Hydrogen Storage Issues for Automotive Fuel Cells

JoAnn Milliken, U.S. Department of Energy
John Petrovic, Los Alamos National Laboratory
Walter Podolski, Argonne National Laboratory

International Workshop on Hydrogen in Materials and Vacuum Systems
11-13 November 2002
Jefferson Lab
Newport News, Virginia
On-Board Hydrogen Storage Challenge

Storing enough hydrogen on vehicles to achieve greater than 300 miles driving range is difficult.

- On a weight basis $\text{H}_2$ has nearly three times the energy content of gasoline.
  - 120 MJ/kg vs. 44 MJ/kg (LHV)
- On a volume basis the situation is reversed.
  - 3 MJ/L (5000 psi), 8 MJ/L (LH$_2$) vs. 32 MJ/L
- Physical storage of hydrogen is bulky.
- Capacity of reversible chemical storage at useful T, P is low.
- Other challenging issues include energy efficiency, cost, and safety.
### 2010 DOE Technical Targets for On-Board Hydrogen Storage

**TO BE REVISED**

<table>
<thead>
<tr>
<th>Units</th>
<th>Target</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Storage Weight Percent</strong></td>
<td>%</td>
</tr>
<tr>
<td><strong>Energy Efficiency</strong></td>
<td>%</td>
</tr>
<tr>
<td><strong>Energy Density</strong></td>
<td>W-h/L</td>
</tr>
<tr>
<td><strong>Specific Energy</strong></td>
<td>W-h/kg</td>
</tr>
<tr>
<td><strong>Cost</strong></td>
<td>$/kW-h</td>
</tr>
<tr>
<td><strong>Operating Temperature</strong></td>
<td>°</td>
</tr>
<tr>
<td><strong>Start-Up Time To Full Flow</strong></td>
<td>sec</td>
</tr>
<tr>
<td><strong>Hydrogen Loss</strong></td>
<td>scc/hr/L</td>
</tr>
<tr>
<td><strong>Cycle Life</strong></td>
<td>Cycles</td>
</tr>
<tr>
<td><strong>Refueling Time</strong></td>
<td>min</td>
</tr>
<tr>
<td><strong>Recoverable Usable Amount</strong></td>
<td>%</td>
</tr>
</tbody>
</table>

- Storage Weight Percent: 6%
- Energy Efficiency: 97%
- Energy Density: 1100 W-h/L
- Specific Energy: 2000 W-h/kg
- Cost: 5 $/kW-h
- Operating Temperature: -40–50°C
- Start-Up Time To Full Flow: 15 sec
- Hydrogen Loss: 1.0 scc/hr/L
- Cycle Life: 500 Cycles
- Refueling Time: <5 min
- Recoverable Usable Amount: 90%
DOE Hydrogen Storage Approaches

- Compressed and liquid hydrogen tanks
- Chemical hydrides
- Carbon structures
- Complex metal hydrides
Compressed/Liquid Hydrogen Storage

Compressed $\text{H}_2$ Storage
Type IV all-composite tanks are available at 5000 psi (350 bar); prototype 10,000 psi tanks completed EIHP-based certification tests.

Packaging volume is still a concern.

Liquid $\text{H}_2$ Storage

- Liquifying $\text{H}_2$ requires substantial energy (40% of HHV)
- Boil-off is an issue for non-pressurized insulated tanks
- Pressurized cryogenic tanks are being developed by LLNL.
The focus of the workshop was on storage materials, with careful consideration of system level requirements.

- Identify and prioritize the most promising approaches to development of viable hydrogen storage materials/technologies
- Identify the technical challenges related to those approaches
- Draft a research and development plan to overcome those challenges
Overarching R&D Questions for All Advanced Materials

- Maximum storage capacity – theoretical model
- Energy balance / life cycle analysis
- Hydrogen absorption / desorption kinetics
- Preliminary cost analysis – potential for low cost, high volume
- Safety
Workshop Format

- **Argonne National Laboratory**
  - August 14-15, 2002
  - Attendees
    - 49 DOE/Laboratory
    - 32 Industry
    - 16 University
  - Plenary session
    - Overview of DOE Program
    - Automaker’s perspective
    - Four technology overview presentations
  - Four breakout groups
    - Advanced/complex hydrides
    - Chemical storage
    - Carbon storage
    - Advanced concepts
DOE target is too low.
Reversible Metal Hydride System

Sodium alanate doped with Ti is reversible but not quite suitable for vehicle applications.

\[ 3\text{NaAlH}_4 \rightleftharpoons \text{Na}_3\text{AlH}_6 + 2\text{Al} + 3\text{H}_2 \rightleftharpoons 3\text{NaH} + \text{Al} + 3/2\text{H}_2 \]

