High Density Hydrogen Storage System Demonstration Using NaAlH₄ Complex Compound Hydrides


United Technologies Research Center
East Hartford, Connecticut

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This presentation does not contain proprietary or confidential information
Overview

- **Timeline**
  - 4/1/02 Start
  - 9/30/06 End
  - 85% Complete

- **Budget**
  - $3.8M Total Program
    - $2.7M DOE
    - $1.1M (28%) UTC
  - $0.8M DOE FY05
  - $0.8M DOE FY06

- **Barriers Addressed**
  - System Gravimetric Capacity: 2 kWh/kg
  - System Volumetric Capacity: 1.5 kWh/L
  - Charging Rate: 1.5 kg H₂/min
  - Safety

- **Partners**
  - UTC Fuel Cells
  - University of Hawaii
  - Hydrogen Components, Inc. (HCI)
  - QuesTek, LLC
  - Albemarle Corporation
  - Spencer Composites
  - Lyons Tool & Die

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UTC Fuel Cells
A United Technologies Company

Lyons Tool & Die

United Technologies Research Center

ALBEMARLE® CORPORATION

HCI

Questek Innovations, LLC

Spencer Composites Corporation
Objectives

**Project Objectives**
- Design, fabricate and evaluate prototype solid state hydrogen storage systems based on catalyzed NaAlH$_4$ which can be used with other reversible complex hydrides of similar thermodynamics with minimal redesign.
- Identify and address key challenges for materials and systems, particularly those which differ from conventional metal hydrides.

**Past Year Objectives**
- **Prototype 1: Evaluation**
  - Test method refinement
  - Absorption / desorption experiments
  - Model verification
- **Prototype 2: Development**
  - Scaled-up media processing & catalysis
  - Optimized finned tube heat exchanger design
  - Powder densification development
Approach

Apply modeling, sub-scale experimentation and full scale development to identify & address critical technologies for complex hydride systems:

- Safety Analysis
- Media Kinetic Experiments & Modeling
- Heat Transfer Analysis & Optimization
- 50 g H₂ Subscale Experiments
- Full Scale Prototype 1
  - Component design & fabrication
  - Assembly hardware
  - Evaluation facility
- Prototype 2
  - Address identified challenges
- Fuel Cell Integration Analysis
Prototype 1 Overview

Prototype 1 elements
- High temperature (250 C) composite vessel
- Optimized aluminum foam based heat exchanger
- Full scale fabrication & testing
- 19 kg of NaAlH$_4$

Adjusted mass fractions

Adjusted volume fractions
Full Scale Testing

Test Conditions
Charging
- Std. discharge: 150°C/vac./16hrs.
- 70 and 100 bar charging (16 hrs):
  - 80 °C
  - 100 °C
Discharging
- Std. charge: 100°C/100bar/16hr
- 2 bar discharging (16 hrs)
  - 90 °C
  - 100 °C

Data
- 2 ranges of Coriolis H₂ mass flow meters
- 2 vessel and 4 system pressure transducers
- 12 vessel & 15 system thermocouples
- 6 strain gauges

Test cell with isolated control

Continued testing up to 25 cycles
Test Methodology and Data

- Totalized mass flow and pressure measurements are used to calculate absorbed/desorbed mass curves.
- A burst flow mode was developed to increase the effective resolution of the mass flow meters.
Absorption Tests

- Ultimate capacity of system is nominally 1 lb. (0.45 kg) of H₂
- Cyclic improvement is apparent for both 80 and 100 C at 70 bar

Challenges identified from first prototype experience
- Material processing scale-up with low cost catalyst
- Powder densification compatible with system fabrication which have been addressed in second prototype development
Prototype 1 Model Comparison

12 TC Locations

943 s (peak T)

FEA

30,000 s

Comparison

Temperature [deg. C]

Time [s]
Prototype 2 Overview

Past year activities

- Scaled-up media processing & catalysis
- Optimized finned tube heat exchanger design
- Powder densification development
- Compact oil manifold
Catalysis Experiments

Materials

Commercial purity NaAlH₄: 87 % NaAlH₄, 5 % Na₃AlH₆, 7 % Al, 1 % inerts

TiCl₃ Costs
- 2001 - $154/m Ti⁺³
- 2002 - $924/m Ti⁺³
- 2005 - $1,955/m Ti⁺³

Alternate Catalysts (2005)
- TiCl₂ - $1,452/m Ti⁺²
- TiF₄ - $157/m Ti⁺⁴
- TiF₃ - $233/m Ti⁺³
- TiCl₃ *1/3AlCl₃ - $46/m Ti⁺³

Compositions Examined
- 6% TiCl₃
- 4% TiCl₃
- 4% CeCl₃
- 6% TiF₃
- 3% TiCl₃ *1/3AlCl₃

PCI Experimental Conditions

Isobaric Absorption
- 150°C/vac/24hrs
- T = 80, 100, 120 & 140 ºC
- P = 68 bar

Isobaric Desorption
- 120°C/68bar/16hrs
- T = 70, 80, 90, 100, 110 & 120 ºC
- P = 1 bar

Isothermal Absorption
- 150°C/vac/24hrs
- T = 120 ºC
- P = 50, 68, 90, 110 bar
Processing Methods

