2005 Annual DOE Hydrogen Program Merit Review

Hydrogen Storage

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Basic Science Research Needs presented by George Thomas

\textsuperscript{1} Laboratory Fellow, change of station assignment to DOE HQ
Overview & Approach
- Challenges & Targets
- Basis for Targets & Current Status
- Research Portfolio & RD&D Plan

Status & Key Accomplishments
- Technology Progress
- Key Activities & Outputs
- Program Planning/Coordination

Future Plans
- Budget
- Upcoming Solicitation & RD&D Needs
**Challenge:** How to store hydrogen on-board to meet performance (wt, vol, kinetics, etc.) , safety and cost requirements and enable > 300 mile range, without compromising passenger/cargo space.

**Targets:** Developed through

<table>
<thead>
<tr>
<th></th>
<th>2010</th>
<th>2015</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>System Gravimetric Capacity= Specific Energy (net)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.0 kWh/kg</td>
<td>3.0 kWh/kg</td>
</tr>
<tr>
<td></td>
<td>(7.2 MJ/kg)</td>
<td>(10.8 MJ/kg)</td>
</tr>
<tr>
<td></td>
<td>(6 wt%)</td>
<td>(9 wt%)</td>
</tr>
<tr>
<td><strong>System Volumetric Capacity=Energy Density (net)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.5 kWh/L</td>
<td>2.7 kWh/L</td>
</tr>
<tr>
<td></td>
<td>(5.4 MJ/L)</td>
<td>(9.7 MJ/L)</td>
</tr>
<tr>
<td></td>
<td>(0.045 kg/L)</td>
<td>(0.081 kg/L)</td>
</tr>
<tr>
<td><strong>Storage system cost</strong></td>
<td>$4/kWh</td>
<td>$2/kWh</td>
</tr>
</tbody>
</table>

These Are System Targets

Material capacities must be higher!

Explanations at [www.eere.energy.gov/hydrogenandfuelcells/](http://www.eere.energy.gov/hydrogenandfuelcells/)
## Focus is on capacity: but many other requirements…

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>2005(7)</th>
<th>2010</th>
<th>2015</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific energy net</td>
<td>kWh/kg</td>
<td>1.5</td>
<td>2.0</td>
<td>3.0</td>
</tr>
<tr>
<td>Energy density net</td>
<td>kWh/L</td>
<td>1.2</td>
<td>1.5</td>
<td>2.7</td>
</tr>
<tr>
<td>Storage system cost</td>
<td>$/kWh</td>
<td>6</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>Cycle life (25-100%)</td>
<td>cycles</td>
<td>500</td>
<td>1000</td>
<td>1500</td>
</tr>
<tr>
<td>Cycle life variation</td>
<td>% of mean (min) @ % confidence</td>
<td>N/A</td>
<td>90/90</td>
<td>99/90</td>
</tr>
<tr>
<td>Max delivery temp.</td>
<td>°C</td>
<td>85</td>
<td>85</td>
<td>85</td>
</tr>
<tr>
<td>Minimum delivery pressure of H₂ from tank, FC=fuel cell, I=ICE</td>
<td>atm (abs)</td>
<td>8 FC 10 ICE</td>
<td>4 FC 35 ICE</td>
<td>3 FC 35 ICE</td>
</tr>
<tr>
<td>Start time to full flow @ 20 °C</td>
<td>sec</td>
<td>4</td>
<td>4</td>
<td>.5</td>
</tr>
<tr>
<td>System fill time (for 5 kg)</td>
<td>min</td>
<td>10</td>
<td>3</td>
<td>2.5</td>
</tr>
<tr>
<td>Loss of useable hydrogen</td>
<td>(g/h)/kg H₂ stored</td>
<td>1</td>
<td>0.1</td>
<td>0.05</td>
</tr>
<tr>
<td>Permeation and leakage</td>
<td>Scc/h</td>
<td>Federal enclosed-area safety standard</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Toxicity</td>
<td></td>
<td>Meets or exceeds applicable standards</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Safety</td>
<td></td>
<td>Meets or exceeds applicable standards</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

These are just some, more available at [www.eere.energy.gov/hydrogenandfuelcells/](http://www.eere.energy.gov/hydrogenandfuelcells/)
Energy Density is Critical

