Survey of Solid State Hydride Tanks for Hydrogen Storage and Energy Conversion Applications

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Summer School Lectures
MH2008
23 June 2008
Outline

• Introduction & Background
  - Metal Hydride (MH) general properties
  - Overview of gas phase applications
  - DOE Targets for Fuel Cell Powered vehicles
• Configurations and System Requirements for Hydride Beds
  - Hydride bed design features
  - Thermal management trades & other issues
• Examples of Hydride Systems
  - Vehicles
  - Compressors
  - Sorption Cryocoolers
• Summary & Conclusions
• Acknowledgments
Family Tree of Hydriding Alloys and Complexes
(TM = transition metal)

$$AB_n + (x/2)H_2 \leftrightarrow AB_nH_x + \Delta Q$$

<table>
<thead>
<tr>
<th>Elements</th>
<th>Alloys</th>
<th>Complexes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Solid Solutions</td>
<td>Intermetallic Compounds</td>
</tr>
<tr>
<td></td>
<td>AB$_5$</td>
<td>AB$_2$</td>
</tr>
<tr>
<td>Other</td>
<td>AB$_3$, A$_2$B$_7$</td>
<td>A$<em>2$B$</em>{17}$, etc.</td>
</tr>
<tr>
<td></td>
<td>Nitrides/Imides</td>
<td>Misc.</td>
</tr>
<tr>
<td></td>
<td>“Stable”</td>
<td>Multiphase</td>
</tr>
</tbody>
</table>

There are Hundreds of MH Phases known – but only relatively few are viable candidates for gas phase applications!
Metal Hydride Pressure-Composition-Temperature (PCT) Properties

\[ \text{M} + x\text{H}_2 = \text{MH}_{x/2} + \Delta Q \]

(Practical Reversible Reactions for Storage are Exothermic)

Reversible \( \text{H}_2 \) Storage capacity = 1.2 wt.\%
Examples of Practical Metal Hydrides

Key Properties of Some Metal Hydrides - Suitable for Gas Phase Applications

<table>
<thead>
<tr>
<th>Alloy Type</th>
<th>Hydride Phase</th>
<th>Maximum H-capacity (wt.%)</th>
<th>Reversible H-capacity (wt.%)</th>
<th>$P_{\text{des}}$ (298 K) (atm)</th>
<th>T (K) for 1 atm $P_{\text{des}}$</th>
<th>$-\Delta H_{\text{plateau}}$ (kJ/mol H$_2$)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>MgH$_2$</td>
<td>7.66</td>
<td>&lt;7.0</td>
<td>~10$^{-6}$</td>
<td>552</td>
<td>74.5</td>
<td>Ni and oxides (e.g., Nb$_2$O$_5$) greatly improve kinetics but only operates @ &gt; 550 K due to thermodynamic limits on pressure</td>
</tr>
<tr>
<td>A</td>
<td>VH$_2$</td>
<td>3.81</td>
<td>1.9</td>
<td>2.1</td>
<td>285</td>
<td>40.1</td>
<td>Two plateaus, difficult to activate</td>
</tr>
<tr>
<td>A</td>
<td>(V$<em>{0.9}$Ti$</em>{0.1}$)$<em>{0.95}$Fe$</em>{0.05}$</td>
<td>3.7</td>
<td>1.8</td>
<td>0.5</td>
<td>309</td>
<td>43.2</td>
<td>Solid Solution (SS) Alloy with bcc phases</td>
</tr>
<tr>
<td>A$_2$B</td>
<td>Mg$_2$NiH$_4$</td>
<td>3.59</td>
<td>3.3</td>
<td>~10$^{-5}$</td>
<td>528</td>
<td>64.5</td>
<td>Not metallic, very slow kinetics &lt; 500 K</td>
</tr>
<tr>
<td>AB</td>
<td>TiFeH$_2$</td>
<td>1.89</td>
<td>1.5</td>
<td>4.1</td>
<td>265</td>
<td>28.1</td>
<td>Two plateaus, hard to activate</td>
</tr>
<tr>
<td>AB</td>
<td>ZrNiH$_3$</td>
<td>1.96</td>
<td>1.1</td>
<td>~5 x 10$^{-6}$</td>
<td>573</td>
<td>68.6</td>
<td>Two plateau, fast kinetics, low pressures</td>
</tr>
<tr>
<td>AB$_2$</td>
<td>TiMn$<em>{1.4}$V$</em>{0.62}$H$_{3.4}$</td>
<td>2.15</td>
<td>1.1</td>
<td>3.6</td>
<td>268</td>
<td>28.6</td>
<td>Two plateau, fast kinetics, low pressures</td>
</tr>
<tr>
<td>AB$_2$</td>
<td>ZrMn$<em>2$H$</em>{3.6}$</td>
<td>1.77</td>
<td>0.9</td>
<td>0.001</td>
<td>440</td>
<td>53.2</td>
<td>Two plateau, fast kinetics, low pressures</td>
</tr>
<tr>
<td>AB$_3$</td>
<td>LaNi$<em>{5.6}$H$</em>{6.5}$</td>
<td>1.49</td>
<td>1.28</td>
<td>1.8</td>
<td>285</td>
<td>30.8</td>
<td>Fast kinetics, but degrades for T &gt; ~350 K</td>
</tr>
<tr>
<td>AB$_5$</td>
<td>LaNi$<em>{4.8}$Sn$</em>{0.2}$H$_{6.0}$</td>
<td>1.40</td>
<td>1.24</td>
<td>0.5</td>
<td>312</td>
<td>32.8</td>
<td>Slow degradation for T &lt; 550 K, Adjust $P_{\text{des}}$ with A-substitution; fast kinetics</td>
</tr>
<tr>
<td>Com.</td>
<td>NaAlH$_4$ (Ti-doped)</td>
<td>5.6</td>
<td>&lt;4.5</td>
<td>--</td>
<td>306/383</td>
<td>47/37</td>
<td>Two plateaus, H$_2$-capacity falls with Ti-doping, Hydrides not metallic, extremely reactive with H$_2$O and O$_2$ (safety issues)</td>
</tr>
</tbody>
</table>
# Metal Hydrides (MH\textsubscript{x}) for Energy Storage and Conversion Applications

