High Density Hydrogen Storage System Demonstration Using NaAlH₄ Complex Compound Hydrides


United Technologies Research Center
East Hartford, Connecticut

Report to the
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This presentation does not contain proprietary or confidential information
Overview

**Objective:** Identify and overcome the critical technical barriers in developing complex hydride based storage systems, especially those which differ from conventional metal hydride systems, to meet DOE system targets.

**Approach:** Design, fabricate and test a sequence of subscale and full scale prototypes involving material development such as safety assessment, catalysis and scaled-up processing.

*Early systems development in parallel with novel materials research has been and will be important to hydrogen storage maturity.*

**Current Systems Focus**
- On-board rechargeable
- Based on NaAlH₄ as representative complex hydride
- Generalize to materials which require moderate charging pressures
Program Plan

- Safety Analysis
- Atomistic/Thermodynamic Modeling
- 50g $H_2$ Prototype System
- Media Kinetic Characterization & Modeling
- Heat/Mass Transfer Analysis
- High Temp. Composite Tank Development
- Component Fabrication
- Assembly System Fabrication
- Evaluation Facility Development
- 1kg $H_2$ CCHSS#1 Assembly
- CCHSS#1 Evaluation

- CCHSS#1 Model Validation
- CCHSS#2 System Design
  - Advanced HX design
  - New media filling method
  - Compact manifold
- Enhanced Media
  - Advanced catalyst concepts
  - High volume synthesis method
- CCHSS#2 Prototype
  - Fabrication
  - Performance Testing
  - Model Validation
- NaAlH$_4$ System Neutralization
  - Process development
  - Prototype 1 decommissioning
- New Materials
  - Powder densification

Program tasks nearing completion.
### Review of Prototypes

<table>
<thead>
<tr>
<th>System Element</th>
<th>LaNi₅</th>
<th>NaAlH₄</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Charging pressure</strong></td>
<td>10 bar</td>
<td>100 bar</td>
</tr>
<tr>
<td><strong>Media volumetrics</strong></td>
<td>50 kg H₂ / m³</td>
<td>25 kg H₂ / m³ **</td>
</tr>
<tr>
<td><strong>Powder loading</strong></td>
<td>Controllable</td>
<td>Challenging</td>
</tr>
<tr>
<td><strong>Expansion forces</strong></td>
<td>High</td>
<td>&lt; 7 bar, &lt; 0.9 g/cc</td>
</tr>
<tr>
<td><strong>Water reactivity</strong></td>
<td>Low</td>
<td>High</td>
</tr>
</tbody>
</table>

** 50% powder relative density, 4% H₂ media capacity

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#### NaAlH₄ Prototypes

1. **Full scale – 19 kg hydride**
   - Aluminum foam

2. **Sub scale – 3.5 kg hydride**
   - Aluminum fins

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Second Prototype Overview

Improvements over first prototype:
- Lighter weight composite vessel with conventional domed end.
- Lighter weight heat exchanger with fins for superior long range heat transport.
- Denser powder packing which is performed within a pre-constructed system, improving both volumetrics and gravimetrics.

Characteristics of second prototype
- Developed at nominally \((1/2)^3 = 1/8^{\text{th}}\) scale or 1/8 kg H2.
- Intermediate size to balance:
  - Fabrication challenges – keep unique supporting hardware to reasonable size and cost.
  - Ability to demonstrate technologies and perform projections.
Prototype 2 Size Scale Replan

Modifying the plan to design, fabricate and test a \((1/2)^3 = 1/8\)th scale system was the **right thing to do**.

- Greater emphasis of resources on powder densification and demonstration of lightweight, as-fabricated system.
- Lower degree of “projecting” to 2.3 wt% and 2.5 wt% systems.
- Recommend this size scale for first prototypes in future efforts.

Original, full scale plan
nominally 25 kg of hydride

Prototype 2
3.5 kg of hydride
Prototype 2 Heat Exchanger Design

Fabricated heat exchanger based on the following design process:

**Low Length Scale FEA**
- Fin unit cell

**Optimize:**
- Fin thickness
- Fin spacing
- Tubing OD
- Tubing spacing

**Larger Length Scale FEA**
- System cross section

**Optimize:**
- Tubing positioning

30% reduction in HX mass
Fabrication

- Finned Tube Heat Exchanger
- Stainless Steel Liner
- Carbon Fiber / Epoxy Overwrap
- 5’ x 5’ x 4’ Assembly
- Glove Box
- Shaker System
Energy density is the product of:

- **Hydride powder density**
- H₂ weight % capacity
- System volumetric efficiency

**Prototype improvement**

- Prototype 1: 200 Wh / L
- Prototype 2: 700 Wh / L

Hydride powder density is as important as H₂ weight % capacity for system volumetric capacity.
Powder Loading – Procedure Development

Development of loading procedure
Results for second prototype hydride powder

- Powder column
  0.72 +/- 0.02 g/cc

- Disassembled finned test article
  > 0.77 g/cc

- Dual axis vibratory shaker
  Controlled amplitudes and frequencies

- Prototype 2
  0.72 to 0.76 g/cc

- Prototype 1
  0.44 g/cc

Consistent densities across multiple configurations & geometries
Milling and Densification (Powder Column)

Ball milling procedures affect not only kinetics, but also powder densification.

