Cold/Cryogenic Composites for Hydrogen Storage Applications in FCEVs

Dallas, TX

October 29, 2015
## DOE H₂ Storage Program Contacts

<table>
<thead>
<tr>
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<th>Title</th>
<th>Phone Number</th>
<th>Email</th>
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</thead>
<tbody>
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</tbody>
</table>

http://energy.gov/eere/fuelcells/fuel-cell-technologies-office
To enable and accelerate the successful commercialization of hydrogen fuel cell technologies through development of advanced hydrogen storage technologies able to cost-effectively meet application performance requirements.

**Light-duty fuel cell electric vehicles**
- Primary focus
- Driving range of at least 300 miles without compromising passenger and cargo space or vehicle performance
- Cost & performance targets established in consultation with automotive OEMs

**High-value, non-automotive applications**
- Secondary Focus
- Support advancement of FCEVs:
  - Infrastructure / supply chain development (e.g., material handling equipment)
  - Leverage prior DOE-supported R&D
- Targets for MHE and portable power established with stakeholder input

Advanced Hydrogen Storage technologies are critical for successful commercialization of hydrogen fuel cell technologies
Dual strategy to address near and long-term needs

**Near-term** – address cost and performance of 70 MPa H₂ storage;

**Long-term** – develop advanced technologies with potential to meet all targets
Challenge of H₂ Storage – Energy Density

Physical Storage

1 bar
- normal
- 0.1 g/L

150 bar
- lab cylinders
- 12 g/L

350 bar
- Gen 1 vehicles
- 24 g/L

700 bar
- Gen 2 vehicles
- 40 g/L

liquid H₂
- 71 g H₂/L
- @ 20 K

Materials Storage

interstitial hydrides
- ~100-150 g H₂/L

complex hydrides
- ~70-150 g H₂/L

chemical storage
- ~70-150 g H₂/L

sorbents
- ≤ 70 g H₂/L

water
- 111 g H₂/L

Efficiently storing adequate amounts of hydrogen in an acceptably small volume
Comparison of H₂ with other fuels

Hydrogen has high energy by mass but low energy by volume
Types of Pressure Vessels

Type I
Type II
Type III
Type IV
Type V

Aluminum/Steel
Polymer
Composite

Source: Lightweighting matters in energy storage (Part 1) (2014)

Type III and type IV vessels face different challenges for cryogenic applications
While performance meets many 2020 targets, certain targets still remain a challenge:

- System cost
- Volumetric Density
- Gravimetric Density
- Fuel Cost
- WtPP Efficiency
Compressed H₂ Critical Storage Costs

Cost breakdown for 700-bar H₂ Storage Tank*

Total System Cost, $/kWh

Systems per Year

2020
Ultimate

Composite Materials & Processing 67%
BOP & Assembly 30%
Other Manufacturing Processes 3%

Total System Cost, $/kWh

10,000 30,000 80,000 100,000 500,000

*Single tank holding 5.6kg H₂ total, cost in 2007$, 500,000 systems/yr – 2013 baseline projections

Composite materials & processing is the largest single cost contributor
Recent progress in reducing cost of H₂ Storage

2$/kWh reduction in cost projected for high manufactured volume (500k/yr)
Type IV 700 bar H₂ storage systems, compared to 2013 baseline cost
Current Program Activities

**Low-cost CF precursors [ORNL/VT]**
- Approach: Melt-spinning process
- Goal: ~30% lower cost than conventional PAN precursor fibers
- Based on prior BASF technology

PAN precursor filaments produced through melt-spinning process

**Low-cost alternative fibers to CF [PPG/Hexagon Lincoln/PNNL]**
- Approach: Ultra-high strength fiber glass
- Goal: New fiber glass with tensile strength exceeding Toray T700 CF at ~50% of cost
- Novel fiber glass manufacturing process
- Characterizing stress rupture properties to determine required safety factor

**Tensile strength analyses**

<table>
<thead>
<tr>
<th>Fiber Glass Chemistry</th>
<th>Melting: $T_1$</th>
<th>$T_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>UD Panel Tensile Strength (MPa)</td>
<td>I</td>
<td>IIa</td>
</tr>
<tr>
<td>Binder: I</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Binder: IIa</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Binder: IIb</td>
<td></td>
<td></td>
</tr>
<tr>
<td>60% FVF</td>
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Reducing cost of composites for use in $H_2$ storage vessels
Reducing cost of \( \text{H}_2 \) storage vessels through alternative manufacturing

