Materials Issues in Hydrogen R&D: Recent Developments in the DOE’s Portfolio

ICMR Symposium on Materials Issues in Hydrogen Production & Storage

University of California, Santa Barbara
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Office of Hydrogen, Fuel Cells and Infrastructure Technologies
Office of Energy Efficiency and Renewable Energy

¹. Sandia National Laboratory, retired, on assignment to DOE
Goal: Technology readiness to enable fuel cell vehicles & hydrogen fuel from diverse domestic resources

Challenges:

Critical Path Technology

- Hydrogen Storage (target: >300-mile range)
- Fuel Cell Cost and Durability (targets: $30 per kW, 5000 hours)
- Hydrogen Cost (target: $2.00 - 3.00 per gallon gasoline equivalent*)

Economic/Institutional

- Codes and Standards (Safety, and Global Competitiveness)
- Hydrogen Delivery (Investment for new Distribution Infrastructure)
- Education (safety and code officials, local communities, state and local governments, students)

*One kilogram of hydrogen contains nearly the same energy as a gallon of gasoline.
Producing Hydrogen

Goal: Hydrogen produced domestically, reducing our dependence on foreign energy sources and providing clean, carbon-free fuel.

Production Pathways: Hydrogen can be produced from renewable, nuclear, and fossil energy resources using a variety of process technologies, including:

- Renewable electrolysis (using wind, solar, or geothermal energy)
- Biomass and renewable liquids
- High temperature thermochemical
  - Nuclear energy
  - High temperature solar
- Biological and photoelectrochemical technologies
- Coal (with carbon sequestration)
- Natural gas

Quick Fact:
The U.S. hydrogen industry currently produces ~9 million tons of hydrogen a year – that’s enough to power about 34 million vehicles.
Distributed Hydrogen Production
Status vs Goal

![Graph showing the status of distributed hydrogen production compared to the goal. The graph includes data points for Dist. NG, Dist. Renewable Liquids, Dist. Water Electrolysis, and Dist. NG. The goal is represented by a horizontal line at $3.00 between 2010 and 2015.](image-url)
NREL is focusing on single material applications that will split water using sunlight as the only energy input.

Goal: Stable III-V nitride material for tandem H\textsubscript{2}O splitting

Synthesize the semiconductor structure with the necessary properties

- GaPN-NREL (high efficiency, stability)
- CuInGa(Se,S)\textsubscript{2} UNAM (Mexico), NREL (Low cost)
- Silicon Nitride –NREL (protective coating and new material)
**BES Priority Research Areas in Hydrogen Production**

**Fossil Fuel Reforming**  
Catalysis; membranes; theory and modeling; nanoscience

- Ni surface-alloyed with Au to reduce carbon poisoning

**Bio- and Bio-inspired H₂ Production**  
Biological enzyme catalysis; nanoassemblies; bio-inspired materials and processes

- Synthetic catalysts for water oxidation and hydrogen activation

**Solar Photoelectrochemistry/Photocatalysis**  
Understanding physical mechanisms; novel materials; theory and modeling; stability of materials

- Dye-Sensitized solar cells

**Nuclear and Solar Thermal Hydrogen**  
Thermodynamic data and modeling; novel materials; membranes and catalysts

- High T operation places severe demands on reactor design and on materials

Source: BES Hydrogen Workshop Report
Hydrogen Storage: The “Grand Challenge”

On-board hydrogen storage to meet all performance (wt, vol, kinetics, etc.), safety and cost requirements and enable a more than 300 mile driving range.

<table>
<thead>
<tr>
<th>Targets</th>
<th>2010</th>
<th>2015</th>
</tr>
</thead>
<tbody>
<tr>
<td>System Gravimetric Capacity (net)= “specific energy”</td>
<td>6 wt.% (7.2 MJ/kg) (2.0 kWh/kg)</td>
<td>9 wt.% (10.8 MJ/kg) (3.0 kWh/kg)</td>
</tr>
<tr>
<td>System Volumetric Capacity (net)= “energy density”</td>
<td>1.5 kWh/L (5.4 MJ/L) (45 g/L)</td>
<td>2.7 kWh/L (9.7 MJ/L) (81 g/L)</td>
</tr>
<tr>
<td>Storage system cost</td>
<td>$4/kWh (~$133/kg H₂)</td>
<td>$2/kWh ($67/kg H₂)</td>
</tr>
</tbody>
</table>

More targets and explanations at [www.eere.energy.gov/hydrogenandfuelcells/](http://www.eere.energy.gov/hydrogenandfuelcells/)
Targets are for Storage System

Reminder: **System** Targets

Material capacities must be higher!

