Hydrogen Storage

Ned T. Stetson

2010 Annual Merit Review and Peer Evaluation Meeting
(8 June 2010)
Goal & Objectives

**Goal:** On-board hydrogen storage for > 300 mile driving range across different vehicle platforms, without compromising passenger/cargo space or performance

Develop on-board storage systems that meet *all* DOE system targets simultaneously.

- **System Engineering / Systems Analysis**
  - Demonstrate the technologies required to achieve the 2015 DOE on-board vehicle hydrogen storage goals
  - Continue storage system analysis/projections for advanced storage system capabilities & development of system models for on-board storage systems
  - Increase emphasis on early market applications

- **Continue R&D on materials for breakthrough storage technologies**
  - Continue new hydrogen storage material discovery R&D for advanced storage systems
  - Strengthen coordination between basic & applied research within DOE and across agencies
**EMPHASIS**

- Systems approach through the Engineering CoE, in collaboration with independent materials development projects, to achieve light-duty vehicle targets.

- Continued close coordination with Basic Energy Science in 2010 & 2011 and improve coordination with National Science Foundation, Advanced Research Projects Agency - Energy, and Energy Frontier Research Centers activities.

- Focus on cost reduction for high pressure tanks.

- Increased analysis efforts for low to high production volumes.

- Increase emphasis on early market storage applications.

**Material Centers are being completed as planned at the end of Fiscal Year 2010.**
Challenges

Compressed gas offers a near-term option for initial vehicle commercialization and early markets

- Cost of composite tanks is challenging
- > 75% of the cost is projected to be due to the carbon fiber layer
- Additional analysis is needed to better understand costs at lower manufacturing volumes

Advanced materials development is still needed for long-term solutions

Materials discovery research is still needed for long-term, advanced materials with full set of properties for materials-based hydrogen storage options!
Progress in Storage Capacity

In just five years of accelerated investment, DOE has made significant progress in near- and long-term approaches.

Projected Capacities for Complete 5.6-kg H₂ Storage Systems

- Projections performed by Argonne National Laboratory using the best available materials data and engineering analysis at the time of modeling
- Analyses included for:
  - Physical storage – liquid, 350 & 700 bar compressed and cryo-compressed
  - Materials-based – reversible sorbents and metal hydrides and off-board regenerable chemical hydrogen systems

However no one system is yet able to meet all targets simultaneously.
Portfolio Management & Progress

Many new material systems have been investigated through the three Materials Centers of Excellence.

### Chemical Hydrogen Storage
- > 130 materials/combinations have been examined
- ~ 95% discontinued
- ~ 5% still being investigated

Ammonia Borane (AB) solid, ammonium borohydride, or mixture of AB with ionic liquids as liquid fuels

### Metal Hydrides

More than 81 distinct material systems assessed experimentally—not including catalyst/additive studies
- ~ 75% discontinued
- ~ 25% still being investigated

Computational/theoretical screening done on more than 20 million reaction conditions for metal hydrides

### Hydrogen Sorption
- ~ 210 materials investigated
- ~ 80% discontinued
- ~ 20% still being investigated
Hydrogen Storage Materials Database

A database has been created to capture materials data from the research projects.

- Database is designed to capture materials data from all projects.
- Database deployed for data input by Material Centers April 2010.
- Public website will be launched first quarter of fiscal year 2011:
  - Site will be searchable by materials properties.
  - Data can be exported in various forms.
  - New materials data can be submitted for addition to public site.
2009 Progress & Accomplishments

Status at 2009 AMR Review

- **Observed H₂ Capacity, weight %**
- **H₂ sorption temperature (ºC)**
- **Temperature for observed H₂ release (ºC)**

**Material capacity must exceed system targets**

**Chemical hydrides**
- LiBH₄/MgH₂
- LiMgN
- NaMn(BH₄)₄
- Na₂Zr(BH₄)₆
- CH Regen.
- Required

**Metal hydrides**
- Mg(BH₄)₂(NH₃)₂
- Mg(BH₄)(AlH₄)
- Mg(BH₄)₂(NH₃)₂
- Li₃AlH₆/Mg(NH₂)₂
- Li₂B₆H₁₁
- Li₃AlH₆/LiNH₂
- 1,6 naphthyridine
- Ca(BH₄)₂
- MgH₂
- Mg-Li-B-N-H

**Sorbents**
- IRMOF-177
- PCN-12
- C aerogel
- carbide-derived C
- B/C
- MOF-74
- bridged cat./IRMOF-8
- MD C-foam
- bridged cat./AX21
- Ti-MOF-16
- M-doped CA
- PANI