<table>
<thead>
<tr>
<th>Application</th>
<th>Required MH\textsubscript{x} Attributes</th>
<th>Other Important Issues</th>
<th>Candidate MH\textsubscript{x}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stationary fuel storage</td>
<td>P\textsubscript{d}$\sim$1-10 atm, very low cost, use waste heat, H-capacity $&gt;$ 2 wt%</td>
<td>Safety, activation, contamination, degradation</td>
<td>TiFe, V-alloys, Mg-alloys, AB\textsubscript{2}-alloys</td>
</tr>
<tr>
<td>Vehicular fuel storage (internal combustion/Fuel cells)</td>
<td>DOE System H-capacity $&gt;$ 6 wt%, cost, P\textsubscript{d}$\sim$1-10 atm, use waste heat, fast kinetics, durability during cycling, safety, contamination</td>
<td>Activation, operating temperature range, cost</td>
<td>AB\textsubscript{2}, Mg-alloys, alanates, &amp; TBD (Note: TiFe, AB\textsubscript{5} alloys have low H-capacities but work well in niche systems)</td>
</tr>
<tr>
<td>Chemical heat pumps and refrigerators</td>
<td>Very fast kinetics, cost, H-capacity, P\textsubscript{d}$\sim$1-5 atm, use waste heat</td>
<td>Hysteresis, degradation during cycling, safety</td>
<td>AB\textsubscript{5}, AB\textsubscript{2}, AB</td>
</tr>
<tr>
<td>Gas gap thermal switches (Used for heat management with sorbent beds.)</td>
<td>P\textsubscript{d} $&lt;$0.05 atm, fast kinetics, low power ($\sim$10 mW), durability during temperature cycling, contamination</td>
<td>Activation, cost, safety, stability, reliability</td>
<td>ZrNi, U, Zr-alloys (AB\textsubscript{2}, A\textsubscript{x}B\textsubscript{y}O\textsubscript{z})</td>
</tr>
<tr>
<td>Compressors (up to \textasciitilde 500 atm) for liquefaction or filling high pressure gas storage tanks</td>
<td>Thermal efficiency (i.e., $\Delta$P/$\Delta$T ratio), fast kinetics, cycling stability, safety, cost</td>
<td>Contamination, power, equipment complexity (multiple staging MH\textsubscript{x} beds), scalability</td>
<td>V-alloys, AB\textsubscript{5}, AB\textsubscript{2}, AB</td>
</tr>
<tr>
<td>Sorption cryocoolers (space flight applications)</td>
<td>$\Delta$P/$\Delta$T ratio, fast kinetics, cycling stability, P\textsubscript{a}$\sim$ constant in absorption plateau, safety, power, reliability</td>
<td>Activation, contamination (H\textsubscript{2} purity during cycling)</td>
<td>LaNi\textsubscript{4.8}Sn\textsubscript{0.2}, V-alloys, AB\textsubscript{5}, AB\textsubscript{2}</td>
</tr>
</tbody>
</table>
Application of Hydride Storage to Fuel Cells

“Required” MHx Attributes for Vehicular Usage:

- H-storage weight capacity > 5 wt.% [DOE 2010 Target ≥ 6.0 Wt.% (System)]
- Volume Density [DOE 2010 Target ≥ 45 g/L (System)]
- Low cost (both materials & processing)
- Desorption Pressure (P_{des}) ~ 1 – 10 bar
- Use waste heat for desorption (<100 °C for PEMFC)
- Fast kinetics (Especially, absorption during refueling process)
- Durability during absorption/desorption & temperature cycling
- Safety & low toxicity