Today’s gasoline tank system:

System includes material, tank, and balance of plant—e.g. insulation, sensors, regulators, first charge, any byproducts/reactants, etc.

6.5 wt%
Improved hydrogen storage technologies that can be packaged in a vehicle are necessary to meet range targets.

Vehicle Range:
- 2015 Target
- 2009 Target

Fuel Economy:
- Dyno (1)
- Window-Sticker (2)
- On-Road (3)(4)
Current Status
No storage technology meets 2010 or 2015 targets

Note: Estimates from developers. To be periodically updated.
Costs exclude regeneration/processing. Complex hydride system data projected. Data points include analysis results.
Many other requirements require optimization and possibly trade-offs.

- Weight
- Volume & conformability
- System cost (& fuel cost)
- Durability/Operability
- Charging/Discharging Rates
- Efficiency
- Fuel Purity
- Environmental Health & Safety

Not just weight %!

Commercially viable & efficient H2 Storage Systems
Strategy & Results
Broad Portfolio Focused on Materials Technologies

Challenges are technology specific: Pros and Cons for each
Tanks (to 10,000 psi), Chemical hydrides (CH), Metal Hydrides (MH), Carbon/Sorbents (S)

<table>
<thead>
<tr>
<th>Key 2010 Targets:</th>
<th>Tanks</th>
<th>CH</th>
<th>MH</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume (1.5 kWh/L)</td>
<td>H</td>
<td>M</td>
<td>M</td>
<td>M/H</td>
</tr>
<tr>
<td>Weight (2.0 kWh/kg)</td>
<td>M</td>
<td>M</td>
<td>M/H</td>
<td>M</td>
</tr>
<tr>
<td>Cost ($4/kWh)</td>
<td>M/H</td>
<td>M/H*</td>
<td>M/H</td>
<td>M/H</td>
</tr>
<tr>
<td>Refueling Time (3 min, for 5 kg)</td>
<td>L</td>
<td>L</td>
<td>M/H</td>
<td>M</td>
</tr>
<tr>
<td>Discharge Kinetics (0.02 g/s/kW)</td>
<td>L</td>
<td>M</td>
<td>M</td>
<td>M</td>
</tr>
<tr>
<td>Durability (1000 cycles)</td>
<td>L</td>
<td>M</td>
<td>M</td>
<td>M</td>
</tr>
</tbody>
</table>

Thermal Mgmt:
Key Issues for MH (CH, C)

- H = High (Significant challenge)
- M/H = Medium/High
- M = Medium
- L = Low (minimal challenge)

For CH, MH and S- assessment based on potential to meet targets, though systems not yet demonstrated in most cases.

*For CH: Storage system may meet cost but fuel cost of $2-$3/kg is challenge for CH regeneration.
An example trade-off for on-board reversible methods is among $\Delta H$, pressure and re-fill time.

**Pressure at 80 C vs. Formation Energy**

- **max. $\Delta S = 145$**
- **ave. $\Delta S = 115 \text{ J/molH}_2\cdot\text{K}$**
- **min. $\Delta S = 96.7$**

**Higher $\Delta H_f$ results in lower equilibrium pressure:**

$\Delta H_f \sim 17 \text{ kJ/molH}_2 \quad 45 \text{ kJ/molH}_2$

$P_{eq} \sim 350 \text{ bar} \quad 5 \text{ bar}$

**Lower $\Delta H_f$ reduces cooling power needs for refueling:**

- e.g., for $\Delta H_f \sim 30 \text{ kJ/molH}_2$
- need 800 kW for 8 kg H$_2$ and 5 minute fill time.
Examples of other important targets to keep in mind….

**Hydrogen Flow Rate at Maximum Power**

- **Discharge Kinetics**
  - $0.02 \text{ g/s/kW}$

For 100 kW fuel cell, need > 2 g/s flow rate

Desorption rate must be available over the entire hydrogen content range of the material

Ref: G. Thomas
…DOE should continue to elicit new concepts and ideas, because success in overcoming the major stumbling block of on-board storage is critical for the future of transportation use of fuel cells.” (NRC Report,p.44)

**Strategy and Program Plans**

- Focus is materials-based technologies
  - Systematic approach
  - Robust theory/simulation and rapid screening
  - Tailor properties

- **Centers of Excellence** ($5-6M/yr) plus independent projects, launched at $150 M over 5 years (plan subject to appropriations)
- ~40 universities, 15 companies, 10 federal labs (including 17 new BES awards)
- Diverse portfolio addresses NAS recommendations

Yakobson, Rice U.
**Results: Examples of Progress (2005-2006)**
New materials with higher capacities being found