**Alternative resin and manufacturing [Materia/MSU/Spencer Composites]**

- **Approach:** low-viscosity, high-toughness resin with VARTM manufacturing process
- **Goal:** 35% reduction in composite costs
- **Potential:** for optimized winding patterns with fewer defects

**Thick panel produced through infusion process with less than 1% voids by volume**

**Optimized cost and performance of COPVs [CTD/ORNL/Adherent Tech.]**

- **Approach:** Graded construction utilizing thick wall effect
- **Goal:** demonstrate potential for 10-25% lower cost through graded-construction approach
- **Identified:** Panex 35™ as potential candidate fiber, evaluating fibers from ORNL

**Potential cost reduction of 1-30%**

<table>
<thead>
<tr>
<th>50% T700 Toray/50% Low Cost Fiber</th>
<th>Low Cost Fiber ($/lb)</th>
<th>$7.00</th>
<th>$10.00</th>
<th>$12.00</th>
</tr>
</thead>
<tbody>
<tr>
<td>T700</td>
<td>$13.00</td>
<td>20.4%</td>
<td>9.1%</td>
<td>1.6%</td>
</tr>
<tr>
<td>Toray</td>
<td>$15.00</td>
<td>24.3%</td>
<td>14.5%</td>
<td>7.9%</td>
</tr>
<tr>
<td>($/lb)</td>
<td>$20.00</td>
<td>30.6%</td>
<td>23.2%</td>
<td>18.3%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>60% T700 Toray/40% Low Cost Fiber</th>
<th>Low Cost Fiber ($/lb)</th>
<th>$7.00</th>
<th>$10.00</th>
<th>$12.00</th>
</tr>
</thead>
<tbody>
<tr>
<td>T700</td>
<td>$13.00</td>
<td>15.9%</td>
<td>6.9%</td>
<td>0.8%</td>
</tr>
<tr>
<td>Toray</td>
<td>$15.00</td>
<td>19.1%</td>
<td>11.2%</td>
<td>6.0%</td>
</tr>
<tr>
<td>($/lb)</td>
<td>$20.00</td>
<td>24.3%</td>
<td>18.3%</td>
<td>14.4%</td>
</tr>
</tbody>
</table>
Current Program Activities

**Alternative materials for BOP [SNL/Hy-Performance Materials]**
- **Approach:** Screening based on fatigue stress and computational material design
- **Goal:** Reductions in BOP of up to 50% in weight and 35% in cost
- **Established baseline** for strain-hardened type 316L SS

**Fatigue life comparisons:** ambient and low-T, as-annealed, pre-charged and in H₂

**New Project: Conformable 700 bar H₂ Storage Systems [CTE/HECR/UT]**
- **Approach:** Development of an over-braided, coiled pressure vessel for 700 bar H₂ storage
- **Goal:** Surpass DOE system targets for specific energy (3.7 kWh/kg) and cost (< $10/kWh)
- **Using proven technology** for self-contained breathing apparatuses as design basis
- **Achieves efficient** onboard vehicle packaging through use of a shaped corrugated core over-braided with aramid fiber for strength
Why cryogenic H₂ storage?

Higher H₂ densities are achievable through use of lower temperatures
Cold-compressed H₂ storage
[PNNL/Ford/Hexagon Lincoln/AOC/Toray]
• Approach: Synergistically consider pressure vessel and operating conditions
• Goal: 30% reduction in system cost over 2013 baseline cost for 700 bar system
• Targeting 500 bar and 200 K operation
• Identified alternative, lower cost resin – being considered for commercial use by a PV manufacturer

~50% reduction in tank mass possible with 500 bar and 200 K operation

<table>
<thead>
<tr>
<th>Current H₂ Tank</th>
<th>Enhanced H₂ Tank</th>
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<tbody>
<tr>
<td>Operating Conditions</td>
<td>700 bar at 15° C</td>
</tr>
<tr>
<td>H₂ Density</td>
<td>40 g/l</td>
</tr>
<tr>
<td>Tank Mass</td>
<td>93.6 kg</td>
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Cryo-compressed H₂ storage
[LLNL/BMW/Linde/Spencer]
• Approach: Develop a thin-lined, pressure capable, cryogenic vessel
• Goal: Demonstrate 3 kWh/kg and 1.7 kWh/L system capacities at 700 bar
• Design incorporates a type III pressure vessel within a MLVSI jacket
• Installed high-efficiency, high-throughput liquid cryo-pump

