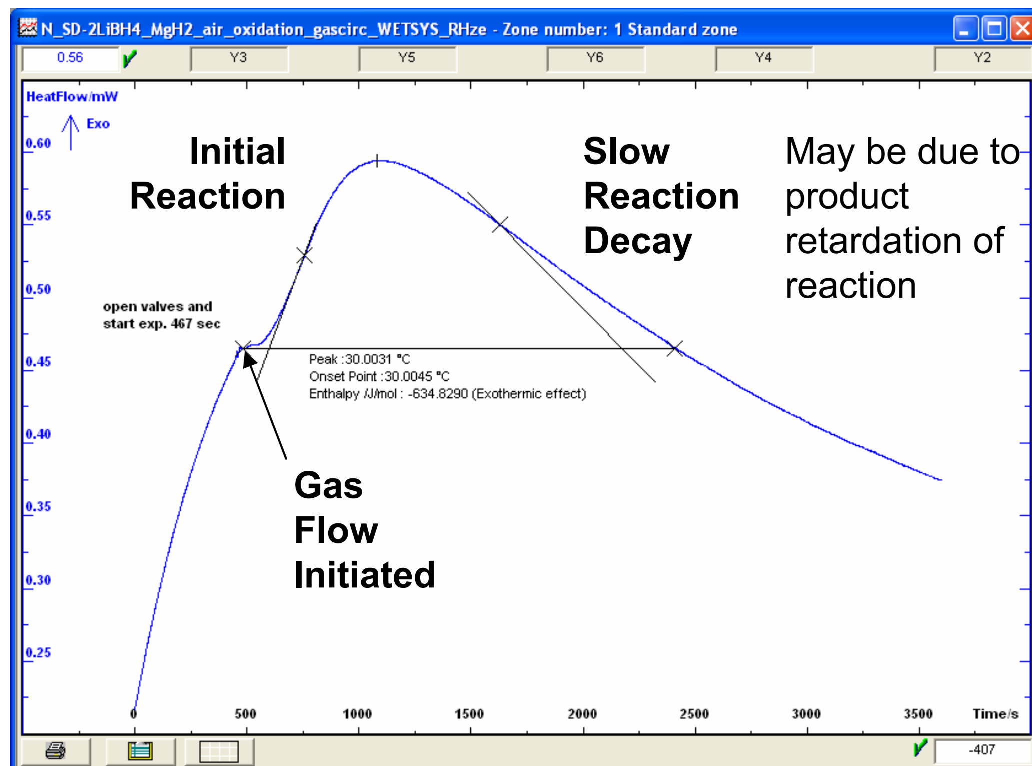
Thermo-chemical Analysis of Dry Air Exposure



$$2LiBH_4 + MgH_2 + 5O_{2(g)} \xrightarrow[0\%RH]{30^{o}C} 2LiOH + 2B(OH)_3 + Mg(OH)_2$$



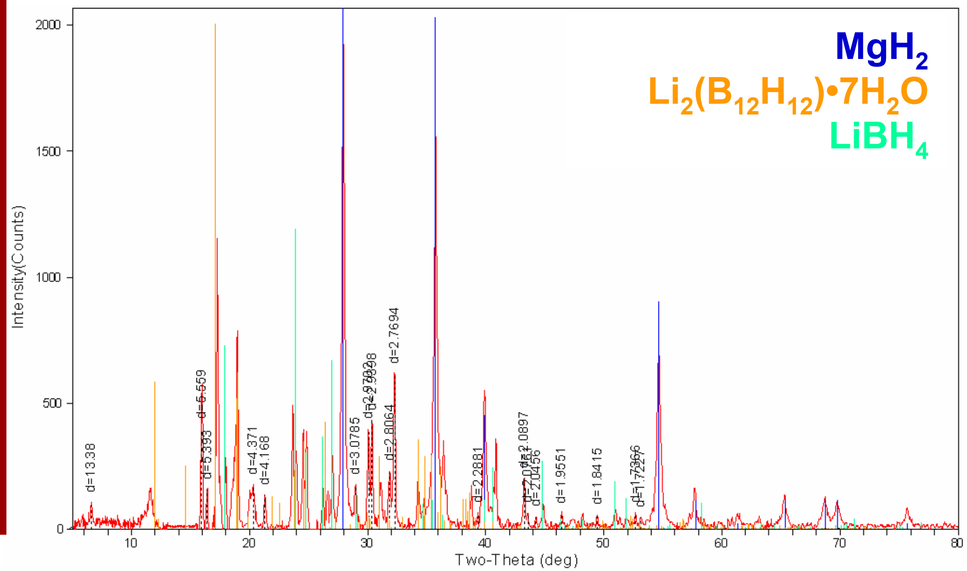
XRD Analysis of Dry Air Exposure

$$2LiBH_4 + MgH_2 + 5O_{2(g)} \xrightarrow[0\%RH]{30^{o}C} XLi_2(B_{12}H_{12})\bullet 7(H_2O) + MgH_2 + LiBH_4 + YLi_iB_jO_kH_l$$

Thermodynamic data to be evaluated

Intermediate oxide/hydroxide/hydrates to be identified and thermodynamic data evaluated

- Oxidation results in intermediate $Li_2(B_{12}H_{12})\bullet 7(H_2O)$
- Water formation results from dissociated H from $LiBH_4$ and O_2
- Numerous unidentified peaks are likely due to unidentified Li_xB_y-oxide/hydroxide/hydrate
- $LiBH_4$ only partially reacted & MgH_2 unreacted