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**Material Capacities for Hydrogen Storage**

<table>
<thead>
<tr>
<th>Advanced Metal Hydrides</th>
<th>Chemical H₂ Storage</th>
<th>Carbon/ Sorbents &amp; New Materials</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li Mg Amides</td>
<td></td>
<td></td>
</tr>
<tr>
<td>~5.5wt%, ~2.8 kWh/L (&gt;200 C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alane</td>
<td></td>
<td></td>
</tr>
<tr>
<td>~7-10 wt%, ~5 kWh/L (&lt;150 C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li borohydrides</td>
<td></td>
<td></td>
</tr>
<tr>
<td>&gt;9 wt%, ~3.5 kWh/l (~350 C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Destabilized Binary hydrides</td>
<td></td>
<td></td>
</tr>
<tr>
<td>~5-7 wt%, ~2-3 kWh/L (250 C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LiMgAlane, M-B-N-H</td>
<td></td>
<td></td>
</tr>
<tr>
<td>~ 7-8.8 wt%, &gt; 1.3 kWh/L (~150-340 C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phenanthroline/organic liquids</td>
<td></td>
<td></td>
</tr>
<tr>
<td>~7 wt%, ~1.8 kWh/L (&gt;150 C)</td>
<td></td>
<td></td>
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<tr>
<td>Ammonia</td>
<td></td>
<td></td>
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<tr>
<td>Borane/Scaffolds</td>
<td></td>
<td></td>
</tr>
<tr>
<td>~6 wt%, ~2-4 kWh/L (&lt;100 C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Metal/carbon hybrids, MetCars</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6 to &gt; 8wt%<em>, ~1.3</em> kWh/l (*theory)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bridged catalysts</td>
<td></td>
<td></td>
</tr>
<tr>
<td>IRMOF-8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>~1.8 wt.% , ~0.3 kWh/L (room T)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Metal-Organic Frameworks</td>
<td></td>
<td></td>
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<tr>
<td>IRMOF-177</td>
<td></td>
<td></td>
</tr>
<tr>
<td>~7 wt%, ~1 kWh/L (77K)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: Material capacities only. No balance of plant. Estimates for volumetric capacities.

*We are excited by these results but there are still issues...*

**Next steps:** Operability (Temperature, pressure, kinetics, etc.)
Heat of formation of reversible hydride impacts both operation and refueling.

Typical $\Delta H_f$ of high capacity hydrides too high for 80°C operation. Need to reduce $\Delta H_f$.

Significant cooling needed for refueling high formation energy hydrides. Lower $\Delta H_f$.

- cryogenic operation (~80°C C operation)
- high temp. operation

$\Delta H$ (kJ/molH2) % of LHV

- 100
- 40%
- 20%
- 0%
Results: MH researchers are finding new materials with favorable thermodynamics but have kinetic limitations.

- TGA for H₂ desorption from LiBH₄ incorporated into nanoporous scaffolds & non-porous graphite control. Lower T₉ in carbon aerogels and activated carbon compared to graphite control.
- Improved cycling capacity for LiBH₄ in scaffold structures. Capacity determined from dehydrogenation after hydrogenation (100 bar H₂, 400°C, 2 hr).
MH researchers are also combining advanced characterization with theoretical modeling to predict promising structures.

**Structural/chemical information**
- TEM structure
- And crystallography
- EDS and EELS
- Chemical and bonding information

**First principles calculations of thermodynamic properties**
- Provides Needed information
- Aids interpretation

**Outcome:** Provides guidance for new alloys with improved properties

- X-ray diffraction – B. Clemens, Stanford
- Neutron diffraction – T. Udovic, NIST
- Monte Carlo – E. Majzoub – SNL
- DFT----- D. Sholl - CMU

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MH Hydride Center of Excellence
MSE Illinois
NIST
Sandia National Laboratories
Carnegie Mellon
Stanford Materials Science
Adsorbent materials generally have too low a binding energy for hydrogen.

Intrinsic H₂ adsorption energy of high surface area materials too low.

Need to increase $E_{ads}$

Significant cooling energy needed for refueling cryogenic systems.

$\Delta H$ (kJ/molH₂) % of LHV

- 100 % of LHV
- 40%
- 20%
- ~80°C operation
- 50
- 0%
- high temp. operation

Increase $E_{ads}$
Results: Carbon and Sorbents are looking at increasing capacity and binding energy.

