Overview

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

Budget
- Proposed Budget: $2M
- Funding received in FY07
  - $300K
- Funding for FY08
  - $500K

Barriers Addressed
- D. Durability/Operability
- A. System Weight and Volume
- Q. Reproducibility of Performance
- F. Codes and Standards

Partners
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- D. Dedrick, Sandia NL, USA
# DoE On-Board Hydrogen Storage
## Technical Targets

<table>
<thead>
<tr>
<th>Target</th>
<th>2007</th>
<th>2010</th>
<th>2015</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt % H₂ (Useable)</td>
<td>4.5</td>
<td>6</td>
<td>9</td>
</tr>
<tr>
<td>Vol. Cap. (kg H₂/L)</td>
<td>0.036</td>
<td>0.045</td>
<td>.081</td>
</tr>
<tr>
<td>Cycles</td>
<td>500</td>
<td>1000</td>
<td>1500</td>
</tr>
<tr>
<td>Minimum rate (g/s)/kW</td>
<td>.02</td>
<td>.02</td>
<td>.02</td>
</tr>
<tr>
<td>Minimum/Maximum pressure (atm) [FC]</td>
<td>8/100</td>
<td>4/100</td>
<td>3/100</td>
</tr>
<tr>
<td>Minimum/Maximum ambient temperature (°C)</td>
<td>-20/50</td>
<td>-30/50</td>
<td>-40/60</td>
</tr>
<tr>
<td>Start time to full flow (s)</td>
<td>4</td>
<td>4</td>
<td>0.5</td>
</tr>
<tr>
<td>System fill time (min)</td>
<td>10</td>
<td>3</td>
<td>2.5</td>
</tr>
<tr>
<td>Safety</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Meet or exceed applicable standards</td>
<td></td>
<td></td>
</tr>
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</table>
Task Plan

- **Task 1: Risk Assessment**
  - Assess the potential risks of using solid state hydrides
  - Develop test protocols and experimental designs to aid in characterization of hypothetical accident scenarios
  - 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.
Materials Test Plan

- All three major classes of condensed hydrogen storage materials are being studied: metal hydrides, chemical hydrides & adsorption hydrides.
- Priority of analysis is being conducted in consultation with the three Materials CoE’s and DoE.

Little Known Investigations Initiated
1. $2\text{LiBH}_4 + \text{MgH}_2$
2. $\text{NH}_3\text{BH}_3$
3. Activated Carbon
4. $\text{AlH}_3$

Some Known Complete Analysis
- $\text{NaAlH}_4 + 2\%\text{TiCl}_3$
- $2\text{LiH} + \text{Mg(NH}_2)_2$
- $\text{Mg}_2\text{NiH}_4$
- $\text{LaNi}_5\text{H}_6$

Materials Prep Plan
- Use Particle Size
  - Fully Charged
  - Partially Discharged
  - Fully Discharged
Background: $2\text{LiBH}_4 + \text{MgH}_2$

$2\text{LiBH}_4 + \text{MgH}_2 + 3\text{m\% TiCl}_3 \rightleftharpoons 2\text{LiH} + \text{MgB}_2 + 2\text{H}_2$


$\text{wt\%} = 11.4\%$

$\Delta H = 40.5 \text{ kJ/mole H}_2$

**discharge**

**Recharge: 100 bar**
Apparatus for Pyrophoricity Test

1. Drop a small amount (< 1 g) of material in a containment box under ambient conditions.

2. Observe material as it falls and for a period of < 5 min. after falling.

3. Check for:
   1. Gas evolution
   2. Spontaneous ignition

4. Video record experiment
2LiBH₄+MgH₂ Pyrophoricity Test

Materials do not undergo reaction in air in 15 minutes (5 minutes for standard test).

Hygroscopic material absorbs H₂O from air.