Cryo-compressed dispensing station at LLNL
In July of 2015, BMW demonstrated 2 prototype fuel cell electric vehicles with cryo-compressed onboard hydrogen storage: an i8 and a 5 Series GT


Cryo-compressed $H_2$ storage can provide significantly longer driving range using the same onboard space for fuel storage
BMW – pursuing cryo-compressed H$_2$ storage

HYDROGEN FUEL CELL-BASED ELECTRIC MOBILITY. BMW CRYOGENIC PRESSURE VESSEL TECHNOLOGY.

BMW DEVELOPED CRYOGENIC PRESSURE VESSEL: CRYO-COMPRESSED HYDROGEN STORAGE, LONGER RANGE, TAKES UP NO MORE SPACE.

<table>
<thead>
<tr>
<th>DOUBLE-WALLED INSULATED PRESSURE VESSEL FOR CRYOGENIC GAS STORAGE</th>
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</thead>
<tbody>
<tr>
<td>Maximum usable storage capacity</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Operating pressure</td>
</tr>
<tr>
<td>Vent pressure</td>
</tr>
<tr>
<td>System weight (incl. H2)</td>
</tr>
<tr>
<td>Refuelling pressure</td>
</tr>
<tr>
<td>Refuelling time</td>
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</table>

INNOVATIONS

+ Active tank pressure control with in-tank heat exchanger
+ Integrated in vehicle body with load-bearing structure
+ Additional fuel cell cooling
+ Cold and ambient refuelling possible (300 – 320 bar)

Comparison of H₂ Storage Systems by Volume (BMW)

Significantly improved energy density for cryo-compressed H₂, especially for larger systems

http://www.stfc.ac.uk/stfc/cache/file/F45B669C-73BF-495B-B843DCDF50E8B5A5.pdf
Comparison of H₂ Storage Systems by Weight (BMW)

Significantly improved specific energy for cryo-compressed H₂ only for larger systems

http://www.stfc.ac.uk/stfc/cache/file/F45B669C-73BF-495B-B843DCDF50E8B5A5.pdf
# Cryo-compressed H₂ System Safety Evaluation

<table>
<thead>
<tr>
<th>Test</th>
<th>Explanation</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vehicle crash</td>
<td>No additional implications compared to vehicle crash with CGH₂ storage expected. Tests will be done during vehicle qualification in 2012/2013.</td>
<td>🟢</td>
</tr>
<tr>
<td>Burst energy</td>
<td>Adiabatic expansion energy in case of sudden vessel failure is mitigated in cryogenic gas storage compared to warm gas storage: Simulation: @ T &lt; 100 K liquefaction during expansion supposable Validation: burst test under warm &amp; cryogenic conditions show significant differences</td>
<td>🟢</td>
</tr>
<tr>
<td>Sudden Vacuum Loss</td>
<td>Validation of safe H₂-discharge via pressure relief devices (and optional vacuum-casing burst disc) in case of Air- or H₂-sided vacuum loss. Imagination of air-side vacuum-loss is mitigated compared to LH₂.</td>
<td>🟢</td>
</tr>
<tr>
<td>Impact damage, penetration, chem. exposure</td>
<td>Vacuum enclosure lowers risk of pressure vessel damage through external impacts. Tests will be done during vehicle qualification in 2012/2013.</td>
<td>🟢</td>
</tr>
<tr>
<td>Permeation and Leakage</td>
<td>Type III pressure vessel with welded boss, joints &amp; vacuum casing eliminates issue of permeation &amp; mitigates risk of leakage compared to CGH₂ storage. Leakage rate &lt;&lt; 3g/day.</td>
<td>🟢</td>
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</tbody>
</table>

http://www.stfc.ac.uk/stfc/cache/file/F45B669C-73BF-495B-B843DCDF50E8B5A5.pdf

*Initial testing has shown systems to be relatively safe*
Cryo-compressed H₂ station open in Munich

Press Release

New hydrogen fuelling station with technology from Linde opens in Munich

Munich, 16 July 2015 – Today, the TOTAL Multi-Energy fuelling station in Detmoldstrasse, Munich, opened its doors to drivers of hydrogen-powered fuel-cell cars. Equipped with innovative refuelling technology from Linde, the station is now home to the only public hydrogen fuelling service in the Bavarian state capital.