Carbon Center & New Materials:

- >7 wt.% at 77K shown on MOFs (> 30 g/L)
- Several cycles reversibility shown
- Four-fold enhancement in H₂ storage via “spillover”

Yaghi, Matzger (UCLA, U MI)

Y. Li and R.T. Yang, JACS (2006)

Yang, et al (U MI)

Results: The Carbon CoE is also using theory to design tailored nanostructures.

Yakobson, Ding, Lin
Rice University
Carbon Center

Theory modeling conducted to predict optimum structures and storage capacities

Y. Zhao, A.C. Dillon, Y.-H. Kim, M.J. Heben, S.B. Zhang, in prep

NREL-Carbon Center
Potential for 6.1-7.7 wt%

MetCars

CNT “Carpet”
Tour, et al, Rice U.
Thermodynamics of chemical (non-reversible) hydrides must also be tailored.

- Heat of reaction for hydrogen release too high
  - Reduce $\Delta E_{\text{react}}$
- Heat of formation too low for material stability at ambient temperatures
  - Increase $\Delta H_f$
- Energy to regenerate chemical hydrides impacts overall fuel efficiency
  - Low energy pathway for regeneration

$\Delta H (\text{kJ/molH}_2)$

- 100% of LHV
- 40%
Results: Chemical carrier research is addressing both on-board kinetics and regeneration chemistry.

- **Organic liquids:** >7 wt.%, 69 g/L
  - 1.5 wt% more than FY05
  - > 100 catalysts screened
  - > Dehydrogenation with 10x less Pt in catalysts

- **NH₃BH₃ in mesoporous scaffolds:**
  - >6 wt% material capacity
  - H₂ release at < 80 C
  - Reduced borazine formation

Rapid dehydrogenation catalysts demonstrated

*U. of Washington, Chemical CoE*

Cooper, Pez, et al, Air Products

Autrey, Gutowski, et al, PNNL
Chemical CoE

Original catalyst development- Jensen, et al (U HI)
Hydrogen Storage – Future Plans

- IPHE Hydrogen Storage Conference Lucca, Italy
- Centers of Excellence Launched
- Testing Workshop
- Updated Roadmap
- Theory Focus Session
- Solicitation Released
- Full Proposals Due Oct 4 06
- Pre-Proposals Due
- FY07 Go/No-go NaBH₄
- Cryo-compressed Tank Assessment
- Go/No Go Single - walled Nanotubes
- Release Solicitation *
- Updated Roadmap
- Test Facility Validation
- Ammonia Paper Released for Comment
- Storage Systems Analysis Working Group Launched
- Mar Jan Sep Dec Mar Jun Sep Dec

*Subject to appropriations
DOE Hydrogen Storage Budget

DOE- EERE
FY2007 Budget Request = $34.6M
FY2006 Funding = $26.6M

DOE- Office of Science
FY2007 Budget Request = $50.0M*
FY2006 Funding = $32.5M*

* For Basic Science within the Hydrogen Fuel Initiative, including hydrogen storage, membranes, catalysts, etc.

Planned funding for Basic Science in Hydrogen Storage in FY06: $7.13M
Difference between the total 04-07 request and available funds is $48.5M

* Budget numbers do not include earmarks
Summary: We need you to solve the Storage “Grand Challenge”!

- New Materials & Concepts are critical - Stress volumetric capacity, kinetics, etc. (not just wt. %!)
- Basic science is essential to develop fundamental understanding & complements applied research & development
- Engineering issues need to be considered
  - System issues, reactor design, thermal mgmt, safety, refueling, testing, etc
- Examples of Essential Capabilities:
  - Modeling & Analysis
  - Combinatorial/high throughput methods
  - Material properties measurements
  - Standardized & accurate testing
2007 Annual DOE Hydrogen Program
Merit Review and Peer Evaluation Meeting
Arlington, VA  May 14-18, 2007

www.hydrogen.energy.gov
For More Information

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**New Hire**  
Carbon/Sorbents, Carbon Center of Excellence

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Relevant Web Sites for DOE-SC-BES Programs:

Core Research Program
http://www.science.doe.gov/bes (Office of Basic Energy Sciences)
http://www.science.doe.gov/bes/dms/DMSE.htm (Division of Materials Sciences & Engineering)
http://www.science.doe.gov/grants/ (Sponsored research details)
http://www.science.doe.gov/bes/dms/Submit_Proposals/submit_proposals.htm
http://www.grants.gov/

http://www.science.doe.gov/bes/dms/Submit_Proposals/1pager.pdf
(1 page information flyer)

Major Research Facilities
http://www.sc.doe.gov/bes/BESfacilities.htm
http://www.science.doe.gov/bes/User_Facilities/dsuf/DSUF.htm

SBIR/STTR
http://sbir.er.doe.gov/sbir