3.7 wt% 1.8 wt%

PEM fuel cell exhaust is near 80°C. Capacity and kinetics are too low.
Metal Hydrides

Conclusions/Recommendations

**Conclusions**
- NaAlH₄ capacity limited to about 5.6 wt%
  - Interim goal (5-year) of 6 wt%
- Need 8 wt% hydrogen material capacity if BOP adds 20%

**Recommendations**
- Continue fundamental studies on NaAlH₄ as model system
- Identify other hydride materials that have storage capacity greater than 6 wt%
- Develop new materials to achieve 8 wt%
- Engineering analyses
  - Preliminary system cost analysis
  - Large scale material production
  - Independent safety consultant/laboratory to understand safety and certification issues
Chemical Hydrides

Three Approaches

**NaBH₄ + 2H₂O → NaBO₂ + 4H₂**  
Millenium Cell DaimlerChrysler  
20 - 35% sol. Stabilized with 1-3% NaOH  
Proprietary catalyst  
Borax in NaOH

**2LiH + 2H₂O → 2LiOH + 2H₂**  
ThermoPower  
Light mineral oil slurry, proprietary stabilizers  
Paste byproduct

Capacity is around 10 wt%, reduced by other materials. Dehydrogenation kinetics are fast. Reactions are irreversible on board vehicle.

**2Na + 2H₂O → 2NaOH + H₂**  
Powerball  
Polyethylene-coated pellets, mechanically cut to expose Na
Chemical Hydride R&D
Recommendations

• Screen chemical complexes
  – Hydrogen storage density potential
  – Thermodynamic energy requirements including regeneration

• Improved/new process chemistry
  – Catalysts
  – Operating conditions (temperature, pressure)

• Well-to-wheels-to-well analysis of top complexes
  – Primary energy use
  – Cost of delivered fuel
  – Emissions
  – Resource depletion
Single-Wall Carbon Nanotubes

- Capacity around 4 wt%
- Doped SWNTs to 7 wt% by NREL
- Ambient temperature, moderate pressure
- SWNTs are made by arc discharge, laser vaporization, CVD, and lithographically
- SWNTs must be purified, cut, and the ends opened

Reproducibility is a critical issue.

Carbon R&D Recommendations

• Conduct definitive experiments to show where and how hydrogen is stored in SWNT and for various forms of carbon
  – develop 2-3 pure SWNT standards for synthesis, purification, activation, and hydrogen adsorption/desorption
  – conduct round-robin testing
    • role of SWRI, other labs, universities, industry

• Better understand the science to engineer carbon for hydrogen storage
  – Baseline theory to elucidate parameters affecting the number and type of binding sites and heat of reaction for a broad range of modified carbon materials
  – Provide “directional” guidance for experiments (and vice-versa)
Advanced Concepts Identified

1. Crystalline Nanoporous Materials
2. Polymer Microspheres
   Self-Assembled Nanocomposites
3. Advanced Hydrides
4. Metals – Organic
5. BN Nanotubes
   Hydrogenated Amorphous Carbon
6. Mesoporous materials
7. Bulk Amorphous Materials (BAMs)
8. Iron Hydrolysis
9. Nanosize powders
10. Metallic Hydrogen
    Hydride Alcoholysis
Advanced Hydride Materials

Hydrogen Generation from LiBH₄

- LiBH₄ (lithium tetrahydroboride)
  - Salt-like, hygroscopic, crystalline material
  - Density 0.68 g/cm³
  - Melting point 275 °C
- \[
  \text{LiBH}_4 = \text{LiH} + \text{B} + 1.5\text{H}_2(\text{g})
\]
  - \(\Delta G\) becomes negative at 450 °C
  - Endothermic reaction
  - 13.8 wt.% H₂ released
- A low temperature H₂ release has been observed
  - 2.3 wt.% H₂ released at 118 °C
  - May be related to an orthorhombic-to-tetragonal crystallographic change
    - Is this a reversible process?