Other Important Issues to Consider:

- Resistance to contamination and common impurities
- Minimal demands for sorbent bed activation

G. Sandrock, in HANDBOOK OF FUEL CELLS, 2003

S. Satyapal, et al., Catalysis Today 120 (2007) 246–256
Goals and Objectives of the US DOE for Hydrogen Storage Systems

S. Satyapal @ 2008 DOE H₂ Program Annual Review 10 June 2008

GOAL: On-board hydrogen storage for > 300 mile driving range across different vehicle platforms, WITHOUT COMPROMISING passenger/cargo space, performance (wt, vol, kinetics, safety, etc.) or cost

Develop on-board storage systems to meet DOE targets, including:
- Capacity
- Operating temperature range (-40 to +85°C)
- Hydrogen supply rate/refueling rate
  ○ 0.02 g H₂ per sec. per kW of power
  ○ Refueling time <3 min. for 5 kg H₂
- System cost
- Fuel cost
- Safety, C&S, reliability, cycle life, efficiency, etc.

See: http://www1.eere.energy.gov/hydrogenandfuelcells/storage/pdfs/targets_onboard_hydro_storage.pdf
US DOE Strategy – Diverse Portfolio to Reach Very Ambitious Goals

National Hydrogen Storage Project

Centers of Excellence
- Metal Hydrides
- Chemical Hydrogen Storage
- Hydrogen Sorption

Independent Projects
- Testing, Material Properties & Analysis Cross Cutting
- Basic Science
- New materials/processes for on-board storage
- Compressed/Cryogenic & Hybrid tanks
- Off-board storage systems

Engineering Center of Excellence

~40 Universities, ~20 Companies, ~15 Federal Laboratories

2. Basic science for hydrogen storage conducted through DOE Office of Science, Basic Energy Sciences
3. Coordinated with Delivery Program element
2008 Status: Material Capacity Vs. Temperature

- Open symbols denote new mat’ls for FY2008
- DOE system targets
- Observed H₂ Capacity, weight %
- H₂ sorption temperature (°C)
- Temperature for observed H₂ release (°C)

Metal hydrides:
- Mg(BH₄)₂(NH₃)₂
- Ca(BH₄)₂
- Mg(BH₄)₂
- MgH₂
- Li₃AlH₆/LiNH₂
- 1,6 naphthyridine

Chemical hydrides:
- Li₃AlH₆/Mg(NH₂)₂
- LiBH₄/MgH₂
- MgH₂
- Li₃AlH₆
- Mg(BH₄)₂(AlH₄)
- LiBH₄/CA
- Mg(BH₄)₂
- Ca(BH₄)₂

Sorbents:
- IRMOF-177
- PCN-12
- C aerogel
- carbide-derived C
- bridged cat./IRMOF-8
- br.dged cat./AX21
- M-doped CA

AB/cat.:
- Li-AB
- AB ionic liq.
- LiMgN
- M-B-N-H
- Li₃AlH₆/Mg(NH₂)₂

B/C:
- B/C
- MOF-74

2008 Status: No Technology Meets DOE Targets

Current focus: DOE system targets
Volume Comparisons for 4 kg Vehicular H₂ Storage

Figure 1 Volume of 4 kg of hydrogen compacted in different ways, with size relative to the size of a car. (Image of car courtesy of Toyota press information, 33rd Tokyo Motor Show, 1999.)

MH\textsubscript{x}-FC Operation is dominated by the P-T relationship

Other Required Metal Hydride Data

• **Energy Transport**
  • Thermal conductivity
  • Specific heat
  • Density (particle & bed)
  • Porosity
  • Thermal contact resistance
  • Heat of reaction (& kinetics)

• **Mass Transport**
  • Mean effective particle diameter
  • Porosity

• **Chemical Kinetics**
  • Kinetics relations for all reactions

• **Bed Expansion**
  • Free bed expansion
  • Constrained expansion stress
    – Stress for fully constrained bed
    – Stress and expansion for partially constrained bed (lock-up of media)

• Potential for component (i.e., powders) segregation due to vibration

Parameters may depend on:
• Temperature
• Pressure
• Composition (depends on T, P & cycling history)
• Internal Stress
• Cycling history (maybe rates of discharge)
Due to expansion of the media against the walls of its container

Expansion Induced Stress Depends On:

- The compressibility of the media as it changes chemical form during hydrogen uptake
- The composition of the media, which at equilibrium, depends on the temperature and gas pressure
- The history of cycling and/or the loading/discharge rates of the media
- The propensity of the media to “lock-up” during expansion. That is, the inability of the media to flow freely so that it occupies the full available volume during expansion

Swelling!
Components for Internal Thermal Management in MH$_x$ Beds

Properties (LaNi$_{4.78}$Sn$_{0.22}$)
- Total mass = 3,675 grams
- Alloy mass = 1,847 grams
- H$_2$ mass = 25.6 grams (285 sL)

Porous (11 % density & 40 ppi) Al Foam used to enhance conduction. Filled with coarse (unactivated) powder @ 3.5 g/cc [~43% bulk density]
Expanded Graphite/MH Compacts-Enhanced Heat Transfer

Fig. 9. (a) Pure graphite pellet, (b) ex situ compact, decomposed, (c) in situ compacts.

