Advancement of Systems Designs and Key Engineering Technologies for Materials Based Hydrogen Storage

United Technologies Research Center

H2
DOE Hydrogen Program
Annual Merit Review
Washington, DC
June 8, 2010

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Overview

- **Timeline**
  - Start: February 2009
  - End Phase 1: July 2011
  - End Phase 2: July 2013
  - End Phase 3 / Project: July 2014
  - Percent complete: 18.0% (spending)

- **Budget**
  - $6.86M Total Program
    - $5.32M DOE
    - $1.55M (22.5%) UTRC
  - FY09: $350k DOE
  - FY10: $870k DOE

- **Barriers**
  - A – J
  - A. System Weight & Volume
  - E. Charging / Discharging Rates
  - J. Thermal Management

- **Targets**
  - All

- **HSECoE Partners**
Objectives

- Design of materials based vehicular hydrogen storage systems that will allow for a driving range of greater than 300 miles
- H\textsubscript{2} storage system focus:
  - Metal hydride
  - Chemical hydride
  - H\textsubscript{2} cryo-sorption materials

Target examples:

<table>
<thead>
<tr>
<th>Performance Measure</th>
<th>Units</th>
<th>2010</th>
<th>2015</th>
<th>Ultimate</th>
</tr>
</thead>
<tbody>
<tr>
<td>System Gravimetric Capacity</td>
<td>g H\textsubscript{2} /kg system</td>
<td>45</td>
<td>55</td>
<td>75</td>
</tr>
<tr>
<td>System Volumetric Capacity</td>
<td>g H\textsubscript{2} /L system</td>
<td>28</td>
<td>40</td>
<td>70</td>
</tr>
<tr>
<td>System fill time (for 5 kg H\textsubscript{2})</td>
<td>minutes</td>
<td>4.2</td>
<td>3.3</td>
<td>2.5</td>
</tr>
<tr>
<td>Fuel Purity</td>
<td>% H\textsubscript{2}</td>
<td>SAE J2719 guideline (99.97% dry basis)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Leverage in-house expertise in various engineering disciplines and prior experience with metal hydride system prototyping to advance materials based H₂ storage for automotive applications.

- Provide a system model for each material sub-class (metal hydrides, adsorption, chemical storage) which shows:
  - 4 of the DOE 2010 system storage targets are fully met
  - Status of the remaining targets must be at least 40% of the target or higher
Center Structure – Roles & Collaborations

Hydrogen Storage Engineering Center of Excellence

- D. Anton, SRNL
- T. Motyka, SRNL

**Materials Operating Requirements**
- D. Herling, PNNL
  - Materials Centers of Excellence Collaboration – SRNL, LANL, NREL
  - Reactivity & Compatibility – UTRC
  - Adsorption Properties – UQTR
  - Metal Hydride Properties – SRNL
  - Chemical Hydride Properties – LANL
  - Media Structure - GM

**Transport Phenomena**
- B. Hardy, SRNL
  - Bulk Materials Handling – PNNL
  - Mass Transport – SRNL
  - Thermal Transport – SRNL

**Enabling Technologies**
- J. Reiter, JPL
  - Thermal Insulation – JPL
  - Hydrogen Purity – UTRC
  - Sensors – LANL
  - Thermal Devices - OSU
  - Pressure Vessels - PNNL

**Performance Analysis**
- M. Thornton, NREL
  - Vehicle Requirements – NREL
  - Tank-to-Wheels Analysis – NREL
  - Forecourt Requirements - UTRC
  - Manufacturing & Cost Analysis - PNNL

**Integrated Power Plant / Storage System Modeling**
- D. Mosher, UTRC
  - Off-Board Rechargeable - PNNL
  - On-Board Rechargeable – GM
  - Power Plant – Ford

**Subscale Prototype Construction, Testing & Evaluation**
- T. Semelsberger, LANL
  - Risk Assessment & Mitigation – UTRC
  - System Design Concepts and Integration - LANL
  - Design Optimization & Subscale Systems – LANL, SRNL, UQTR
  - Fabricate Subscale Systems Components – SRNL, LANL
  - Assemble & Evaluate subscale Systems – LANL, JPL, UQTR

Leading / Project Tasks

Additional Project Tasks

Supporting
Engineered Compaction

- Objective: Improve volumetric capacity and thermal conductivity through powder compaction
- Coordinated through GM

Press inside glovebox

Pellets for thermal Conductivity measurements

Thermal conductivity analyzer

Density increased by 63% (39% reduction in volume)

Density [g/cm³]