Hydrolysis of LiBH$_4$-Organics

Organics combined with LiBH$_4$ to reduce the severity and heat of the hydrolysis reaction

$$\{M(L)BH_4\}_x + 4xH_2O \rightarrow 4xH_2 + xMOH + xB(OH)_3 + xL$$

M = lithium
L = organic ligand

Molecular weight of organics in the range of 300 g/mol

# Chemical Reactions of Hydrides With Alcohols (Alcoholysis)

Controlled and convenient production of $\text{H}_2$ at room temperature and below


<table>
<thead>
<tr>
<th>Hydride</th>
<th>wt. % of $\text{H}_2$ (in respect to the hydride weight)</th>
<th>Litres of $\text{H}_2$ obtained per 1 kg of hydride</th>
<th>Total $\text{H}_2$ capacity (including the weight of the hydride and the alcohol - methanol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiH</td>
<td>25.4</td>
<td>2845</td>
<td>5.0</td>
</tr>
<tr>
<td>LiAlH$_4$</td>
<td>13.2</td>
<td>1478</td>
<td>7.2</td>
</tr>
<tr>
<td>Li$_3$AlH$_6$</td>
<td>16.8</td>
<td>1882</td>
<td>6.1</td>
</tr>
<tr>
<td>LiBH$_4$</td>
<td>23.1</td>
<td>2592</td>
<td>9.4</td>
</tr>
<tr>
<td>NaH</td>
<td>8.3</td>
<td>933</td>
<td>3.6</td>
</tr>
<tr>
<td>NaAlH$_4$</td>
<td>9.3</td>
<td>1045</td>
<td>5.9</td>
</tr>
<tr>
<td>Na$_2$AlH$_6$</td>
<td>8.9</td>
<td>996</td>
<td>4.6</td>
</tr>
<tr>
<td>NaBH$_4$</td>
<td>13.3</td>
<td>1490</td>
<td>7.3</td>
</tr>
<tr>
<td>Li$_2$Be$_2$H$_7$</td>
<td>22.0</td>
<td>2460</td>
<td>7.1</td>
</tr>
<tr>
<td>Li$_2$BeH$_4$</td>
<td>22.5</td>
<td>2516</td>
<td>6.7</td>
</tr>
<tr>
<td>MgH$_2$</td>
<td>15.3</td>
<td>1716</td>
<td>4.5</td>
</tr>
<tr>
<td>CaH$_2$</td>
<td>9.6</td>
<td>1074</td>
<td>3.8</td>
</tr>
<tr>
<td>FeTiH$_2$</td>
<td>5.7</td>
<td>641</td>
<td>2.6</td>
</tr>
<tr>
<td>ZrH$_2$</td>
<td>4.3</td>
<td>484</td>
<td>2.6</td>
</tr>
<tr>
<td>TiH$_2$</td>
<td>8.1</td>
<td>905</td>
<td>3.5</td>
</tr>
<tr>
<td>MgAl$_2$H$_6$</td>
<td>11.7</td>
<td>1307</td>
<td>6.7</td>
</tr>
<tr>
<td>LiAlH$_7$</td>
<td>11.9</td>
<td>1329</td>
<td>8.1</td>
</tr>
<tr>
<td>ZrAl$_2$H$_8$</td>
<td>6.6</td>
<td>737</td>
<td>4.6</td>
</tr>
</tbody>
</table>

\[ \text{MH}_x + x \text{ROH} \rightarrow \text{M(OR)}_x + x \text{H}_2 \uparrow \]

- LiH + CH$_3$OH $\rightarrow$ LiOCH$_3$ + H$_2$
- NaH+ CH$_3$OH $\rightarrow$ NaOCH$_3$ + H$_2$
- LiH + C$_2$H$_5$OH $\rightarrow$ LiOC$_2$H$_5$ + H$_2$
- MgH$_2$ + 2 C$_2$H$_5$OH $\rightarrow$ Mg(OC$_2$H$_5$)$_2$ + 2 H$_2$
Hydrogen Adsorption by Boron Nitride Nanotubes

Figure 1: The morphologies of BN nanotubes: (a) multiwall nanotubes and (b) bamboo-like nanotubes. Scale bar: 100 nm.

Figure 2: The hydrogen adsorption as a function of pressure in multiwall BN nanotubes and bamboo nanotubes at ~10 MPa is 1.8 and 2.6 wt %, respectively, in sharp contrast to the 0.2 wt % in bulk BN powder. The values reported here have an error of <0.3 wt %.

Comparison of Carbon and Zeolite Hydrogen Physisorption

• Physisorption at 77 °K and 1 bar pressure
• Activated carbon Norit 990293
  – BET surface area 2030 m²/gm
  – 2.1 wt.% hydrogen adsorbed
    • Highest level of all carbon materials that were examined
• Zeolite ZSM-5
  – BET surface area 430 m²/gm
  – 0.7 wt.% hydrogen adsorbed
    • Highest level of all silica-based materials that were examined

Zeolite A

- \(\{\text{Na}_{12}[^{\text{Al}}_{12}\text{Si}_{12}\text{O}_{48}]\}\_8\)
- 8-ring channel
- Three-dimensional channels along \(<100>\) directions
- Channel diameter 0.42 nm

Hydrogen Storage In Zeolite A

0.05 wt.% H₂ was reversibly stored in Zeolite A at 300 °C

H₂ molecules believed to be stored in the sodalite cages

• Only 20-25% of sodalite cages contained an H₂ molecule
  • Reasons for this partial cage filling were unclear

Can zeolites be chemically designed to store significantly more hydrogen?

