Overview

Timeline

- Start: February 1, 2009
- End: December 31, 2015
- 99% Complete (as of 3/1/16)

Budget

- Total Center Funding:
  - DOE Share: $35,275,000
  - Cost Share: $3,322,000
  - FY '15 Funding: $895,000
  - FY '16 Funding: $150,000
- Prog. Mgmt. Funding
  - FY '15: $300,000
  - FY’16: $0

Barriers

A. System Weight and Volume
B. System Cost
C. Efficiency
D. Durability
E. Charging/Discharging Rates
G. Materials of Construction
H. Balance of Plant (BOP) Components
J. Thermal Management
K. System Life-Cycle Assessment
O. Hydrogen Boil-Off
P. Understanding Physi/Chemi-sorption
S. By-Product/Spent Material Removal

Partners

[Logos of various partners]
HSECoE Technical Objectives

Using systems engineering concepts, design innovative material-based hydrogen storage system architectures with the potential to meet DOE performance and cost targets.

- Develop and validate system, engineering and design models that lend insight into overall fuel cycle efficiency.

- Compile all relevant materials data for candidate storage media and define required materials properties to meet the technical targets.

- Design, build and evaluate subscale prototype systems to assess the innovative storage devices and subsystem design concepts, validate models, and improve both component design and predictive capability.
Adsorbent System Overview

Approach

Fuel Cell Components (outside HSECoE scope)

Type 1 Pressure Vessel

Vacuum shell
Multilayer insulation in evacuated space
LN₂ vessel wall chilling channel

Media/HX

H2 out
H2 in
LN2 in
LN2 out
Adsorbent Heat Exchanger Types

HexCell
Flow Through Chilled H₂ Cooling

MATI
Isolated LN₂ Flow Cooling

Gain Volumetric Density
in going from loose powder to compacted pucks
at expense of Cost

Evaluation of Novel HX Design to Prove Efficacy & Utility
MATIC Heat Exchanger & Test Systems

Demonstrate performance of subscale system evaluations and model validation of a 2L adsorbent system utilizing a MATI thermal management system having 54 g available hydrogen, internal densities of 0.10g/g(m+H₂) gravimetric, and 27 g/l volumetric.

Demonstrate a two liter hydrogen adsorption system containing a MATI internal heat exchanger provided by Oregon State University characterizing its performance against each of the sixteen performance DoE Technical Targets for On-Board Hydrogen Storage Systems.
MATI Performance Tests – Puck Cooling Profiles

Entire system at ambient temperature and vacuum with LN\textsubscript{2} flowed through MATI

- Significant temperature differential, up to 70 K, between pucks on top two plates, #1 & 2, and pucks on bottom 3 plates, #3-5.
NDE analysis indicates significant blockage of outlet passage resulting in reduced LN2 flow and degraded cooling efficiency.
20% increase in average bed temperature at 300 SLPM vs 50 SLPM H₂ flow due to faster adsorption.

13% decrease in total grams of hydrogen into system at 300 SLPM compared to 50 SLPM H₂ flow due to warmer adsorbent.

Thermal models for the MATI system were not completed due to personnel changes at OSU, thus comparison of models and experiments could not be made.
MATI Discharging – Varied H₂ flow  
constant GN₂ flow at 150 SLPM

- Slower outgoing hydrogen flow allows for greater heating of the adsorbent.
- Max. average bed temperature decreases (160, 112 and 85 K respectively) with increasing H₂ flow rate.
- Total mass of H₂ through the mass flow meter decreased (92, 91 and 84 grams) with increasing H₂ flow rate due to chilled system.
Accomplishment

**MATI 60 & 100 bar H₂ Cycling**

- Performed with vessel start conditions of 5 bar and ~80 K
- Cycles performed to 60 and 100 bar max. pressure
  - Depending on gas supply, 10 consecutive cycles for 60 bar and 4 consecutive cycles for 100 bar
- Adsorption conditions: 300₁ SLPM H₂, LN₂ 150 SLPM (gas equivalent)
  - Adsorptions halted once pressure reached (60 or 100 bar) regardless of vessel temperature, system switched over to perform desorption
- Desorption conditions: 130² SLPM H₂, GN₂ 150 SLPM
  - Desorption halted once pressure reached (5 bar) regardless of vessel temperature, system switched over to perform adsorption