Pressure [kpsi]

7X improvement of thermal conductivity

Thermal conductivity [W/m/K]

Density [g/cm³]
Properties of Compacted Metal Hydride

- **H₂ Absorption (120°C, 110 bar)**

  ![H₂ Absorption Graph](image)

  **NaAlH₄ +4% TiCl₃**

  **Time [hrs]**

  **H₂ Absorption [wt. %]**

  - 0.0%
  - 0.5%
  - 1.0%
  - 1.5%
  - 2.0%
  - 2.5%
  - 3.0%
  - 3.5%
  - 4.0%
  - 4.5%

  **Pellet**

  **Powder**

  **Comparable H₂ absorption and desorption rate before and after compaction**

- **Biaxial flexure screening test for compressed pellets**

  ![Biaxial Flexure Test](image)

  **Integrating pellet reinforcement and thermal conductivity enhancement in compacted material**

  **Reinforced NaAlH₄**

  **Probability Plot for Strength[kpsi]**

  Weibull - 95% CI

  Complete Data - LSXY Estimates

  Table of Statistics
  - **Shape**: 5.12553
  - **Scale**: 1.54030
  - **Mean**: 1.41628
  - **StDev**: 0.31735
  - **Median**: 1.43400
  - **IQR**: 0.433734
  - **Failure**: 15
  - **Censor**: 0
  - **AD***: 0.954
  - **Correlation**: 0.993
Objective: Optimization of hydrogen storage system heat exchanger for fast refueling time

Approach:
- Co-developed and validated COMSOL™ model of NaAlH₄ bed with SRNL
- Incorporated improved material properties after compaction (ρ, k)
- Performed parametric study to optimize heat exchanger design for fast refueling time
- Developed lumped parameter model for System Level Modeling
Technical Accomplishments and Progress

HX Design for Fast Refueling Time

- Different bed designs are optimal for specific refueling times

NaAlH₄ is a good model material for designing engineering tools but can not achieve gravimetric capacity targets at fast refueling times.
**H₂ Purity**

- **Objective:** Develop system methods to improve discharged hydrogen purity / quality for acceptable PEM fuel cell durability

**Impurities of Concern:**

- **NREL H₂ Forecourt**

```
<table>
<thead>
<tr>
<th>Storage material</th>
<th>Impurity</th>
<th>SAE guideline</th>
<th>HSECoE Estimate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonia</td>
<td>Borazine</td>
<td>???</td>
<td>0.4-3.0%*</td>
</tr>
<tr>
<td>Borane</td>
<td>Diborane</td>
<td>???</td>
<td>1-5 ppm</td>
</tr>
<tr>
<td>Metal Amides</td>
<td>Ammonia</td>
<td>0.1 ppm</td>
<td>20-200 ppm</td>
</tr>
<tr>
<td></td>
<td>Ammonia</td>
<td>0.1 ppm</td>
<td>200-800 ppm</td>
</tr>
</tbody>
</table>
```

*LANL: 0.01-0.08 mol Borazine/ mole of AB reacted

**Initial focus on Ammonia**
## Technical Accomplishments and Progress
### Preliminary Purification System Comparison

<table>
<thead>
<tr>
<th>Factor</th>
<th>Conventional Palladium Membrane</th>
<th>Regenerable Physical Adsorption</th>
<th>Chemical Adsorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight</td>
<td>Heavy</td>
<td>Heavy(^1)</td>
<td>Light</td>
</tr>
<tr>
<td>Volume</td>
<td>Big</td>
<td>Big</td>
<td>Small</td>
</tr>
<tr>
<td>Cost</td>
<td>Expensive</td>
<td>Affordable</td>
<td>Affordable</td>
</tr>
<tr>
<td>(H_2) loss</td>
<td>2-5%</td>
<td>High(^1)</td>
<td>Low</td>
</tr>
<tr>
<td>Pressure</td>
<td>(&gt;50) psig</td>
<td>High pressure preferred</td>
<td>Atmospheric or high pressure</td>
</tr>
<tr>
<td>Temperature</td>
<td>300-400ºC</td>
<td>RT</td>
<td>RT(&lt;T&lt;150ºC</td>
</tr>
<tr>
<td>Purity</td>
<td>99.99999999%</td>
<td>99.97%</td>
<td>99.97%</td>
</tr>
<tr>
<td>Life expectancy</td>
<td>(&gt;5) years</td>
<td>(&gt;2) years</td>
<td>3 month replacement</td>
</tr>
</tbody>
</table>