• H₂ molecules stored in both sodalite and α cages

Modeling of Hydrogen Storage in Zeolite A

Modeling suggests that Zeolite A can store at least 2 wt.% H₂ if all cage sites are filled.

Large Pore Zeolite UTD-1

- High silica zeolite
  - SiO$_2$/Al$_2$O$_3$ ratio ~ 70
- 14-ring channel
- One-dimensional channel along [001]
- Channel dimensions of 1.0 x 0.75 nm

Hydrogen storage in large pore zeolites has never been examined

Mesoporous MCM-41 Material

- Hexagonal array of uniform mesoporous channels ranging from 2-10 nm

Synthesis of Ordered Carbon Molecular Sieves by Templating

- Mesoporous silica molecular sieve MCM-48 impregnated with sucrose
- Sucrose converted to carbon by heating to 800-1100 °C in vacuum or inert atmosphere
- Silica framework dissolved in aqueous solution of NaOH and ethanol

SiO\textsubscript{2} Xerogels and Aerogels

- **Xerogels**
  - Produced by conventional drying of wet silica gel
- **Aerogels**
  - Produced by liquid-to-gas drying of wet silica gel
  - Supercritical fluid drying

**Structural Properties of SiO\textsubscript{2} Aerogels**

- Bulk density: 0.003-0.500 g/cm\textsuperscript{3}
- Porosity: 80\% - 99.8\%
- Mean pore diameter: 20-150 nm
- BET surface area: 100-1600 m\textsuperscript{2}/gm

Porous Metal-Organic MOF-5

- Chemical formula \( \text{Zn}_4 \text{O} (\text{BDC})_3 (\text{DMF})_8 (\text{C}_6\text{H}_5\text{Cl}) \)
  - \( \text{BCD} = 1,4 \)-benzenedicarboxylate
  - \( \text{DMF} = \text{dimethylformamide} \)
- \( \text{ZnO}_4 \) tetrahedral clusters linked together by \( \text{C}_6\text{H}_4\text{-C-O}_2 \) “struts”
- Cubic crystal structure
- 1.294 nm spacing between centers of adjacent clusters

Mesoporous Organosilica Material

benzene-silica hybrid material

Nanosize Metal and Ceramic Powders

- Nanosize metal and ceramic powders are commercially available
  - 10 - 100 nm diameters

- Nanosize metal powders
  - Au, Ag, Ni, Ti, Mo, Pt, W

- Nanosize ceramic powders
  - $\text{Al}_2\text{O}_3$, $\text{ZrO}_2$, $\text{CeO}_2$, $\text{CuO}$, $\text{MgO}$
    - $\text{SiO}_2$, $\text{TiO}_2$
Gold-Thiol Single Molecule Electrical Junctions

Single benzene-1,4-dithiolate molecule between atomically-sharp gold electrodes

Hydrogen Production by Grinding of Powders

- “In wet grinding in liquid media including water or alcohol, it has been confirmed that a considerable amount of hydrogen is generated and causes an abnormal increase in pressure of a closed mill pot, even when the feed materials hardly react with them.”

- Steel milling balls used to mill ceramic materials react with water to form hydrogen

- \(3 \text{Fe} + 4 \text{H}_2\text{O} = \text{Fe}_3\text{O}_4 + 4 \text{H}_2\)
  - 3.3 wt.% \(\text{H}_2\) including both \(\text{Fe}\) and \(\text{H}_2\text{O}\)

Hydrogen Storage in Modified Iron Oxides

Additives accelerate reduction and oxidation reactions at lower temperatures

Al, Cr, Zr, Ga, V the most effective

Effects of Mechanical Milling on Hydrogen Storage in Graphite

- 200 µm graphite powder
- Planetary milling with steel balls and vial


Solubility of Hydrogen in Polymers

Hydrogen has a very low solubility in polymers: \( \sim 0.0003 \) wt.% \( \text{H}_2 \) at 25 \( ^\circ \text{C} \)

Next Steps

- Prepare workshop proceedings
- Hold workshop to address remaining R&D issues for compressed hydrogen tanks
- Update targets and draft 5-yr R&D Plan
- Draft hydrogen storage solicitation
- Accelerate development of standard test facility
- Discuss advanced storage concepts further to refine recommendations and resolve controversial aspects
For More Information

www.anl.gov/g8
www.eren.doe.gov/hydrogen/news
www.hydpark.ca.sandia.gov