₁-adsorption rate to meet scaled Technical Target of 3 min. fill time
₂-desorption rate to meet scaled US-06 max. flow rate

100 bar Cycling, Adsorption Curves

1<sup>st</sup> cycle

2<sup>nd</sup> cycle

3<sup>rd</sup> & 4<sup>th</sup> cycle

- Twenty cycles performed at 60 bar and eight cycles performed at 100 bar
- No degradation in capacity observed.
Demonstrate performance of subscale system evaluations and model validation of a 2L adsorbent system utilizing a HexCell heat exchanger having 46g available hydrogen, internal densities of 0.13g/g gravimetric, and 23.4g/L volumetric.
HexCell Charging (100 SLPM, 80 bar)

• Initial conditions: 85K, 1.7 bar
• Approximate full charging time 30 minutes
  • Vessel Inlet hydrogen = 280 g
  • Vessel Outlet hydrogen = 242 g
  • Mass of MOF5 = 270 g at 217 kg/m³

• Modeling agrees with experimental data to within 10°C
• Flow-through is an effective cooling system.
• Achieved weight capacity of ~ 4.1 %
• Achieved volumetric capacity of ~19 g/l
• 14% H₂ Adsorbed
Accomplishment

**HexCell Charging (100 SLPM, 80 bar)**

- **Initial conditions:** 85K, 1.7 bar
- **Approximate full charging time:** 30 minutes
- **Vessel Inlet hydrogen:** 280 g
- **Vessel Outlet hydrogen:** 263 g
- **Mass of MOF:** 270 g at 217 kg/m³

- Initial start 150 K inlet H₂ warms tank and MOF before steady state cooling dominates.
HexCell Charging (100 vs. 500 SLPM, 80 bar)

- Initial condition: 2 bar, 85 K

- Higher flow through rate results in higher maximum temperature due to greater availability of fresh gaseous hydrogen.
- Doubling flow through rate decreased charge time >30%.
• Models agree with experimental results within 15 K.
• Error results from non-uniform heating rod thermal distribution.
HexCell Discharging with Heat (11 SLPM, 40 bar)

Accomplishment

- Manual heater output control results in potential local overheating and requires periodic cycling to meet hydrogen demand.
HexCell Cycling Tests

Conditions:
- Pressure swing 5 – 60 bar
- Quasi isothermal (submerged in LN2)
- Flow-through charging at 200 SLPM H₂
- Discharging H₂ at 130 SLPM.

Accomplishment:
- Temperature swing stabilized after four cycles
- Cycling results in no system capacity degradation observed after 24 cycles.
## Comparison of HexCell, MATI and Type 4 Systems

<table>
<thead>
<tr>
<th></th>
<th>What we did: 2 liter Materials &amp; HX Only (measured)</th>
<th>What we could do: 5.6 Kg H₂ Full Scale Type I Tank w/BoP (projected)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>HexCell</strong></td>
<td>90K,80bar ⇔ 85K,1.7bar</td>
<td>80K,100bar ⇔ 160K,5bar</td>
</tr>
<tr>
<td>Gravimetric Density</td>
<td>0.112 g/g</td>
<td>0.032 g/g</td>
</tr>
<tr>
<td>Volumetric Density</td>
<td>23.6 g/l</td>
<td>18.9 g/l</td>
</tr>
<tr>
<td><strong>MATI</strong></td>
<td>84.5K,100bar ⇔ 83.7K,1.1bar</td>
<td>80K,100bar ⇔ 160K,5bar</td>
</tr>
<tr>
<td>Gravimetric Density</td>
<td>0.092 g/g</td>
<td>0.031 g/g</td>
</tr>
<tr>
<td>Volumetric Density</td>
<td>37.2 g/l</td>
<td>21.0 g/l</td>
</tr>
<tr>
<td><strong>Physical Storage, Type 4 Tank</strong></td>
<td>293K,700bar ⇔ 293K,5bar</td>
<td></td>
</tr>
<tr>
<td>Gravimetric Density</td>
<td>0.026 g/g</td>
<td></td>
</tr>
<tr>
<td>Volumetric Density</td>
<td>20.1 g/l</td>
<td></td>
</tr>
</tbody>
</table>