\(^1\) Assuming on-board regeneration

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Chemical adsorption cartridge selected for Ammonia
Adsortion System Development

Technical Accomplishments and Progress

Process Flow Diagram

Test apparatus

\[ \text{NH}_3 \text{ adsorbent} \]
- Mesh size: 20x30 mesh (0.84x0.60 mm)
- Tap Density: 0.673 g/cm³
- BET surface area: 673 m²/g
- Pore volume: 0.338 cm³/g
- Average Pore Diameter (4V/A by BET): 20.1 Å

NH\(_3\) breakthrough curves

Flow rate dependence NH\(_3\) breakthrough time

Cartridge weight for 3-month replacement interval

Adsorbent based H\(_2\) purification cartridge for NH\(_3\) appears viable
Integrated Framework for Vehicle Simulation

- **Objective:** Evaluate combined power plant / storage system configurations to determine hydrogen storage system requirements and predict overall performance.

- **Progress:**
  - Framework structure developed and implemented in Simulink™
  - Different storage system types coexist within same framework
  - Results generated for comparing storage systems against DOE targets on a common basis

**Technical Accomplishments and Progress**

**System Results for comparison with DOE targets**

- **H₂ Storage Systems**
  - UTRC NaAlH₄
  - GM NaAlH₄
  - GM H₂ cryo Adsorbent (AX-21)
  - PNNL Chemical Hydride (solid AB)

**Vehicle level model (NREL)**

- **Fuel Cell System (Ford)**
  - Vehicle
  - Fuel Cell
  - Storage systems

UTRC leading IPP/SSM technical area and providing support to all partners for implementing their contributions.
NaAlH₄ system example:

- Power demand curves from HSSIM (NREL)
- Lumped heat transfer model parameters from COMSOL™ model of NaAlH₄ bed
- Single “cold start” from 20°C:
  - H₂ stored in free volume is burned to raise temperature
- Drive cycle repeats indefinitely
  - Drive cycles were not designed for vehicles with materials based H₂ storage systems
- Minimum delivery pressure: \( P_{\text{min}} = 3 \text{ bar} \)
- Results show drive cycle is tracked correctly until after 5 kg H₂ have been delivered to the fuel cell.
- More details in presentation by GM

Performance comparison of all three hydrogen storage systems on a common basis
<table>
<thead>
<tr>
<th>Task</th>
<th>FY10</th>
<th>FY11</th>
</tr>
</thead>
<tbody>
<tr>
<td>Improve properties through compaction with reinforcing material</td>
<td></td>
<td></td>
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<tr>
<td>Quantify impact of pressure gradients inside consolidated metal</td>
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<tr>
<td>hydride powder on H(_2) absorption and desorption kinetics</td>
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<tr>
<td>Evaluate small test article with structured media</td>
<td></td>
<td></td>
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<tr>
<td>Evaluate alternative reversible metal hydride materials in common</td>
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<tr>
<td>H(_2) storage framework with current engineering tools</td>
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<tr>
<td>Improve capacity of on-board H(_2) purification cartridge for ammonia</td>
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<td>Develop and assess methods for removing boron containing species</td>
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<td></td>
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<tr>
<td>Qualitative risk assessments of novel systems</td>
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<tr>
<td>Improve definition of Balance of Plant (BOP) components in system</td>
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<tr>
<td>model and establish a common bill of materials</td>
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<tr>
<td>Implement initial cost model library for storage systems</td>
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<tr>
<td>Identify technology gaps and prioritize concepts</td>
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<td></td>
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<tr>
<td>Quantify hydrogen storage system performance against DOE targets for Go/No-Go decision on April 30, 2011</td>
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Summary

Relevance: Design of materials based vehicular hydrogen storage systems that will allow for a driving range of greater than 300 miles

Approach: Leverage in-house expertise in various engineering disciplines and prior experience with metal hydride system prototyping to advance materials based H₂ storage for automotive applications

Technical Accomplishments and Progress:

- Developed method that improved volumetric capacity and thermal conductivity through compaction
- NaAlH₄ is a good model materials but can not achieve gravimetric capacity targets at fast refueling times
- Hydrogen purification cartridge for adsorbing NH₃ appears viable
- Established Simulink framework that enables performance comparison of all three hydrogen storage materials against DOE targets on a common basis

Collaboration: Active collaboration with all partners in center, for instance between Ford, GM, PNNL and NREL on system level modeling

Future Work: Work towards milestones on quad charts of each of the technical areas and technical teams and towards Go/No-Go decision on April 30, 2011
Acknowledgements

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