**Today’s Vehicles**

- Fuel Cell Efficiency, Conformable Tanks

**2015 Target**

- Liquid H₂ (20K, 1 bar)
- Compressed H₂ (300K)
- Gasoline

**Today’s gasoline “tank”:** fuel tank, fuel filler tubes, gas cap, hoses, fuel lines, fuel pump, fuel filter, carbon vapor canister, leak detection device, purge control solenoid, rollover check valve, tank hanger straps, clips, and other small fasteners

**For Hydrogen Systems:** Also include insulation, sensors, regulators, first charge, any byproducts/reactants, etc.
Portfolio stresses longer-term solutions but continues some R&D on viable options for the transition phase.
No current hydrogen storage technology meets the targets.

**Volumetric & Gravimetric Energy Capacity**

- **2015 target**
  - Chemical Hydrides: 1.0 kWh/L, 1.4 kWh/kg
  - Complex Metal Hydrides: 0.6* kWh/L, 0.8* kWh/kg
  - Liquid H2: 1.2 kWh/L, 1.7 kWh/kg
  - 10000 psi gas: 0.8 kWh/L, 1.6 kWh/kg
  - 5000 psi gas: 0.5 kWh/L, 1.9 kWh/kg

- **2010 target**
  - Chemical Hydrides: 1.5 kWh/L, 6 wt%
  - Complex Metal Hydrides: 0.8 kWh/L, 9 wt%
  - Liquid H2: 2.0 kWh/L, 3.0 kWh/kg
  - 10000 psi gas: 1.4 kWh/L, 2.0 kWh/kg

**System Cost, $/kWh**

- **2015 target**
  - Chemical Hydrides: $8
  - Complex Metal Hydrides: $16
  - Liquid H2: $6
  - 10000 psi gas: $18
  - 5000 psi gas: $15

- **2010 target**
  - Chemical Hydrides: $4

* Estimations from developers - to be continuously updated
* Projection
* Regeneration costs excluded
National Hydrogen Storage Project

Centers of Excellence

Metal hydrides

Chemical Hydrogen Storage

Carbon-Based Materials

Basic Science

Testing & Analysis

Cross Cutting

New materials/processes for on-board storage

Compressed/Cryogenic & Hybrid approaches

Off-board storage systems

Independent Projects

2. Basic science for hydrogen storage conducted through DOE Office of Science, Basic Energy Sciences
3. Coordinated with Delivery program element
Hydrogen Storage
“Grand Challenge” Partners

Centers of Excellence

**Metal Hydride Center**

- **National Laboratory:** Sandia-Livermore
- **Industrial partners:** General Electric HRL Laboratories Intematix Corp.
- **Universities:** CalTech Stanford Pitt/Carnegie Mellon Hawaii Illinois Nevada-Reno Utah
- **Federal Lab Partners:** Brookhaven JPL NIST Oak Ridge Savannah River

**Carbon Materials Center**

- **National Laboratory:** NREL
- **Industrial partners:** Air Products & Chemicals
- **Universities:** CalTech Duke Penn State Rice Michigan North Carolina Pennsylvania
- **Federal Lab Partners:** Lawrence Livermore NIST Oak Ridge

**Chemical Hydrogen Center**

- **National Laboratories:** Los Alamos Pacific Northwest
- **Industrial partners:** Intematix Corp. Millennium Cell Rohm & Haas US Borax
- **Universities:** Northern Arizona Penn State Alabama California-Davis UCLA Pennsylvania Washington

**Independent Projects**

**New Materials & Concepts**
- Alfred University
- Carnegie Institute of Washington
- Cleveland State University
- Michigan Technological University
- TOFTEC
- UC-Berkeley
- UC-Santa Barbara
- University of Connecticut
- University of Michigan
- University of Missouri

**High-Capacity Hydrides**
- UTRC
- UOP
- Savannah River NL

**Carbon-based Materials**
- State University of New York
- Gas Technology Institute
- UPenn & Drexel Univ.

**Chemical Hydrogen Storage**
- Air Products & Chemicals
- RTI
- Millennium Cell
- Safe Hydrogen LLC

**OffBoard, Tanks, Analysis & Testing**
- Gas Technology Institute
- Lawrence Livermore
- Quantum
- Argonne Nat’l Lab & TIAx LLC
- SwRI
Continuum of Knowledge Transfer Across Stages of Development