### Summary

- Compacted MOF-5/MATI/Type I tank surpasses compressed gas at 700 bar/Type 4 tank in gravimetric and volumetric capacity!
Accomplishment

Full Scale Type 1 HexCell System Design Concept

- Internal LN2 cooling channel
- MLVI Insulation

System Capacity:
5.6 kg useable H₂ under US06 Drive Cycle

Operating Conditions:
80K-160K
100bar-5bar

System Components:
Type 1 Al Tank (1.8m x 0.46m dia.)
7 x 100W heaters
HexCell HX - 9mm hex/76µm foil
60-100 layer MLVI – 25.4mm
Internal LN2 tank cooling channel

Full Scale System:
Tank 107.0kg 109.0l
HX 9.8kg 3.6l
MOF 35.1kg 166.4l
BoP 16.7kg 16.5l
Total 174.5kg 295.8l

- Model completed and being used to simulate drive cycle response.
Accomplishment

Adsorbent System FMEA

Complete the failure mode and effects analysis (FMEA) associated with real-world operating conditions for a MOF-5-based system, for both HexCell and MATI concepts based on the Phase 3 test results. Report on the ability to reduce the risk priority numbers (RPN) from the phase 2 peak/mean and identify key failure modes.

Key Failure Modes
- Material uptake/discharge rates insufficient due to hydrogen impurities
- Material uptake/discharge rate insufficient due non-uniform thermal conductivity
- Impact damage to system
- Pressure relief valve does not open upon accidental over pressurization
- Loss of useable hydrogen rate insufficient due to performance/damage of thermal isolation system
- MATI
  - Material uptake/discharge rate insufficient due non-uniform flow in micro-channel plates
- HexCell
  - Material uptake rate insufficient due to inhomogeneous adsorbent packing density
Remaining Adsorbent Engineering Issues

- Build and test fully functional prototype adsorption system, including tank cooling channel concept, to assess real life charging characteristics.
- Develop charging control algorithms to minimize charging time and H$_2$ flow through.
- Develop discharge control algorithm to meet drive cycle hydrogen demands.
- Denser MOF compacts would yield higher volumetric capacities.
- The effectiveness of enhanced thermal conductivity methods such as MATI pins need to be demonstrated.
- Manufacturing methods of MOF/HX systems in a sealed Type I pressure vessel needs to be demonstrated.
- Optimized refueling stations needs to be designed to meet recirculation demands imposed by either MATI or HexCell systems.
Continuing Efforts

Model Updates (*NREL*, *PNNL*, *SRNL*)

Develop a stand-alone isotherm data fitting routine to convert raw excess adsorption H$_2$ data into its D-A parameters.

Update the adsorbent hydrogen storage equations for additional theoretical formulations (such as UNILAN and/or 2-state Langmuir).

Update the built-in material properties database to include new adsorbents (such as AC, HKUST-1, etc.).

MATI System Modeling (*SRNL*)

Complete a fluid-flow model to examine flow distribution within the MATI channels and the feasibility of the “unit cell” assumption.

Complete and validate a prototype-scale COMSOL model of MATI system and upload to WEB site.
## Materials Based Hydrogen Storage Systems Summary

<table>
<thead>
<tr>
<th></th>
<th>Mass*</th>
<th>Volume*</th>
<th>Cost*</th>
<th>Gravimetric Density</th>
<th>Volumetric Density</th>
<th>Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(kg)</td>
<td>(liters)</td>
<td>($)</td>
<td>(gH₂/g system+gH₂)</td>
<td>(gH₂/liter system)</td>
<td>($)/kWh</td>
</tr>
<tr>
<td><strong>Metal Hydride System</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaAlH₄/Ti</td>
<td>457</td>
<td>489</td>
<td>8008</td>
<td>1.2%</td>
<td>11.5</td>
<td>43.0</td>
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<tr>
<td><strong>Chemical System</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AB</td>
<td>122</td>
<td>136</td>
<td>3011</td>
<td>4.6%</td>
<td>41.0</td>
<td>16.5</td>
</tr>
<tr>
<td>AlH₃</td>
<td>164</td>
<td>151</td>
<td>4133</td>
<td>3.4%</td>
<td>37.0</td>
<td>22.2</td>
</tr>
<tr>
<td><strong>Adsorbent System</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HexCell/MOF-5</td>
<td>174</td>
<td>296</td>
<td>2720</td>
<td>3.2%</td>
<td>18.9</td>
<td>14.6</td>
</tr>
<tr>
<td>MATI/MOF-5</td>
<td>178</td>
<td>267</td>
<td>2897</td>
<td>3.1%</td>
<td>21.0</td>
<td>15.5</td>
</tr>
<tr>
<td><strong>Compressed Gas</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Type 4 Tank/700 bar</td>
<td>212</td>
<td>278.6</td>
<td>2740</td>
<td>2.6%</td>
<td>20.1</td>
<td>14.8</td>
</tr>
<tr>
<td><strong>2020 DOE Target</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* 5.6kg usable hydrogen