2LiBH₄+MgH₂ not pyrophoric.
Instrumented Apparatus for Self-Heating

- Fill the 25mm³ sample holder with material
- Sample holder pre-fitted with micro thermocouples
- Heat sample to 150°C
- Observe temperature within sample spatially resolved to determine if self-heating occurs
2LiBH₄+MgH₂ Self-Heating

- Sample begins to self-heat within 30 seconds of exposure in the oven
- Maximum Temperature observed = 447°C

- Reaction initiates at sample surfaces and propagates towards the interior
- Consistent with diffusion of air/water vapor into the packed powder sample
1. Pack a triangular prism mold 20mm x 10mm x 250mm with material

2. Place material on fire resistant base, with thermocouples fitted underneath at 35mm intervals

3. Introduce flame at one end of packed material

4. Observe whether flame propagation occurs
   1. Measure rate of propagation
   2. Monitor linear temperature distribution
$2\text{LiBH}_4 + \text{MgH}_2$ Burn Rate

Flame rapidly moves to right and continues to burn for several minutes.
2LiBH$_4$·MgH$_2$ Burn Rate Measurement

- Variations in max temperature attributed to variations in packing density.
- Burn rate is very similar to NaAlH$_4$
- Burn rate = 52 mm/sec
- Burn rate for NaAlH$_4$ = 51 mm/sec$^1$

Experimental Setup of Water Contact Tests

**Water Immersion**
1. Drop ~ 20 mg of material into excess of H₂O (250 ml)
2. Check for:
   a) Gas evolution
   b) Spontaneous ignition
3. Video record experiment

**Surface Contact**
1. Drop ~ 20 mg of material onto filter paper on the surface of an excess of H₂O (250 ml)
2. Check for:
   a) Gas evolution
   b) Spontaneous ignition
3. Video record experiment

**Water Drop**
1. Contact a small pile (~ 2 g) of material with a few drops of H₂O
2. Check for:
   1. Gas evolution
   2. Spontaneous ignition
3. Video record experiment
2LiBH$_4$·MgH$_2$ Water Immersion

Material does not ignite on dropping in excess water.
2LiBH$_4$·MgH$_2$ Surface Contact

Conflagration of hydrides and hydrogen gas

Material ignites on restricted contact with water and air
$2\text{LiBH}_4 \cdot \text{MgH}_2$ Water Drop

Conflagration of hydrides and hydrogen gas

Material ignites when enough heat and hydrogen are generated

MgH$_2$-Hydrophobic - LiBH$_4$-Hydrophilic
Standardized Tests for $2\text{LiBH}_4\cdot\text{MgH}_2$

<table>
<thead>
<tr>
<th>UN Test</th>
<th>Result</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrophoricity</td>
<td>Pass</td>
<td>No combustion event. Hygroscopic material absorbed $\text{H}_2\text{O}$ from air.</td>
</tr>
<tr>
<td>Self-Heat</td>
<td>Fail</td>
<td>Self-heated $\sim$300°C within 30 sec.</td>
</tr>
<tr>
<td>Burn Rate</td>
<td>Fail</td>
<td>Flame propagated at a burn rate of 52 mm/sec.</td>
</tr>
<tr>
<td>Water Drop</td>
<td>Fail</td>
<td>2 $\text{H}_2\text{O}$ drops required for near-instant combustion.</td>
</tr>
<tr>
<td>Surface Contact</td>
<td>Fail</td>
<td>Restricted $\text{H}_2\text{O}$ surface contact results in combustion</td>
</tr>
<tr>
<td>Water Immersion</td>
<td>Fail</td>
<td>No combustion event recorded. $\text{Gas}$ evolved at longer times. (5 min)</td>
</tr>
</tbody>
</table>

- Material is classified as packing class 4.3 – Dangerous When Wet
- Same packing class as pure components
Thermodynamic Assessment of Environmental Exposure

- Thermodynamic analysis completed for all materials available in the data base

Gibbs Free energy of lowest energy reaction
\[ \Delta G \text{ (kJ/mol) at } 373 \text{ K} \]

\[ \Delta G \text{ (kJ/mol) at } 373 \text{ K} \]

- Thermodynamics predict greatest energy release for oxygen reactions
- Generally, thermodynamic calculation did not predict experimentally observed products
Thermo-Chemical Analysis of Water Contact

Calorimetric signal from mixing ~ 10 mg 2LiBH₄ + MgH₂ and 1ml water at 40°C and 70°C

- More complete reaction or additional reactions occurring at 70°C.
- Investigating NMR and Raman of products to elucidate reactions.