Basic Research

Use theory & fundamental experimentation to generate knowledge:
- Fundamental property & transport phenomena
- Novel material structures, effect of morphology.
- Understand reaction mechanisms

Applied Research & Development

Use theory & experimentation to design & develop high-performance materials
- Leverage knowledge from basic research, develop new materials
- Optimization of materials and testing to improve performance
- Use engineering science to design system packaging & balance of plant components

Technology Validation & Demonstration

Test Systems in Real World Conditions
- Gain knowledge on integration with power plant with fuel delivery infrastructure
- Apply lessons learned back to R&D
Basic material properties are a key issue in hydrogen storage.

**Hydrogen Densities of Materials**

- Liquid fuels
- Intermetallic hydrides too heavy

**2010 system targets**
- Liquid fuels
- 700 bar
- 350 bar

**2015 system targets**
- Liquid fuels

**Materials**
- Mg$_2$NH$_4$
- TiH$_2$
- LaNi$_5$H$_6$
- FeTiH$_{1.7}$
- CaH$_2$
- NaH
- KBH$_4$
- CH$_4$ (liq)
- C$_8$H$_{18}$
- NH$_3$
- C$_2$H$_6$
- C$_2$H$_5$OH
- C$_3$H$_8$
- CH$_3$OH
Program focus is on high energy density materials.

Some of the materials under study in CoE's

**Hydrogen Densities of Materials**

- **Hydrogen mass density (mass %)**
- **Hydrogen volume density (kg H₂ m⁻³)**

- **Materials**:
  - CH₄ (liq)
  - C₂H₆
  - C₃H₈
  - C₆H₁₈
  - C₂H₅OH
  - Mg₂NH₄
  - TiH₂
  - LaNi₅H₆
  - MgH₂
  - NH₃BH₃(1)
  - NH₃BH₃(2)
  - NH₃BH₃(3)
  - Mg(OMe)₂H₂O
  - Mg(OH)₂
  - AlH₃
  - LiNH₂(1)
  - LiNH₂(2)
  - KBH₄
  - NaAlH₄
  - NaBH₄
  - LiBH₄
  - NaH
  - 11M aq NaBH₄
  - C₆H₁₈
  - hexahydrotriazine
  - decaborane

**2010 system targets**
- 700 bar
- 350 bar

**2015 system targets**
No current material meets system requirements.
Other material property issues include thermodynamic properties.

For reversible systems, equilibrium between gas and solid given by:

\[ P = \exp(-\Delta H/RT + \Delta S/R) \]

or

\[ \ln P = -\Delta H/RT + \ln P_{T\inf} \]

\(\Delta H\) = enthalpy (kJ/mol \(H_2\)),

\[ d(\ln P)/d(1/T) = \Delta H/R \]

van’t Hoff plot

- **MnNi5**
- **MnNi4.5Al0.5**
- **LaNi5**
- **CaNi5**
- **LaNiAl**
- **TiCr.8**

<table>
<thead>
<tr>
<th>(\Delta H) (kJ/mol (H_2))</th>
<th>% of LHV</th>
</tr>
</thead>
<tbody>
<tr>
<td>ionic, covalent hydrides</td>
<td>100</td>
</tr>
<tr>
<td>70-80 kJ/mol (H_2)</td>
<td>40%</td>
</tr>
<tr>
<td>intermetallic, complex hydrides</td>
<td>30%</td>
</tr>
<tr>
<td>30-55 kJ/mol (H_2)</td>
<td>20%</td>
</tr>
<tr>
<td>carbons</td>
<td>20%</td>
</tr>
<tr>
<td>4-20 kJ/mol (H_2)</td>
<td>10%</td>
</tr>
<tr>
<td>cryogenic containment</td>
<td>0%</td>
</tr>
<tr>
<td>0-100°C containment</td>
<td></td>
</tr>
<tr>
<td>high T containment</td>
<td></td>
</tr>
</tbody>
</table>
BES workshop was held to identify basic research needs.