LmNi_{4.85}Sn_{0.25}

Test Beds Parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>RB-A (Al-foam)</th>
<th>RB-A (graphite)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass of matrix/compact (g)</td>
<td>32.6</td>
<td>12.12</td>
</tr>
<tr>
<td>Mass of hydride (g)</td>
<td>531.1</td>
<td>530.93</td>
</tr>
<tr>
<td>Total mass (g)</td>
<td>563.7</td>
<td>543.05</td>
</tr>
<tr>
<td>Mass ratio</td>
<td>0.0614</td>
<td>0.0228</td>
</tr>
<tr>
<td>Measured free gas volume (ml)</td>
<td>65.85</td>
<td>65.37</td>
</tr>
<tr>
<td>ε_{Al/Gr}</td>
<td>0.0911</td>
<td>0.0762</td>
</tr>
<tr>
<td>ε_{Met}</td>
<td>0.5343</td>
<td>0.5341</td>
</tr>
<tr>
<td>ε = ε_{Al/Gr} + ε_{Met}</td>
<td>0.6254</td>
<td>0.6103</td>
</tr>
<tr>
<td>Porosity Ψ (%)</td>
<td>37.46</td>
<td>38.97</td>
</tr>
</tbody>
</table>

λ_{Eff} (W/mK) 8.0 19.5
TC (W/K) ~16 ~12

Hydrogen Absorption Rates are very similar
HTF = Heat Transfer Fluid

H₂ gas porous tube
Other Storage Vessel Options

Ergenics, Inc.
Solid State Hydrogen Energy Solutions

Low cost, high surface area Ring Manifold heat exchanger

Miniature Storage Units for Hydrogen compression and FC Powered Radios
Sodium Alanate Experiences Significant Physical Changes during Hydrogen Sorption

Total Theoretical Capacity = 5.6 wt% hydrogen

\[ \text{NaAlH}_4 \Rightarrow \frac{1}{3} \text{Na}_3 \text{AlH}_6 + \frac{2}{3} \text{Al} + \text{H}_2 \Rightarrow \text{NaH} + \text{Al} + \frac{3}{2} \text{H}_2 \]

3.7 wt.% 1.9 wt.%

Fully cycled material thermal conductivity varies >70% with phase and gas pressure

Characteristic equations
- \( \text{NaH + Al (H}_2) \): \( K_{th} = 0.068 \ln(P) + 0.71 \)
- \( \text{Na}_3 \text{AlH}_6 \): \( K_{th} = 0.061 \ln(P) + 0.50 \)
- \( \text{NaAlH}_4 \): \( K_{th} = 0.037 \ln(P) + 0.51 \)

Initial packing density: 0.62 g/cc

- Morphology changes with cycle and influences thermal properties
- Gas pressure enhances thermal conductivity

Dedrick, et al., JALCOM 389 (2005) 299
First full scale vessel: Store ~1 kg H₂ with 19 Kg Ti-doped NaAlH₄

- Development of system design tools focused on complex hydrides
- High temperature composite vessel
- Powder densification
- Full scale fabrication & testing

• D. Mosher, et al., 2007 DOE Hydrogen Annual Rev. Proc., Project ID STP 33
**UTRC Prototype 2: Improve Thermal Conductivity & Powder Density**

Full scale – 19 kg hydride
Aluminum foam

(1/2)^3 = 1/8 scale – 3.5 kg hydride
Aluminum fins

**Volumetrics Overview**

Energy density is the product of
- **Hydride powder density**
- H₂ weight % capacity
- System volumetric efficiency

Prototype improvement
- Prototype 1: 200 Wh / L
- Prototype 2: 700 Wh / L

**Prototype 2**
0.72 to 0.76 g/cc
Prototype 1
0.44 g/cc

Hydride powder density is as important as H₂ weight % capacity for system volumetric capacity
UTRC Prototype 2 Gravimetrics

- 3.5 kg NaAlH$_4$
- 0.72 g/cc
- 2.0 wt% system
  (150 C desorption)
UTRC Prototype 2: Improve Thermal Conductivity & Powder Density

Comparison of (a) temperatures and (b) hydrogen mass flow for the exothermic hydrogen absorption. Dashed lines are for the model.