ΔH₄₀°C = 223 kJ/mol
ΔH₇₀°C = 294 kJ/mol
Kinetics of Water Contact: $2\text{LiBH}_4 + \text{MgH}_2$

Integrated Heat of Reaction

- **70°C**
- **40°C**

1 hour

Different reaction products is further evidence of differences in reaction pathway previously identified.
Thermo-Chemical Analysis of Humid Air Exposure

Conditioned Temperature & Humidity
Gas Inlet

Calorimetric Apparatus

Reaction profile resembles multi-step reaction or surface spallation effect, not a single step reaction.
Gas Product Analysis

2LiBH₄ +MgH₂ calorimetry in air at 70°C and 30% RH

Heat flow signal during gas sampling (sample time ~ 1 min.) vs. H₂% determined via Gas Chromatography (GC)

- Hydrogen concentration in gas stream tracks heat flow signal
- Flammable concentrations of hydrogen observed
Gas versus Liquid Hydrolysis/Oxidation Comparison

Heat flow during hydrolysis with 40°C humid air 20% humidity and 40°C liquid water

- Liquid water 40°C
- Vapor water 20%RH 40°C

Total energy released
- Water 225kJ/mol
- Vapor 270kJ/mol

Maximum Normalized Heat Flow (mW/mg)

- Liquid Water
- Gas: Air 30% RH
- Gas: Argon 30% RH

Water quantity:
- Liquid: t=0, mol actual/mol stoichiometric=32%
- Gas: t_{stoichiometric}=3.5 hours, t=12 hours, mol actual/mol stoichiometric=350%

- Liquid water hydrolysis displays maximum heat flow
- Oxygen in air is only a small contributor to heat flow signal
Reactivity Comparison

Fully Charged

2LiBH₄
MgH₂

Fully Discharged

Mg (28% wt)
MgB₂ (32 %)
LiH (17%)
Hydroxide products (22%)

Discharged material state more reactive:

**Charged**

\[ \text{LiBH}_4 + \frac{1}{2} \text{MgH}_2 + 4 \text{H}_2\text{O(l)} = \text{LiOH} + \frac{1}{2} \text{Mg(OH)}_2 + \text{H}_3\text{BO}_2 + 4\text{H}_2(g) \]
\[ \Delta H = -675 \text{ kJ/ formula unit} \]

**Discharged**

\[ \text{LiH} + \frac{1}{2} \text{MgB}_2 + 4 \text{H}_2\text{O(l)} = \text{LiOH} + \frac{1}{2}\text{Mg(OH)}_2 + \text{H}_3\text{BO}_2 + 2\text{H}_2(g) \]
\[ \Delta H = -760 \text{ kJ/formula unit} \]
Preliminary NH$_3$BH$_3$ Testing Initiated

- **1) Calorimetry**
  Argon gas flow with 30% RH at 40°C
  Small exothermic reaction
  *products under analysis*

- **2) UN test**
  - **Water drop**

  ![Image of water drop](image1)
  ![Image of reaction product](image2)

  $\Delta H = -5$ kJ/mol

  No reaction with addition of H$_2$O drops
Preliminary experiments suggest:

- Exposure of media to humid environment leads to:
  - Exothermic reaction and H$_2$ generation
  - Low thermal conductivity of media causes temperature to rise
  - H$_2$ at surface and in pores burns if & when auto ignition temperature of 571°C is reached
  - Burning of H$_2$ initiates pyrolysis of media

Correlations will be developed, in terms of non-dimensional parameters, that:

- Predict whether H$_2$ ignition occurs
  - Predict time to ignition
- Predict whether pyrolysis occurs

Correlations will be developed on salient material properties of media and dimensions of media pile
Task 2 Plans

- Summarize results of calorimetric tests and UN tests in a DOE report for the LiBH₄ + MgH₂ material system
- Continue liquid phase and gas phase calorimetry of NH₃BH₃
- Identify amorphous reaction products (Raman, NMR)
- Assess risks based on observed thermo-chemical release
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 $\text{NH}_3\text{BH}_3$, $2\text{LiBH}_4 + \text{MgH}_2$, $2\text{LiH} + \text{Mg(NH}_2)_2$, $\text{AlH}_3$ & $\text{NaAlH}_4$.
- Perform calorimetric experiments of mitigation strategies for water exposure at $0<T<50^\circ\text{C}$.
- Perform calorimetric experiments of mitigation strategies for conditioned air exposure at $0<T<100^\circ\text{C}$, $0<\%\text{RH}<100\%$.
- Identify reaction products.
- Assess mitigation strategies effectiveness based on observed thermo-chemical release.
SRNL FYs ’07 & ‘08 Work

- Coordinate IPHE team to complete experimental analysis, compile results and disseminate findings and conclusions.
- Complete standardized tests UN hazards analysis tests on \( \text{NH}_3\text{BH}_3, 2\text{LiH} + \text{Mg(NH}_2)_2 \) & \( \text{AlH}_3 \).
- 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.