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Task 2 Plans

- Evaluate theoretical thermodynamics for water and air exposures initially of NH_3BH_3, $2LiBH_4$+MgH_2, 2LiH+$Mg(NH_2)_2$ & AlH_3 followed by $NaAlH_4$, Mg_2NiH_4 & $LaNiH_6$.
- Perform calorimetric experiments for water exposure at $0<T<50^oC$
- Perform calorimetric experiments for conditioned air exposure at $0<T<100^oC$, 0<%RH<100%
- Identify reaction products
- Identify thermodynamic properties of reaction products as required and reconcile thermodynamic and experimental results.
- Assess risks based on observed thermo-chemical release

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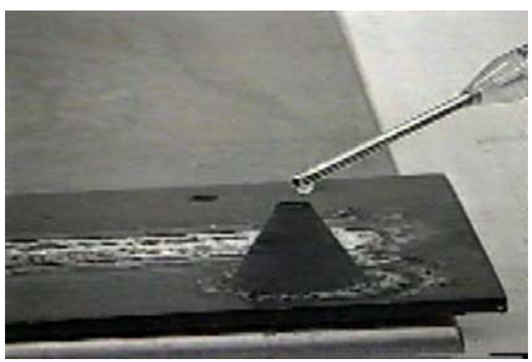
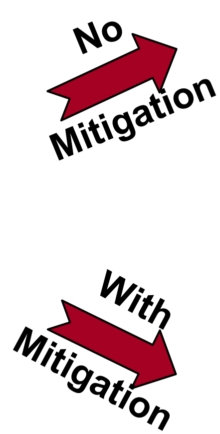
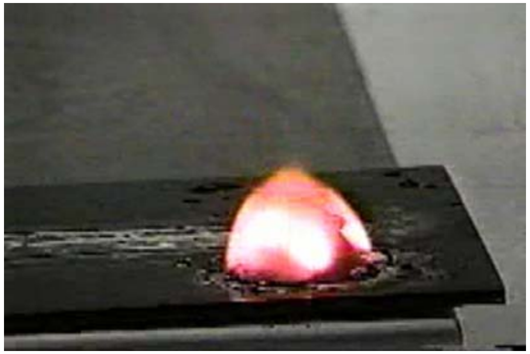
Task 3: Risk Mitigation

System risk analyses will be performed and methods of mitigating these risks including 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. The fundamental effectiveness of these mitigations methods will be determined with identification of the most successful identified.







Task 3 Plan

- Identify risk mitigation strategies including contaminants and poisons which will reduce exothermic releases.
- Evaluate theoretical thermodynamics of mitigation strategies for water and air exposures initially on NH_3BH_3, $2LiBH_4+MgH_2$, $2LiH+Mg(NH_2)_2$, AlH_3 & $NaAlH_4$.
- Perform calorimetric experiments of mitigation strategies for water exposure at $0<T<50^oC$.
- Perform calorimetric experiments of mitigation strategies for conditioned air exposure at $0<T<100^oC$, $0<\%RH<100\%$.
- Identify reaction products.
- Identify thermodynamic properties of reaction products as required and reconcile thermodynamic and experimental results.
- Assess mitigation strategies effectiveness based on observed thermo-chemical release.

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Task 4: Prototype System Testing

Evaluation tests on risk mitigations strategies will be performed to validate their efficacy. Prototype vessels of approximately one liter in volume will be filled with promising hydrogen storage materials and tested for vessel rupture, water ingestion, humid air ingestion etc. to determine the effect of larger contained amounts of hydride. These tests will be derived from internationally accepted standards for testing chemical and pressurized containers with the aim of setting standards for testing solid state hydrogen storage containment. Time will be allotted for interacting with standards setting agencies to guide development of these practices.

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Institut de recherche sur l'hydrogène
Université du Québec à Trois-Rivières

Forschungszentrum Karlsruhe
in der Helmholtz-Gemeinschaft

Participation Matrix

	SRNL	FZK	AIST	SNL	UTR	UTRC
1.0 Risk Assessment						
1.1 Perform Formal Risk Assessment						x
1.2 Bulk Tests	x	x	x	x	x	
1.3 Dust Cloud Tests		x	x			x
2.0 Thermodynamics & Chemical Kinetics						
2.1 Calorimetry	x					
2.2 RT-XRD						x
2.3 TGA MS				x		
2.4 Kinetics Modeling	x			x		
3.0 Risk Mitigation						
3.4 Risk Mitigation Strategy	x			x		x
3.1 Calorimetry	x					
3.2 TGA/MS				x		
3.3 Hazards Tests	x					x
3.5 Surface Analysis		x				
4.0 Prototype System						
4.1 System Design		x				
4.2 System Reaction Modeling				x	x	x
4.3 Subscale prototype testing					x	
4.4 System Design Strategy		x			x	
4.5 Materials Preparation		x			x	
4.6 Sytem Evaluation		x				

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SRNL FYs '07 & '08 Work

- Coordinate IPHE team to complete experimental analysis, compile results and disseminate findings and conclusions.
- Complete laboratory safety protocols, initiate and complete standardized tests UN hazards analysis tests on NH_3BH_3, $2LiBH_4$+MgH_2, $C_{[a]}$ & AlH_3.
- Complete thermodynamic assessment of environmental exposure reactions.
- Perform calorimetric experiments on environmental exposure reactions, assess reaction products and chemical kinetics as a function of T & %RH.
- Determine chemical reaction & thermal discharge rates to assess risks.

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Publication in Press

Fundamental Safety Testing and Analysis of Hydrogen Storage Materials & Systems

D. Anton, D. Mosher,

M. Fichtner, D. Dedrick, R. Chahine, E. Akiba and N. Kuriyama

Proceedings of the

2nd International Conference on Hydrogen Safety

September 11-13, 2007

San Sebastian, Spain

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