**Ultimate**
- CH Regen.
- Required

**2015**
- Li-AB
- AB/cat.
- MD C-foam
- ?

**2015 Progress & Accomplishments**
- Status at 2009 AMR Review
Open symbols denote new materials since 2009 AMR

Material capacity must exceed system targets

Metal hydrides

Chemical hydrides

Sorbents

Observed H₂ Capacity, weight %

H₂ sorption temperature (°C)

Temperature for observed H₂ release (°C)
**Focus on model development and material evaluation**

**Modeling of Storage Systems**

- **DOE Technical Targets**
  - Media kinetics/isotherm data
  - Media thermal and transport property data
  - Vessel component performance data
  - Novel component performance data
  - Prototype designs
  - Prototype data
- **Acceptability Envelope**
  - Integrated storage system models (3D, 2D, sensitivity/scoping)
  - Storage system design concepts
- **System Architect Analysis**
  - Applying Acceptability Envelope Model to Various Materials
  - Graph showing Li-Mg-N materials may be the most promising metal hydrides for further consideration

**Acceptability Envelope**

The “Acceptability Envelope” or “BlackBox Analysis” determines range of characteristics necessary for coupled media and system to meet storage system performance targets

**System Architect Analysis**

Applying Acceptability Envelope Model to Various Materials

- NaAlH₄, LiNH₂, MgH₂, Mg₂NiH₄

L(m) is the distance between heat transfer elements in meters
Systems evaluated against complete set of performance targets

2010 Progress: Engineering CoE

Metal Hydrides
(NaAlH₄)

Chemical Hydride System
(Solid Ammonia-Borane Bed)

Adsorbent System Status
(AX-21 Cryo-Adsorbent)
**Hydride Destabilization**

- Destabilization results in lower $\Delta H$ and $T_{1\text{ bar}}$

**LiBH$_4$/Mg$_2$NiH$_4$ system**

- $\Delta H = 15$ kJ/mol-H$_2$ and $\Delta S = 62$ J/K-mol-H$_2$ are the lowest reported so far for a reversible system

(HRL)

---

**AlH$_3$ Regeneration**

- ElectroCatalytic Additive found to increase steady-state current by 80%
- Dramatic increase in production rates.

(SRNL)

**Role of Additives on H$_2$ release from Mg(BH$_4$)$_2$**

- Small amount of boron hydrides (15 – 58 amu) (<0.2wt%) is released
- Other transition metal halides were tested but were not as effective
- The catalysts have little or no effect on rehydrogenation

List what additives were used

(BNL)

---

**AlH$_3$ Generated Electrochemically**

- ElectroCatalytic Additive found to increase steady-state current by 80%
- Dramatic increase in production rates.

(SRNL)
Understanding the role of additives in hydrogen uptake reactions

Role of Ti on the reaction of H₂ with Al

- Ti on clean Al surface critical for dissociating molecular hydrogen.
- Enables formation of mobile AlHₓ entities on the surface

Chemical Hydrogen Storage Material

Impurities

PNNL and LANL developed methods for quantification and strategies for mitigation of impurities released during hydrogen release from ammonia borane.

Catalysts and additives reduce the release of borazine into the gas stream.
Coupling exothermic BHNH release with endothermic H-C-C-H in the same molecule is a successful approach. Quantitative conversion by NMR gives ammonia borane for multiple spent fuel forms. Improvements in process efficiency and capital cost should result from the lower mass throughput (relative to previous process).

New Materials from University of Oregon:
- Prepared models of compound 1 at stages of dehydrogenation
- Demonstrated simple regeneration chemistry

Coupling exothermic BHNH release with endothermic H-C-C-H in the same molecule is a successful approach.

Material (1)

More readily available model of (1)

Rehydrogenates under mild conditions
2010 Progress: Sorbents

Accomplishments: Cryosorbents

Stabilization of MOFs with High Surface Areas by the Incorporation of Mesocavities with Microwindows

PCN-61  PCN-66  PCN-68

PCN-68: 6033 m²/g Langmuir (5109 m²/g BET) and ~ 7.2 wt% excess H₂ capacity

• Achieved H₂ uptake of 5.1 w% at 77K and 0.6 w% at RT
• Observed H₂ isosteric heat of adsorption up to ~10 kJ/mol over selected POPs
• Polyporphyrin can serve as platform for exchanging transition metals for H-M interaction