- 0.64 g/cc
- 0.85 g/cc
- 0.72 g/cc

Used for projection

Prototype 2 material
Material Quality Assurance – Batch Testing

At desorption temperatures ramping from 100 to 150 °C, capacity is nominally 3.5 to 3.7 wt%
Prototype 2 Testing Apparatus

- Addition of secondary vessel for risk reduction
- First test – modified Sievert’s apparatus approach with 100 bar dosing
Absorption Test

- Hydrogen was added to the prototype in doses from an accumulator volume.
- System charging pressure is reduced from its starting value of $\approx 100$ bar after dosing.
- The first point includes both compressed gas and absorbed hydrogen storage.
- Desorption: $150$ C & $\approx 1$ atm.

Kinetics will be improved with constant 100 bar test conditions

136 g after $\approx 3$ hrs.
**Weight and Volume**

- **Hydride material:** 3.5 kg, 0.72 g/cc
- **Gravimetric capacity:** $\frac{136}{6846} = 0.020$ (g H2 / g System)
- **Volumetric capacity:** $\frac{136}{6450} = 0.021$ (g / cc)

**Weight**

- Liner / Manifold: 20.1%
- Overwrap: 7.5%
- Heat Exchanger: 14.4%
- Other Internal: 1.6%
- Filter & Cap: 2.5%
- Vessel / Manifold: 27.6%
- H2 Valve: 2.3%

**Volume**

- Solid: 41.8%
- Void: 34.2%
- Heat Exchanger: 19.1%
- Hydride (full densification): 3.7%
- Hydride (partial densification): 1.1%
- Filter & Other Internals: 4.5%
- Vessel / Manifold / Externals: 71.5%
Absorption Test – Temperatures

- Four internal thermocouples located at ¼ length and as given in the figure.
- Sheathed type K with 0.032” diameter—some averaging.
- Apparent exothermic reaction for slightly less than 1 hr.
- Pressure data only at dosing points, not continuous.
- Detailed model comparisons will be made with subsequent data.
Testing Status

Modifications and Issues:
- Improvements in oil temperature management.
- Significant noise in pressure transducer data was reduced.
- Addition of Coriollis force flow meter – will use burst flow to improve accuracy.
- After being dormant for almost 2 months, a leak has occurred:
  - Pressurization to 1420 psi was normal, 1510 psi resulted in rapid leak rate.
  - Due to possible ejection of powder into secondary containment vessel, our neutralization process was applied before removing the lid. Upon opening secondary vessel, no ejected powder was noted.
  - The system was leaked check with helium and the source confirmed to be the O-ring. A metal-to-metal seal was used to keep the Viton O-ring from being exposed to hydride which did not perform as expected. A Kalrez O-ring is now being installed.
System Scaling and Projection

**Elements of preliminary projection:**

- Potential hydride mass = 0.85 g/cc * 4900 cc = 4165 g for subscale
- Scaling vessel to full size (10X)
  - Liner retains 0.020” thickness; liner mass scales as (Volume)^^(2/3)
  - Hydrogen valve has the same mass
- Resulting full scale gravimetric efficiency is 0.63 (kg hydride / kg system)
- At 0.85 g/cc, 140 C and 100 bar, the compressed gas storage is effectively 0.25 wt% (kg H2 gas / kg hydride).
- With a 3.4 wt% material, system would be
  \[(3.4\% + 0.25\%) \times 0.63 = 2.3\%\]

All of these projection elements have been demonstrated separately, substantiating that such a 2.3 wt% system could be constructed with the currently developed technology.
## Performance Metrics and Projections