Prototype 2
0.72 to 0.76 g/cc

Prototype 1
0.44 g/cc
Compact High Temperature PEM Fuel Cell system Utilizing Integrated NaAlH₄ Beds


Concept diagram of integrated PEMFC/MH bed

Solid model of MH bed and fuel cell integration

HT (upper limit ~ 200 ºC) PEM fuel cell from TU-Denmark produced ~55 W operating @ ~160 ºC when using 8.8 LPM H₂ & 8.3 LPM air during tests at SNL.

NaAlH$_4$ Bed Integration and Test Summary

**Integrated MH Bed & FC Stack**

Two Tests done @ 160 °C [Much lower Power due to H$_2$ & air from damaged HT-PEMFC stack] – MH beds supplied enough hydrogen to produce 71W

<table>
<thead>
<tr>
<th>Test #</th>
<th>Absorption time (hrs)</th>
<th>Flow (SLPM)</th>
<th>Operation time (min)</th>
<th>Usable Hydrogen</th>
<th>Ave Power (W)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>121</td>
<td>0.77</td>
<td>65.8</td>
<td>4.55g (2.6 wt%)</td>
<td>6.9</td>
</tr>
<tr>
<td>2</td>
<td>14</td>
<td>0.80</td>
<td>62.6</td>
<td>4.50g (2.6 wt%)</td>
<td>3.5</td>
</tr>
</tbody>
</table>

Test 2 MH Bed & FC Stack Performance

Total of 173 grams of MH  

No follow-up work done to date!
Examples of Hydride Storage Systems On “Vehicles”

Information extracted from “Open Literature” sources and DOE Hydrogen Program Reviews & Annual Reports
MH Beds Developed @ SNL for FC Powered Golf Cart [1998]

<table>
<thead>
<tr>
<th>Requirement</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen Supply</td>
<td></td>
</tr>
<tr>
<td>Total hydrogen stored</td>
<td>~160 grams</td>
</tr>
<tr>
<td>Maximum delivery rate</td>
<td>~25 slm</td>
</tr>
<tr>
<td>Refueling time</td>
<td>≤ 10 minutes</td>
</tr>
<tr>
<td>Environmental Temperature Range</td>
<td>-5 °C to ~ 65 °C</td>
</tr>
<tr>
<td>Overall Size</td>
<td>Fit in space ~ 3&quot; x 20&quot; x 21&quot;</td>
</tr>
<tr>
<td>Bed Heating</td>
<td>“normal” steady state operation</td>
</tr>
<tr>
<td></td>
<td>water, fuel cell waste heat (≤2.5 kW max)</td>
</tr>
<tr>
<td></td>
<td>startup</td>
</tr>
<tr>
<td></td>
<td>batteries, 12 - 36 V, ~ 600 - 1000 kJ max</td>
</tr>
</tbody>
</table>
Hydride Bed Modules (two alloys)

C15 – AB₂ Alloy: Ti(24.6)Zr(8.3)Mn(48.1)V(13.9)Fe(3.4)Ni(1.8)

Hy-Stor 208: MmNi₄.₅Al₀.₅ [Higher Pressure Bed]

MH bed modules were built & tested but never integrated into the golf cart.
**H₂ Hybrid Electric Bus - Augusta, GA [1997-1998]**
(Westinghouse Savannah River Co., et al.)

Schematic of the hydrogen-powered hybrid power system

- Hydrogen storage vessels
- IC engine
  - 230 kW
  - 70 kW
  - (6 kg/hr)
- Generator
- Power Control
- AC motor
- Batteries
- 170 kW
- Wheels
- 100 kW

Advantages
- IC engine at high efficiency
- Ultra low emissions

**Two Fuel Containers (15 kg H₂):**
- 24 Hydride Storage Vessels (Each)
  - 26.6 Kg hydride alloy
  - Al foam
  - Engine coolant via U-tubes
  - 10 µm sintered metal filters

**Lm₁.₀₆Ni₄.₉₆Al₀.₀₄ (Lm =La 55.7%, Ce 2.5%, Pr 7.7%, Nd 34.1%)**

[H/M = 0.86 @ 40°C, P_{des} = 13.3 bar @ 60°C ]
SRTC PEMFC Vehicle “Gator” Uses MHₓ Tanks
(Demonstration in York & Columbia, SC, 1998-2001)

![Gator Vehicle Image](image)