# DOE Record #15013

- AB chemical system surpasses DOE 2020 volumetric target
- AlH₃ chemical system surpasses 700 bar Type 4 tank gravimetric and volumetric capacities
- MATI/MOF-5 adsorbent system surpasses 700 bar Type 4 tank volumetric capacity
- HexCell/MOF-5 adsorbent system surpasses 700 bar Type 4 tank cost metric
Technical Back-Up Slides
Accomplishment

Risk Management: Pressure Vessel Cryogenic Leaks

- Teflon seals observed to leak at LN2 temps.
- This issue could affect schedule and cost (as of 3/31 3-4 months behind schedule)
- Tank Seal Tiger Team formed with weekly telecoms scheduled
- Numerous approaches attempted to solve both waist and large plug leaks
- Waist seal solved with composite Teflon/steel washer allowing testing of HexCell system.
- Large opening seal not solved due to lack of mating surfaces – New stainless steel flange tanks designed, manufactured, tested and delivered allowing MATI system testing.

Problem Identified

Small Opening Leak

Large Opening Leak

Main Body Leak

Potential Solutions Investigated

SO: Crush Seal

WB: Teflon coated steel washer/w external clamp

Final Solutions Implemented

HexCell HX

MATI HX

2L Flange Tank
MATI Prototype Decommissioning

- Pucks were in good condition after testing.
- Any noticeable chips due to handling (pucks fit very tightly into MATI).
- Any significant amounts of loose powder due to assembly/disassembly.
- Only trace amounts found in bottom of vessel after MATI and pucks removed.
Summary of Metal Hydride Requirements

- Low enthalpy materials (i.e. $\Delta H < 27 \text{ kJ/mol-H}_2$), can operate with just the waste heat of the fuel cell for discharge, while high enthalpy materials require extra $\text{H}_2$ ($\sim 10\%$) for combustion and additional BoP.

- A material $\text{H}_2$ absorption kinetics needs to be 3-8X greater than catalyzed NaAlH$_4$, at charging pressures <100 bar.

- Materials with both high gravimetric capacity and low enthalpy of formation need to be developed.

\[
\frac{dC}{dt} = A \exp\left(-\frac{E_a}{RT}\right) \left(\frac{P_e - P}{P_e}\right) (C)^\chi
\]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>Range*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gravimetric Capacity, $\Delta H$&lt;27 kJ/mol</td>
<td>$g_{\text{H}<em>2}/g</em>{\text{media}}$</td>
<td>11%</td>
</tr>
<tr>
<td>Gravimetric Capacity, $\Delta H$&lt;40kJ/mol</td>
<td>$g_{\text{H}<em>2}/g</em>{\text{media}}$</td>
<td>17%</td>
</tr>
<tr>
<td>Equilibrium Pressure, $P_e$</td>
<td>bar</td>
<td>$5&lt;P_e&lt;100$</td>
</tr>
<tr>
<td>Exponential, $\chi$</td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Activation Energy, $E_a$</td>
<td>kJ/mol</td>
<td>3.05</td>
</tr>
<tr>
<td>Pre Exponential, $A$</td>
<td></td>
<td>$6.2 \times 10^8$</td>
</tr>
<tr>
<td>Bulk Density</td>
<td>$g_{\text{media}}/\text{volume}_{\text{media}}$</td>
<td>70% Crystal Density</td>
</tr>
<tr>
<td>Thermal Conductivity, $\kappa$</td>
<td>W/m K</td>
<td>$&gt;10$</td>
</tr>
</tbody>
</table>