- **SPEX mill**
  - 5 grams
  - 40 g / 16 Hz

- **Tumble mill**
  - 0.5 kg
  - 1 g / 1 Hz

- **High capacity shaker**
  - 0.5 kg
  - 15 g / 10 Hz

- **Attrition mill**
  - kg quantities
  - 60 – 350 RPM
Scaled-up Processing

Large scale processing 68 & 110 bar charging pressures

Large scale processing with a low cost catalyst results in effective capacities for NaAlH₄ between 3.2% and 3.5% after cycling.
Heat Exchanger Design

(Air conditioner HX)

Unit cell FEA

Design variables:
- Fin thickness
- Fin spacing
- Tubing OD
- Tubing spacing

Heat exchanger design and optimization based on a single fin unit cell and variable properties to estimate performance of the entire system

30% reduction in HX mass
Reaction Kinetics Model

Recalibration for attrition milled 3% TiCl3 / AlCl3 material

\[ \text{NaH} + \text{Al} + \frac{3}{2} \text{H}_2 \overset{r_1}{\leftrightarrow} \overset{r_2}{\frac{1}{3}} \text{Na}_3\text{AlH}_6 + \frac{2}{3} \text{Al} + \text{H}_2 \overset{r_3}{\leftrightarrow} \overset{r_4}{\text{NaAlH}_4} \]

H₂ absorption: model vs. experiment
Heat Exchanger Design

Conduct higher length scale simulations of vessel cross section using effective properties determined from lower length scale fin unit cell simulations

**Effective thermal conductivity**

- Thermal conductivity
- Baseline
- 2 X
- 1/2 X
- NaAlH4 only

**Maximum T uniformity & kinetics**

Different tubing placements in vessel cross-section can result in similar performance

Optimal design developed which shows only minor improvement in absorption rate with increasing effective thermal conductivity (i.e. 2X fin mass).
Combination of
• **Hydride powder bulk density**
• \( \text{H}_2 \) weight % capacity
• System volumetric efficiency
determine energy density

Hydride powder bulk density is as important as \( \text{H}_2 \) weight % capacity for system volumetric capacity
Powder Densification Approach

- Densification approach must be compatible with prototype fabrication method: composite vessel elevated T curing and NaAlH$_4$ safety concerns ⇒ fabricate composite vessel before powder loading.
- Goal to have lightest weight heat exchanger and pressure vessel ⇒ construct optimized finned tube heat exchanger within conventional dual domed vessel, requiring hydride powder loading through a reduced size port.

NaAlH$_4$ and other lightweight complex hydrides are considerably more difficult to pack than conventional metal hydrides (LaNi$_5$). Creates challenge to densely load NaAlH$_4$ within the HX structure through a small port.
Powder Densification Experiments

Develop powder loading procedure with a versatile, instrumented vibratory apparatus and progression of experimental configurations.

- Powder column
  - Fundamental studies
- Finned test article
  - Capable of disassembly
- Dual axis vibratory shaker
  - Controlled amplitudes and frequencies
- Prototype 2
  - Demonstration
# NaAlH$_4$ Material States

## Powder Bulk Densities, [g/cc]

<table>
<thead>
<tr>
<th>Material State</th>
<th>Process 1</th>
<th>Process 2</th>
<th>Process 3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>As-received</td>
<td>As-received</td>
<td>As-received</td>
</tr>
<tr>
<td>Original</td>
<td>0.462</td>
<td>0.391</td>
<td>0.334</td>
</tr>
<tr>
<td>Vibratory settling</td>
<td>0.740</td>
<td>0.465</td>
<td>0.399</td>
</tr>
<tr>
<td>Enhanced settling</td>
<td>0.751</td>
<td>0.669</td>
<td>0.629</td>
</tr>
</tbody>
</table>

Material processing and compositional state have a significant influence on particle morphology and densification.
Powder Densification Results

Enhancement methods developed in addition to baseline vibratory settling

Average densities obtained
- Powder column: 0.75 g/cc
- Finned HX: 0.65 g/cc

Improvement over Prototype 1 actual average density of 0.44 g/cc and peak density of 0.6 g/cc
Future Work

- Conduct continued safety studies including decommissioning of Prototype 1.
- Fabricate Prototype 2 components and assemble.
- Test Prototype 2 – 9/30/06 Milestone.
- Compare system performance of Prototype 2 with modeling.
- Project material and system requirements to meet performance goals of 2.5 wt% and 4.5 wt% systems.
- Conclude contract with final report.
Summary

- First full scale NaAlH₄ prototype has been designed, fabricated and tested to identify and reprioritize key and in some cases unanticipated challenges (powder densification).
- Large scale processing method demonstrated with low cost catalyst having cyclic capacities up to 3.5 wt%.
- Finned tube heat exchanger designed with approximately 30% weight reduction.
- Powder loading and densification process developed compatible with composite vessel manufacture which has achieved densities between 0.65 and 0.75 g/cc.

<table>
<thead>
<tr>
<th>Requirement</th>
<th>Units</th>
<th>DOE 2007 Targets</th>
<th>Prototype 1 Adjusted</th>
<th>Prototype 2 Projected</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gravimetric Density</td>
<td>kWh/kg, kg H₂/kg</td>
<td>1.5, 0.045</td>
<td>0.27, 0.008</td>
<td>0.67 to 0.77, 0.020 to 0.023</td>
</tr>
<tr>
<td>Volumetric Density</td>
<td>kWh/L, kg H₂/L</td>
<td>1.2, 0.036</td>
<td>0.18, 0.0054</td>
<td>0.50 to 0.60, 0.015 to 0.018</td>
</tr>
</tbody>
</table>
Supplemental Slides
Not Required