### Design Parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Requirement</th>
<th>GATOR 1</th>
<th>GATOR 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Storage Type</td>
<td>Metal Hydride</td>
<td>MmNi5Al</td>
<td>FeTiMn</td>
</tr>
<tr>
<td>Desorption Temperature</td>
<td>45-55 deg. C</td>
<td>45 deg. C</td>
<td>50 deg. C</td>
</tr>
<tr>
<td>Desorption Pressure (mid-point)</td>
<td>100 psig</td>
<td>110 psig</td>
<td>95 psig</td>
</tr>
<tr>
<td>Refueling Pressure (H₂ supply)</td>
<td>&gt;100 psig</td>
<td>100 &amp; 300 psig</td>
<td>100 &amp; 300 psig</td>
</tr>
<tr>
<td>Max. H₂ Delivery Rate</td>
<td>105 liters per min</td>
<td>&gt;350 slpm</td>
<td>&gt;350 slpm</td>
</tr>
<tr>
<td>H₂ Storage Capacity</td>
<td>&gt;1.8 kg</td>
<td>2.2 kgs</td>
<td>2.2 kgs</td>
</tr>
<tr>
<td>Storage System Volume (per side)</td>
<td>&lt;90 liters</td>
<td>55 liters</td>
<td>55 liters</td>
</tr>
<tr>
<td>Storage System Weight (per side)</td>
<td>&lt;150 kg</td>
<td>143 kgs</td>
<td>122 kgs</td>
</tr>
<tr>
<td>Refueling Time @ 300 psig</td>
<td>&lt;60 minutes</td>
<td>30 min to 90%</td>
<td>20 min to 90%</td>
</tr>
</tbody>
</table>
An 80 cc, 4 stroke, air-cooled, single cylinder gasoline ICE scooter was converted to run on hydrogen fuel at ECD.

**Performance Data**

- Range: 35 Km
- Fuel Consumption: 3.8 grams/Km
- Average Speed during the test: Approx 20 mph
- Top Speed during the test: 25 mph
Metal Hydride Beds for ICE Powered Passenger Vehicles

Ovonic™ Solid H₂ Onboard Storage Vessel

Type Bed used on a 2002 Model Prius Hybrid (Ni-MH batteries)

Specifications (Prototype)

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Charging Pressure</td>
<td>up to 2,000 psig</td>
</tr>
<tr>
<td>Charging Time</td>
<td>10 min. to 90% capacity</td>
</tr>
<tr>
<td>Storage Capacity</td>
<td>3 kg H₂</td>
</tr>
<tr>
<td>Total Weight</td>
<td>190 kg</td>
</tr>
<tr>
<td>Total Volume</td>
<td>60 liters (840mm Length x 328mm OD)</td>
</tr>
<tr>
<td>Operating Temp.</td>
<td>-20°C to 60°C</td>
</tr>
</tbody>
</table>

60 Liter Vessel

<table>
<thead>
<tr>
<th></th>
<th>Metal Hydride @ 2,000 psig</th>
<th>Compressed H₂ @ 3,600 psig</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂ Capacity (kg)</td>
<td>3.0</td>
<td>0.88</td>
</tr>
<tr>
<td>Total weight (kg)</td>
<td>190</td>
<td>25.2</td>
</tr>
<tr>
<td>Weight %</td>
<td>1.58</td>
<td>3.49</td>
</tr>
<tr>
<td>Volume (g / liter)</td>
<td>50</td>
<td>14.7</td>
</tr>
</tbody>
</table>

MH Bed in Trunk

Hydrogen ICE Vehicles with 200 mile range storing 3.5 kg H₂ (2005 model)

2002 Prototype

Two MHₓ Vessels (2005)

2005 Prototype

Comments:

(1) ECD proprietary metal hydride \([C14 \ AB2 \ alloy]\)

(2) Initial \(H₂\) fill @ ~100 bar, but stores/operates @ \(\leq 20\) bar

(3) Weighs 150% more than 350 bar \(H₂\) gas vessel with same capacity, but 3 times capacity of same volume size gas tank.
Toyota HP Tank/LT Metal Hydride Storage Vessel

Figure 1. Schematic view of high-pressure MH tank

Figure 2. Concept of charge and discharge system

Figure 6. PCT diagram of Ti-Cr-Mn alloy
Table I. Specification of each tank system

<table>
<thead>
<tr>
<th></th>
<th>Low-pressure MH tank</th>
<th>High-pressure tank</th>
<th>High-pressure MH tank</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen storage capacity</td>
<td>3.5 kg/tank 120 L</td>
<td>3 kg/tank 180 L</td>
<td>7.3 kg/tank 180 L</td>
</tr>
<tr>
<td>Tank weight</td>
<td>300 kg</td>
<td>&lt; 100 kg</td>
<td>420 kg</td>
</tr>
<tr>
<td>Hydrogen filling time</td>
<td>0.5-1 hour</td>
<td>5-10 min.</td>
<td>5 min./80%</td>
</tr>
<tr>
<td>With external cooling facility</td>
<td></td>
<td></td>
<td>Equal to high-pressure tank without external cooling facility</td>
</tr>
<tr>
<td>Hydrogen release at low temperature</td>
<td>Impossible at low temperature</td>
<td>Possible</td>
<td>Possible even at 243 K</td>
</tr>
<tr>
<td>Control ability</td>
<td>Difficulty in acceleration</td>
<td>Good</td>
<td>Good</td>
</tr>
<tr>
<td>Safety</td>
<td>Low pressure (&lt; 1 MPa)</td>
<td>High pressure (35 MPa)</td>
<td>High pressure (35 MPa)</td>
</tr>
</tbody>
</table>

As of May 2008, Toyota has NOT integrated these HP-MH beds on any Demo vehicle!