Summary of Chemical Hydrogen Requirements

- Slurry or liquids are optimal for mass transport and must be stable both before and after reaction.
- Efficient chemical hydrogen regeneration needs to be developed to address fuel cost and WTPP efficiency gap.
- Hydrogen gas stream clean up has been demonstrated with the loss of gravimetric density.
- Chemical hydrogen which can discard spent fuel environmentally (one-way) optimal business solution.

\[
\frac{dC}{dt} = A \exp\left(-\frac{E_a}{RT}\right) (C)^n
\]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>Range*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gravimetric Capacity (liquids)</td>
<td>g H₂ / g material</td>
<td>~ 0.078 (0.085)†</td>
</tr>
<tr>
<td>Gravimetric Capacity (solutions)</td>
<td>g H₂ / g material</td>
<td>~ 0.098 (0.106)†</td>
</tr>
<tr>
<td>Gravimetric Capacity (slurries)</td>
<td>g H₂ / g material</td>
<td>~ 0.112 (0.121)†</td>
</tr>
<tr>
<td>Endothermic Heat of Reaction</td>
<td>kJ / mol H₂</td>
<td>≤ +17 (15)†</td>
</tr>
<tr>
<td>Exothermic Heat of Reaction</td>
<td>kJ / mol H₂</td>
<td>≤ -27</td>
</tr>
<tr>
<td>Kinetics: Activation Energy, Eₐ</td>
<td>kJ / mol</td>
<td>117-150</td>
</tr>
<tr>
<td>Kinetics: Pre-exponential Factor, A</td>
<td></td>
<td>4 x 10⁹ – 1 x 10¹⁶</td>
</tr>
<tr>
<td>Maximum Reactor Outlet Temperature</td>
<td>°C</td>
<td>250</td>
</tr>
<tr>
<td>Media H₂ Density</td>
<td>kg H₂ / L</td>
<td>≥ 0.07</td>
</tr>
<tr>
<td>Regeneration Efficiency</td>
<td>%</td>
<td>≥ 66.6%</td>
</tr>
<tr>
<td>Viscosity</td>
<td>cP</td>
<td>≤ 1500</td>
</tr>
</tbody>
</table>

* To meet 2020 targets
† (if hydrogen gas clean-up needed)

Summary of Adsorbent Requirements

- Volumetric density improved with microchannel MATI HX design via MOF compaction demonstrated.
- Charge time target requires external tank and H₂ cooling.
- Low enthalpy adsorbents ($\Delta H < 15$ KJ/mol) require low temperatures, MLVI, and eventual loss of hydrogen in dormancy.
- Method of fabricating higher density powder compact need to be developed without loss of adsorption sites to address volumetric density.

$$n_a = \frac{n_{max}RT}{(E_{max} - E_{min})} \ln \left( \frac{e^{-\Delta S_0/R} + \frac{P}{P_0} e^{E_{max}/RT}}{e^{-\Delta S_0/R} + \frac{P}{P_0} e^{E_{min}/RT}} \right)$$

$$n_{Total} = n_a + c(V_v - V_p)$$

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>Range*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum Excess Capacity, $n_{max}$</td>
<td>mol H₂/kg_media</td>
<td>~ 200</td>
</tr>
<tr>
<td>Minimum Binding Energy, $E_{min}$</td>
<td>KJ/mol</td>
<td>~ 4.49</td>
</tr>
<tr>
<td>Maximum Binding Energy, $E_{max}$</td>
<td>KJ/mol</td>
<td>~ $E_{min}$</td>
</tr>
<tr>
<td>Entropy, $\Delta S_0$</td>
<td>J/mol K</td>
<td>≤ -65</td>
</tr>
<tr>
<td>Reference Pressure, $P_0$</td>
<td>bar</td>
<td>1</td>
</tr>
<tr>
<td>Absolute Pressure, $P$</td>
<td>bar</td>
<td>5&lt;P&lt;100</td>
</tr>
<tr>
<td>Bulk Density, $\rho_{bulk}$</td>
<td>Kg/m³</td>
<td>181</td>
</tr>
<tr>
<td>Bed Void Volume, $V_v - V_p$</td>
<td>m³/kg_media</td>
<td>0.00391</td>
</tr>
<tr>
<td>Temperature, $T$</td>
<td>K</td>
<td>77&lt;T&lt;160</td>
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</table>

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