- Understanding the fundamental factors governing material behavior
- Applying these principles to modify material performance
- Identifying new materials and new classes of materials
- Designing of new materials at the nanoscale
- Theory, modeling and simulation of materials and molecular processes
Workshop laid foundation for 2005 BES solicitation.

• 227 full proposals were received
• Five technical focus areas:
  – Novel materials for hydrogen storage (50 proposals)
  – Membranes for separation, purification and ion transport (52 proposals)
  – Design of catalysts at the nanoscale (56 proposals)
  – Solar hydrogen production (49 proposals)
  – Bio-inspired materials and processes (20 proposals)

*Stay tuned for further announcements!*
Tanks: Performance close to targets - Next steps are cost and hybrid approaches.

### Specific Energy | Energy Density | Cost
--- | --- | ---
2015 Targets (2010) | 3.0 kwh/kg (2.0) | 2.7 kwh/L (1.5) | $2/kWh (4)
5,000 psi System | 1.9 kwh/kg | 0.5 kwh/L | $15/kWh
10,000 psi System | 1.6 kwh/kg | 0.8 kwh/L | $18/kWh

**Status**

- Primary driver is material cost
- 40 - 80% is carbon fiber cost

**Future focus:** Cost reduction, advanced concepts, conformability

Density improvements possible with cryo-compressed H

Aceves, et al, LLNL

* 5 kg storage using one tank; volume of 500,000 tanks/year
Storage Accomplishments - Metal Hydrides

System Engineering:
- Preliminary 1-kg hydrogen system prototype developed (Anton, et al, UTRC)
- With composite vessel, ~50% of system is balance of plant

Materials Development:
- Mg modified Li-amides demonstrate 5 wt% materials-based capacity, reversible with potential up to 10 wt% (Luo, Wang, et al, SNL)
- Absorption demonstrated down to 180°C with Mg substitution
- Over 100 cycles demonstrated for Li/Mg amide system (Luo, Gross, et al, SNL)

660 Wh / kg  530 Wh / L

H wt.% (material only)  0.005 wt% loss/cycle
• Doped single-wall nanotubes (SWNTs) synthesized and capacity measured to be ~2.5 - 3 wt.% hydrogen storage

• Binding energies calculated and optimum compounds theoretically predicted for potential storage materials

\[ \text{Cp}[\text{ScH}_2(\text{H}_2)_4] \quad 0.23 \text{ eV} \]

\[ \text{C}_{48}\text{B}_{12}[\text{ScH}]_{12} \leftrightarrow \text{C}_{48}\text{B}_{12}[\text{ScH}(\text{H}_2)_5]_{12} \]

Potential for 8.8 wt%

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Heben, Dillon, et al
NREL, Golden, CO
Storage Accomplishments - Chemical Hydrides

- Identified chemical hydride with 5.5 wt% materials-based H₂ storage capacity
  - N-ethylcarbazole
  - Cooper, Pez, et al, Air Products
  - Demonstrated several cycles
  - 40 catalysts screened for dehydrogenation

- Mesoporous scaffolds internally coated with ammonia borane show hydrogen release at < 100 °C and reduce borazine formation
  - Autrey, et al, PNNL
Independent Testing and Analysis

- **Standardized Test Facility**
  - Independent laboratory, SwRI
  - Construction complete
  - Test protocols developed
  - Website planned
  - Validation underway (double-blind testing)

- **Storage Systems Analyses**
  - Storage Systems Analysis Working Group formed (March, ’05)
  - Need for independent analyses: Performance, cost, life cycle energy & environmental impact, toxicity, safety
  - Breakdown of system into components (TIAX, ANL, Quantum, UTRC, Safe H2, Millennium Cell)

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**Graph**
- **Sodium Alinate**
  - 1.7 wt%
- **Compressed Hydrogen Storage**
  - **Need to reduce weight**

**2007 Target**
- = 4.5 wt%
IPHE Hydrogen Storage Technology Conference
June 20-22, 2005, Barga, Lucca, Italy

- Forum for Technical experts in hydrogen storage worldwide
- Track global progress- inventory of projects & expertise
- Objectives: Promote leveraging of global R&D
  - Identify and reduce duplication
  - Create and strengthen partnerships
  - Initiate process, identifying clear guidelines for IPHE projects
  - Gather feedback from global technical community on issues to be addressed by IPHE
  - Accelerate collaborative research projects
  - Recommendations to IPHE Committees