HP-MH: Ti-Cr-Mn (C14 AB\textsubscript{2} Laves) Stores 1.9 Wt.% @ 22kJ/molH\textsubscript{2}
Sandia RATLER: Robotic All Terrain Lunar Exploration Rover

Conversion of a battery powered vehicle to hydrogen fuelcell operation

RATLER™ operating in the field

Fuel cell/hydride Power System
• **H Power fuel cells (2 units)**
  – nominal 24 volts, 100 watts per unit
  – air cooled (fan)
  – low pressure H₂ and air
  – internal stack humidification

• **Hydride storage assemblies (2 units)**
  – 120 liters H₂ capacity each assembly (approx. 200 kwh electrical)
  – 4 psig H₂ regulated delivery
  – air cooled (no liquid loop)

• Severe volume limitations

**Hydride storage assembly**

- **Compact ‘six-pack’ vessel.**
  – Stainless steel construction - easily welded.
- **Forced air operation**
  – High external surface area
  – Channeled air flow
- **C-15 AB₂ Alloy ( Ti, Fe, Mn )**
  – Low pressure operation from 0°C to 60°C.
  – Low temperature activation
- **1.1 wt.% hydrogen capacity (hydride + structural hardware)**
Effective heat transfer reduced loading time

Convective cooling: 200 min.

Forced air: 80 min.

Internal structure: 50 min.

Proprietary internal structure adds < 1% to weight of beds
Four-Ton Mine Locomotive

HB/FC Powerplant
- Power: 14 KW (gross)
- Current: 135 A
- Voltage: 104 V
- Weight: <550 kg
- Volume: <650 L
- Energy: 48 KWh
- Operating time: 8 h
- Recharge time: ~½ h

Performance Capability Favors the Hydride Bed/ Fuelcell Powerplant!

- Bed Weight ~ 350 kg
- Hydride: GfE C15 AB₂ (216 kg alloy @ 1.4 wt.%)
- Capacity = 3 kg H₂
  - 0.86 wt.%
  - 17 g/L H₂
- Delivery Rate_{max} ~ 170 slm
  - 0.25 g H₂/s
- Refueling time ~ 1 h
Underground Field Tests
Placer Dome Gold Mine, Balmertown, Ontario

- Two week test period
- Locomotive put on production level 27 – 4,000 feet down
- 760 tons of ore and rock moved
- 30 hours actual operating time
- 67,000 litres (~6 kg) of hydrogen consumed
- No failures or downtime encountered
- Metal-hydride bed transported to surface for refueling
- Capable of longer operational shift than battery version
Two removable MH modules stored total of 13.6 kg H₂ (External recharging)

- Ergenics/Hera USA developed & built
- Operating Pressure < 7 bar
- Refill times < 10-15 minutes

Plan to complete integration, test, & mine demos in FY-07

[Status is unknown]
German Navy Class 212 Submarine

- Hybrid Diesel/Lead Acid + Air Independent Fuel Cell Propulsion System
- FC delivers 300 kW for silent slow cruising up to 18 knots
- Metal hydride hydrogen storage (GfE TiMnₓ alloy stores H₂ @ ~2 wt.%) & liquid oxygen
- H₂ desorbing hydride tanks consumes ~30% waste heat from FC
- Designed 1992, four ordered 1994, first completed 2003
- Nearly 20 FC powered submarines sold on international market.
Hydride/Hydrogen Compressors

Ergenics, Inc.
Solid State Hydrogen Solutions

Six-stage (85°C H₂O)

\[ P_i = 1 \text{ bar (0.1 MPa)} \]
\[ P_f = 210 \text{ bar (21 MPa)} \]

Single Stage (Electric)

\[ P_i = 17 \text{ bar (1.7 MPa)} \]
\[ P_f = 410 \text{ bar (41 MPa)} \]
The metal hydride compressor uses thermal rather than electrical energy

- Multi-stage metal hydride hydrogen compressor creates work (pressurized gas) from heat.
- Ergenics engineers the composition of hydride alloys to operate at different pressures.
- Staging progressively higher pressure alloys lets the hydride compressor achieve very high pressures, using only the energy in hot water or hot air.

**Step 1:** Low pressure hydrogen is absorbed by an alloy at ambient temperature.

**Step 2:** Hot fluid heats the alloy causing the hydrogen to be released with an exponential increase in pressure.
Newly designed hydride heat exchangers have been fabricated
- 1/16" diameter tubes in a spiral geometry

Ring Manifolds are the modular building blocks for efficient, cost-effective design.

They are stacked together to form very high surface area heat exchangers.

Heat exchangers are internally insulated to reduce sensible heat loss.