Cryo-compressed H₂ stations open to the public in Munich, Germany
However, R&D still needed

• Dormancy – time until system has to vent due to pressure build up from heat leakage and warming of stored hydrogen
  – Insulation efficiency – high R factors required
  – Insulation degradation – stability of vacuum systems
    • Outgassing of volatile components from composites
    • Hydrogen permeation

• Durability of composites in high pressure and thermal cycle environments
  – Match of CTE between composites and liners
  – Cycling between brittle and elastic phases
  – Effects of micro-cracking

• Certification protocols
  – Standard duty cycles – how to define
  – Accelerated test procedures
DOE has issued an RFI on Advanced Thermal Insulation and Composite Material Compatibility:

- Aim is to obtain feedback and opinions from industry, academia, research laboratories, government agencies, and other stakeholders on advanced thermal insulation for sub-ambient temperature alternative fuel storage systems.
- This RFI requests information regarding specifically:
  - How to maintain vacuum stability of systems
  - Use of advanced composites within the systems
  - Accelerated test methods to determine performance and applicability of materials and systems for long-term cold and cryogenic based alternative fuel storage systems for onboard vehicle applications
- Alternative fuels could include hydrogen or natural gas stored on board the vehicle at sub-ambient temperatures as a compressed gas, liquefied gas, or adsorbed onto a porous material.

RFI Link under DE-FOA-0001420: https://eere-exchange.energy.gov/
Email questions about the RFI to H2Storage@ee.doe.gov with "question" in the subject line
Objectives:

- Increase understanding on the technical challenges that are unique to composite materials and processing at cold and cryogenic temperatures for automotive applications. Including:
  - Material compatibility
  - Failure mechanisms
  - Durability and Fatigue
  - Material Characterization
  - Modeling and analysis

- Inform funding and policy decision making to advance physical hydrogen storage research, development and deployment efforts

**Frank, open and honest discussion and recommendations based on your expertise are what we are looking for!**
<table>
<thead>
<tr>
<th>Time</th>
<th>Session</th>
<th>Details</th>
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<tbody>
<tr>
<td>8:30</td>
<td>Panel Presentations and</td>
<td>Ford Motor Company – Mike Veenstra</td>
</tr>
<tr>
<td></td>
<td>Discussions: Moderator – John</td>
<td>Pacific Northwest National Laboratory – David Gotthold</td>
</tr>
<tr>
<td></td>
<td>Gangloff (DOE - FCTO)</td>
<td>Lawrence Livermore National Laboratory – Gene Berry</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Composite Technology Development, Inc. – Pat Hipp</td>
</tr>
<tr>
<td>10:00</td>
<td>Break</td>
<td></td>
</tr>
<tr>
<td>10:15</td>
<td>Breakout Session I – Mechanics</td>
<td>Identifying constituent materials (i.e. fibers, resins, additives) that are recommended for cold / cryogenic temperatures with pressure cycling.</td>
</tr>
<tr>
<td></td>
<td>and Materials</td>
<td>Microstructural failure mechanisms at cold / cryogenic temperatures.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Vacuum exposure on composite materials at cold / cryogenic temperatures.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Durability and fatigue due to Coefficient of Thermal Expansion issues.</td>
</tr>
<tr>
<td>11:15</td>
<td>Break</td>
<td></td>
</tr>
<tr>
<td>11:30</td>
<td>Breakout Session II – Processing</td>
<td>Composite manufacturing processes suitable for cold / cryogenic applications</td>
</tr>
<tr>
<td></td>
<td>Characterization, and Analysis</td>
<td>Material characterization methods for part verification and validation.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Safety codes and standards status for cold / cryogenic temperature composites</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Modeling and analysis tools for cold / cryogenic temperature composites.</td>
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<tr>
<td>12:30</td>
<td>Adjourn</td>
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</tbody>
</table>
Acknowledgements

For panel session participation:
Michael Veenstra (Ford)
David Gotthold (PNNL)
Gene Berry (LLNL)
Pat Hipp (CTD)

For workshop organization and facilitation:
John Gangloff (DOE/ORISE)
David Gotthold (PNNL)

For discussions and information:
Jesse Schneider (BMW)

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Thank you

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