**Complex Compound Hydride Storage System (CCHSS) Performance Metrics**

<table>
<thead>
<tr>
<th>Characteristics &amp; Metrics</th>
<th>Units</th>
<th>Material &amp; Version:</th>
<th></th>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>Material gravimetric capacity</td>
<td>% kg H₂ / kg hydride</td>
<td>NaAlH₄</td>
<td>3.4%</td>
<td>3.4%</td>
<td>6.5%</td>
<td>8.0%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂ charging pressure</td>
<td>bar</td>
<td>Prototype 2</td>
<td>100</td>
<td>100</td>
<td>70</td>
<td>50</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Packed powder density</td>
<td>kg hydride / m³ powder</td>
<td>Projected</td>
<td>720</td>
<td>850</td>
<td>800</td>
<td>850</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Material volumetric capacity</td>
<td>kg H₂ / m³ powder</td>
<td>TBD hydride</td>
<td>24</td>
<td>29</td>
<td>52</td>
<td>68</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>System gravimetric efficiency</td>
<td>kg hydride / kg system</td>
<td>TBD hydride</td>
<td>0.515</td>
<td>0.63</td>
<td>0.67</td>
<td>0.75</td>
<td></td>
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</tr>
<tr>
<td>System volumetric efficiency</td>
<td>m³ powder / m³ system</td>
<td>TBD hydride</td>
<td>0.76</td>
<td>0.76</td>
<td>0.7</td>
<td>0.7</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Normalized compressed gas</td>
<td>% kg H₂ gas / kg hydride</td>
<td>TBD hydride</td>
<td>0.5%</td>
<td>0.3%</td>
<td>0.3%</td>
<td>0.2%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>System gravimetric capacity</td>
<td>% kg H₂ / kg system</td>
<td>DOE Targets</td>
<td>2.0%</td>
<td>2.3%</td>
<td>4.5%</td>
<td>6.1%</td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>gravimetric capacity</td>
<td>kWh / kg</td>
<td>2007</td>
<td>0.66</td>
<td>0.8</td>
<td>1.5</td>
<td>2.0</td>
<td></td>
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<tr>
<td>System volumetric capacity</td>
<td>kg H₂ /m³</td>
<td>2010</td>
<td>21.1</td>
<td>24.0</td>
<td>37.8</td>
<td>48.6</td>
<td></td>
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</tr>
<tr>
<td>System volumetric capacity</td>
<td>kWh / L</td>
<td></td>
<td>0.70</td>
<td>0.80</td>
<td>1.26</td>
<td>1.62</td>
<td></td>
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</tr>
</tbody>
</table>

### Notes

- a: Improved catalysts & processing
- b: Demonstrated powder packing enhancement
- c: Improved densification & size scaling
- d: Materials discovery
- e: Reduction of charging pressure & vessel mass

**Need 8 wt% material and 75% mass efficiency of system to meet 6 wt% system**
## Evaluation of New Materials – System Integration

<table>
<thead>
<tr>
<th>Compound</th>
<th>Theoretical Rev. H₂ wt fraction</th>
<th>Initial Density kg H₂/liter</th>
<th>Vibratory Settling kg H₂/liter</th>
<th>Enhanced Settling kg H₂/liter</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiMg(AlH₄)₃*</td>
<td>0.089</td>
<td>0.010</td>
<td>0.014</td>
<td>0.019</td>
</tr>
<tr>
<td>M-B-N-H System A *</td>
<td>0.088</td>
<td>0.033</td>
<td>0.041</td>
<td>0.042</td>
</tr>
<tr>
<td>M-B-N-H System B *</td>
<td>0.082</td>
<td>0.035</td>
<td>0.044</td>
<td>0.044</td>
</tr>
<tr>
<td>NaAlH₄- best result **</td>
<td>0.056</td>
<td>0.026</td>
<td>0.041</td>
<td>0.042</td>
</tr>
</tbody>
</table>

* Densification of as-received new materials, with no further processing.
** 6% TiF₃-NaAlH₄, dehydrided, and paint shaken, close to “as-received.”

Use of systems development methods to evaluate novel materials.
Second prototype system development resulted in significant gravimetric and volumetric improvements:

<table>
<thead>
<tr>
<th>Metric</th>
<th>Units</th>
<th>As-Fabricated</th>
<th>Projected</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Prototype 1</td>
<td>Prototype 2</td>
<td>Prototype 1</td>
</tr>
<tr>
<td>Gravimetric efficiency</td>
<td>$kg \text{ hyd.} / kg \text{ sys.}$</td>
<td>0.14</td>
<td>0.515</td>
</tr>
<tr>
<td>Gravimetric density</td>
<td>$% \text{ kg H}_2 / kg \text{ sys.}$</td>
<td>0.4%</td>
<td>2.0%</td>
</tr>
<tr>
<td>Powder density</td>
<td>$g / cc$</td>
<td>0.44</td>
<td>0.72</td>
</tr>
<tr>
<td>Volumetric density</td>
<td>$kWh / L$</td>
<td>0.20</td>
<td>0.70</td>
</tr>
</tbody>
</table>