Each heat exchanger contains 3 stages to compress hydrogen from 0.5 bara to 100 bara.
Cryogenic Applications of Metal Hydrides
(BETSCE – JPL System flew in 1996)

BETSCE Sorption Cooler (flown on Space Shuttle STS-77 May, 1996) produced solid H$_2$ at T = 11 K

LaNi$_{4.8}$Sn$_{0.2}$ and ZrNi metal hydride beds absorbed, stored, and compressed H$_2$ to 100 atm pressure for a J-T cryogenic refrigerator to make liquid then solid hydrogen.
Planck Mission

• Planck is the third Medium-Sized Mission (M3) of ESA's Horizon 2000 Scientific Programme. It is designed to measure the anisotropies of the Cosmic Microwave Background (CMB)

• Two instruments
  – HFI (100 GHz to 857 GHz)
  – LFI (30 - 70 GHz)

• Cryogenic Cooling chain
  – HFI (0.1 K)
    • 0.1 K Open cycle dilution cooler
    • 4 K Mechanical Joule-Thomson
    • 20 K Sorption Joule-Thomson
  – LFI (Array of tuned radio receivers @ 20 K)
    • 20 K Sorption Joule-Thomson
Planck Spacecraft to Launch in 2009

Planck will be launched in 2009 by an Ariane-5 launcher together with another ESA space observatory, the Far-infrared and Submillimetre Telescope (IRIST). The two satellites will separate shortly after launch and proceed to different orbits. They will be operated independently.

About four months after launch Planck will reach its final destination: a so-called 'Lissajous orbit' around a virtual point in space known as the 2nd Lagrangian point of the Sun-Earth-Moon system. The L2 point is located about 1.5 million kilometres away from the Earth - four times the distance to the Moon. From this position Planck will be able to elude the emission from the Earth, the Moon and the Sun, which would otherwise confuse the signal from the cosmic background.

Schematic of Planck Spacecraft

- **Dimensions:** ~ 4 m by 4.5 m
- **Mass:** ~1500 kg
- **Mission Operating Life:** >21 months
- **Power Available:** ~1 kW
Continuous Hydrogen Sorption Cryocoolers

A Closed-Cycle Joule-Thomson (J-T) Device Producing Liquid H\textsubscript{2} @ T ~ 20 K

**Example:** Planck Sorption Cooler (PSC) to launch in 2008

- Performance of PSC Compressor Element Hydride Beds
  - Desorb: ~50 atm @ 6.5 mg/s (4.3 slpm)
  - Absorb: < 0.6 atm @ 2.2 mg/s (1.4 slpm)
The PSC GGHS for Compressor Beds

- The Gas-Gap Heat Switch (GGHS) allows variable thermal isolation of the inner $\text{LaNi}_{4.78}\text{Sn}_{0.22}H_x$ sorbent bed.
- The PLANCK GGHS design utilizes a small bed of $\text{ZrNiH}_x$ hydride in an auxiliary Gas-Gap Actuator (GGA).

Hydrogen has largest Heat Conductivity ($\lambda$)

<table>
<thead>
<tr>
<th>Gas</th>
<th>Continuum $\lambda_0$ [10$^4$ W/cm-K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>17.3</td>
</tr>
<tr>
<td>Helium</td>
<td>14.4</td>
</tr>
<tr>
<td>Air</td>
<td>2.4</td>
</tr>
<tr>
<td>Argon</td>
<td>1.6</td>
</tr>
</tbody>
</table>

GGHS lets the PSC-CE meet its performance requirements with only ~22% of power needed compared to mounting sorbent bed directly to radiators – **without GGHS this cryocooler cannot operate** on available power from Planck spacecraft!
Both Flight PSC units on mounting panels for integration onto spacecraft @ Alcatel (France)
Summary and Conclusions

• Metal Hydride (MH) storage beds have been developed for various niche applications including prototype passenger vehicles powered by ICE and PEMFC.

• All designs are compromises between conflicting properties and performance requirements:
  ➢ Gas containment pressure vessels trade-off size, weight, ease of fabrication, etc.
  ➢ Thermal management issues of hydride reactions usually dominate designs and system performance levels.
  ➢ Practical MH tanks tend to weigh at least 2-3+ times of hydride material and to have bed volumes that are least twice the bulk material density.
  ➢ Ideally, MH beds are durable and robust but very few long term cycling assessments of “full size” operating systems especially on recovery of degraded or compromised hydrides.
  ➢ Rapid (< 5 min) on-board refueling of 5+ Kg hydrogen will release >0.5-1.0 MW heat for hydrides with heat of formation > 30 kJ/mol and probably cannot be achieved with current configurations and materials.

• Current complex hydrides bring additional challenges with lower thermal conductivities, slow reaction kinetics, powder densities, safety issues due to high chemical reactivities.
Acknowledgments

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• Ned Stetson
• Mauro Prina
• Dave Pearson
• Dave DaCosta

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