Key Organizers:
P. Garibaldi, S. Malyshenko, M. Steen, G. Sandrock, M. Conte, C. Filiou, S. Satyapal

Limited Attendance: www.iphe.net or http://www.engconfintl.org/5ar.html
Key Activities and Outputs (2005-2006)

- Water Availability Model
  - Help guide chemical hydrogen storage researchers

- Position Paper on Ammonia
  - Draft for public comment, June 2005

- Review Targets & Update
  - June-August 2005

- Purity Specification Guidelines
  - Tolerance of storage materials to various contaminants
  - Coordination with Fuel Cell, Production & Delivery Program Elements
    - Input to storage systems
    - Output from storage systems
Go/No-Go Decision on Carbon Nanotubes (4Q FY 06)

Decision Planning & Implementation

- **Measurement Technique Validation**
  - ✔ Verify storage capacity measurement with 2 different techniques
  - ✔ Verify accuracy with standards
  - ✔ On-site peer review to inspect & verify measurement techniques (Jan. ‘04)

- **Interim Milestone:**
  - ✔ Demonstrate 3 wt % (materials-based storage capacity - Aug. ‘04)

- **Interim Milestone:**
  - o Demonstrate 4 wt % (materials-based storage capacity)

- **Milestone:**
  - o Reproducibly demonstrate 4 wt% in external laboratory (4Q FY 2005)

- **Go/no go Point:**
  - o Reproducibly demonstrate 6 wt% (materials-based storage capacity) in external laboratory (4Q FY 2006)

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Shift funds to materials with potential to meet 2010 targets
Budget: FY 2005 vs. FY 2006 Request

FY2006 Budget Request = $29.9M
FY2005 Appropriation = $24.4M

- **Emphasis:**
  - Continue Centers of Excellence and new materials projects to focus on 2010 hydrogen storage goals of 2.0 kWh/kg, 1.5 kWh/liter, $4/kWh
  - Independent Testing & Analysis

- **Budget Distribution:**
  - Centers of Excellence: $16.7M
  - Independent Projects & Support: $13.2M
  - Total: $29.9M
**Key Milestones**

2005
- Complete construction of materials test facility (4Q, 2004)
- Demonstrate 4 wt% storage capacity on carbon nanotubes (4Q, 2005)

2006
- Complete prototype complex metal hydride system (2Q, 2006)
- Go/no go based on 6 wt% storage capacity on carbon nanotubes (4Q, 2006)

2007
- Down-select reversible metal hydrides (4Q, 2007)
- Down-select regeneration processes for chemical hydrides (4Q, 2007)

2008
- Down-select new materials / concepts (4Q, 2006)
Hydrogen Storage – Future Plans

Centers of Excellence Kick-off Meetings

IPHE Hydrogen Storage Conference Lucca, Italy

2005
Jan
Mar
Jun
Sep
Nov

Storage Systems Analysis Working Group Launched

Annual Program Review

2006
Jan
Mar
Jun
Oct
Dec

Testing Workshop

Preproposals Due

Basic Science Theory/Modeling Workshop

Hydrogen Storage Systems Analysis WG
Fuel Cell Seminar, Palm Springs

Announce new Solicitation Plans (“Grand Challenge” cont’d)

Release Solicitation* Subject to appropriations

Complete Safety Plans Storage Projects

Annual Program Review
For More Information, Contact:

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- **Carole J. Read**: Metal Hydrides, Metal Hydride Center of Excellence  
  – Phone 202-586-3152; carole.read@ee.doe.gov
- **John Petrovic**: New concepts and materials, Laboratory Fellow, Change of Station assignment from LANL  
  – Phone 202 586-8058; john.petrovic@ee.doe.gov
- **New Hire**: Materials science/engineering expertise junior/mid-level scientist/engineer- to be posted

- **Sunita Satyapal**: Hydrogen Storage Team Leader, Carbon Center of Excellence, Tanks, Analysis, IPHE activities  
  – Phone 202-586-2336; sunita.satyapal@ee.doe.gov

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