Nanostructured polyporphyrin based organic polymer

- Derived from 195 K and 298 K isotherms
- FeTTPP
- PTTPP
- ANL/Univ. of Chicago
- H₂ uptake capacity study

TAMU; Data by GM
2010 Progress: Sorbents

Accomplishments: Towards Room Temperature & Moderate Pressure Conditions

**Weak Chemisorption Materials**
Pt/ Carbon from Pyrolyzed Sucrose on Silica Sphere Template

- **Excellent Kinetics:** < 5 min to saturation
- Adsorption of hydrogen still increasing at 150 bar
- Minimal irreversibility. Multiple cycles with no loss of sorption capacity or water formation.
- Demonstrates unique features of pyrolyzed sucrose that is used for “bridging” to MOFs
- Unexpected capacity on “small” surface area, 600 m2/g (Pt content 10wt%)
- Possibility of “hidden” pore structure needs to be determined

**Boron substituted carbons**

- **Quantitative B-H interactions observed for the first time**
  - Neutron data shows, for the first time, a large rotational splitting indicative of enhanced H₂ interactions in a substituted carbon
  - DRIFTS observes reversible H interaction in B-C materials
- Experimental results confirm calculations that B-C increases ΔH values
The carbon fiber composite layer accounts for about 75% and 80% of the 350-bar and 700-bar base case system costs, respectively.

Based on manufacturing volumes of 500,000 units per annum, weight and volume under review

The Storage Program is currently funding ORNL to develop lower cost precursors (i.e., melt spinnable PAN and polyolefins) and reduced production costs for high-strength carbon fibers.

<table>
<thead>
<tr>
<th>Precursor and Conversion</th>
<th>Estimated CF Cost $/lb CF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Baseline – Wet spun PAN precursor conventionally converted</td>
<td>$11.43</td>
</tr>
<tr>
<td>Melt spun PAN, advanced ORNL conversion</td>
<td>$ 6.11</td>
</tr>
</tbody>
</table>

With conventional processing using a carbon fiber-grade (CF) PAN, precursor is over 50% of the carbon fiber cost.
Cryogenic pressure vessels offer potential to exceed 2015 H2 storage goals

ANL/TIAAX analyses indicate that scaling vessel size to store 5.6 kg H₂ for a passenger vehicle reduces capacities to 5.5 wt% H₂ at 42 g H₂/L at lower cost than a 700-bar Compressed gas tank.

### 5.8 kg Base Case Weight = 102 kg
**5.5 wt% based on 5.6 kg usage LH₂**

<table>
<thead>
<tr>
<th>Component</th>
<th>Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Balance of Tank</td>
<td>102 kg</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>5.8 kg</td>
</tr>
<tr>
<td>RI Port</td>
<td>Regular Valves</td>
</tr>
<tr>
<td>Outer Shell</td>
<td>MLVI</td>
</tr>
<tr>
<td>Carbon Fiber Layer</td>
<td>Linear and Fittings</td>
</tr>
</tbody>
</table>

### 5.8 kg Base Case Volume = 131 L
**43 g H₂/L based on 5.6 kg usable LH₂**

<table>
<thead>
<tr>
<th>Component</th>
<th>Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>Balance of Tank</td>
<td>131 L</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>5.8 kg</td>
</tr>
<tr>
<td>Outer Shell</td>
<td>MLVI</td>
</tr>
<tr>
<td>Carbon Fiber Layer</td>
<td>Linear and Fittings</td>
</tr>
<tr>
<td>Other BOP</td>
<td>Valves</td>
</tr>
<tr>
<td>Regulator</td>
<td>Fill Port</td>
</tr>
</tbody>
</table>

### 5.8 kg Base Case Factory Cost¹ = $2,200
**$12/kWh based on 5.6 kg useable LH₂**

<table>
<thead>
<tr>
<th>Component</th>
<th>Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>$2,200</td>
</tr>
<tr>
<td>Assembly and Inspection</td>
<td>Fill Port</td>
</tr>
<tr>
<td>Outer Shell</td>
<td>MLVI</td>
</tr>
<tr>
<td>Carbon Fiber Layer</td>
<td>Linear and Fittings</td>
</tr>
<tr>
<td>Valves</td>
<td>Other BOP</td>
</tr>
</tbody>
</table>

---

¹ Factory cost is based on the assumed factory cost of $12/kWh and includes the factory cost, materials, and transportation to the balance of tank.
Metal Organic Frameworks Adiabatic Liquid H₂ Refueling Analysis

Refueling: 7.1 MJ evaporative cooling load
- 62% for ΔH, 38% for sensible cooling and PV work

Discharge options
- Constant Q (1.2 kJ/g of H₂ discharged), 1.9 kW
- Variable Q, heat supplied only if tank P < 4 atm, 6.3-kW peak Q

System gravimetric capacity peaks at ~150 atm but the volumetric capacity increases slowly with storage pressure

Borane Liquid Mixture Analysis

Onboard release system: Preliminary ANL analysis of ionic liquid/ammonia borane liquid mixtures developed in Sneddon’s group at U. Penn with material capacities up to 11 wt. %, and fast release rates above 85 °C identified:

- Substantial spent fuel recycle to manage exothermic release
- Heat rejection and startup/shutdown are key challenges

Performance & Cost Metric | MOF -177 | Units
--- | --- | ---
System Gravimetric Capacity | 4.1 | Wt% |
System Volumetric Capacity | 34.1 | Kg·H₂/m³ |
Storage System Cost | 18 | $/kWh |
Fuel Cost | 4.6 | $/gge |
Cycle Life (1/4 full tank) | 5500 | Cycles |
Min Delivery Pressure | 4 | atm |
System Fill Rate | 1.5 – 2 | Kg·H₂/min |
Min Dormancy (full tank) | 2.8 | W – d |
H₂ Loss Rate (Max) | 0.9 | g/h/kg·H₂ |
WTT Efficiency | 41.1 | % |
GHG Emissions (CO₂ eq) | 19.7 | kg/kg·H₂ |
Ownership Cost | 0.15 | $/mile |
Congratulations to the 3 Presidential Awardees:

• **Professor Susan Kauzlarich** – UC Davis, a 2009 recipient of the *Presidential Award for Excellence in Science, Mathematics and Engineering Mentoring*—and a partner of the Chemical Hydrogen Storage Center of Excellence

• **Dr. Jason Graetz** – Brookhaven National Laboratory, a 2009 recipient of the *Presidential Early Career Award for Scientists and Engineers*—and a partner of the Metal Hydride Center of Excellence

• **Dr. Craig Brown** – NIST, a 2009 recipient of the *Presidential Early Career Award for Scientists and Engineers*—and a Partner of the Hydrogen Sorption Center of Excellence
Summary

Major Upcoming Milestones

**Physical Storage**

- Initially tasks were not planned beyond FY2010 because physical storage was not seen as a pathway towards meeting the ultimate targets.
  - Physical Storage will be used for early automotive market penetration as well as other early markets;
  - Additional tasks will be planned and added for out years, especially focusing on cost reduction.

**Material-based Storage**

- Three Material-based Centers of Excellence established in FY2004 and are being completed in FY2010;
- Hydrogen Storage Engineering Center of Excellence established in FY2009 as a 5-year effort;
- New materials R&D efforts are needed to further develop storage materials and to support the engineering efforts.
Session Instructions

- This is a review, not a conference.
- Presentations will begin precisely at the scheduled times.
- Talks will be **20 minutes** and **Q&A 10 minutes**.
- Reviewers have priority for questions over the general audience.
- Reviewers should be seated in front of the room for convenient access by the microphone attendants during the Q&A.
- Please mute all cell phones, BlackBerries, etc.
Reviewer Reminders

- Deadline for final review form submittal is **June 18th**.

- ORISE personnel are available on-site for assistance. A reviewer lab is set-up in room 8216 and will be open Tuesday – Thursday from 7:30 AM to 6:00 PM and Friday 7:30 AM to 3:00 PM.

- Reviewer feedback session – **Thursday, at 6:15pm (after last Hydrogen Storage session)**, in this room.
For More Information

Storage Team Contacts

Ned T. Stetson  
**Acting Hydrogen Team Leader**  
**Metal Hydrides**  
202-586-9995  
ned.stetson@ee.doe.gov

Grace Ordaz  
**Chemical Hydrogen Storage Materials**  
202-586-8350  
grace.ordaz@ee.doe.gov

Carole Read  
**Hydrogen Sorbents**  
202-586-3152  
carole.read@ee.doe.gov

Monterey Gardiner  
**Physical Storage, Engineering**  
202-586-1758  
monterey.gardiner@ee.doe.gov

Golden Field Office Project Officers:  
Jesse Adams  
James Alkire  
Paul Bakke  
Katie Randolph

Technical Support:  
Robert C. Bowman, Jr. (ORNL)  
Anita Vanek (BCS)  
Kristian Whitehouse (Navarro)