Thermomechanical Cycling of Thin Liner High Fiber Fraction Cryogenic Pressure Vessels Rapidly Refueled by LH$_2$ pump to 700 bar

Salvador Aceves,
Guillaume Petitpas, Vernon Switzer
Lawrence Livermore National Laboratory
June 17, 2014

This presentation does not contain any proprietary, confidential, or otherwise restricted information
Overview

Timeline

• Start date: January 2014
• End date: December 2016

Budget

• FY13 DOE Funding: 0
• Planned FY14 DOE Funding: $1.35M (DOE)
• Total project Value: $5.5M
• DOE Share: $4M
• Cost Share: $1.5M

• Funded Jointly by Storage, Delivery and TechVal

Barriers

• A. System weight and volume
• D. Durability/Operability
• N. Hydrogen venting

Partners

• Spencer Composites
  custom cryogenic pressure vessel
• Linde 875 bar LH₂ pump supply, operation & maintenance
• BMW thermal insulation, performance requirements, automotive perspective

DOE AMR meeting June 17, 2014
Project history: Increasingly compact \( \text{H}_2 \) storage

1997 | 1999 | 2001 | 2003 | 2005 | 2007 | 2009 | 2011 | 2013

- LH\(_2\) proof of concept
- ISO certification (gunfire, bonfire, drop)
- \( \text{LN}_2 \) cycle test
- Thermodynamic simulation
- Zero boil-off simulation
- Onboard integration
- LH\(_2\) refueling
- Burst simulations
- 2 bar LH\(_2\) refueling
- Full scale para/ortho-H\(_2\) measurement
- 350 bar 30 day dormancy test
- Subscale radiation

**System density, \( \text{gH}_2/\text{L}_{\text{sys}} \)**

- 10.4 kg mobile LH\(_2\), 15.5 L
- 45 kg LH\(_2\), 225 L (steel jacket)
- 7 m\(^3\) LH\(_2\), 1400 kg empty
- 88 kWh (<8000)
- 275 bar MWP
- 350 bar MWP

6 min 8 kgH\(_2\) 350 bar
Single flow refuel

<table>
<thead>
<tr>
<th>Year</th>
<th>Gen 3</th>
<th>Gen 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>2003</td>
<td>300 L, 350 bar</td>
<td>225 L, 280 bar</td>
</tr>
<tr>
<td>2005</td>
<td><strong>350 bar 30 day dormancy test</strong></td>
<td></td>
</tr>
<tr>
<td>2007</td>
<td>Burst simulations</td>
<td></td>
</tr>
<tr>
<td>2009</td>
<td><strong>2 bar LH(_2) refueling</strong></td>
<td></td>
</tr>
<tr>
<td>2011</td>
<td><strong>Heat transfer studies w/ ( \text{LN}_2 )</strong></td>
<td></td>
</tr>
</tbody>
</table>

DOE AMR meeting June 17, 2014
Relevance: Chief objective of highest H₂ & system density with preferred diameter, capacity, cycle life & safety will simultaneously maximize progress toward other targets

1. Demonstrate 700 bar fueling with LH₂ pump
   • Measure final density, time, electricity
   • Use commercial 163 L 700 bar vessel

2. Develop 60 L H₂ 700 bar prototypes with thin liner, high fiber fraction, small diameter
   • Custom design & fabrication for cryogenics
   • Demonstrate 1600 bar strength with LN₂

3. Cycle cryogenic vessels & LH₂ pump
   • Long duration and accelerated testing
   • Multiple vessels, 1250-1750 fuelings (each)
   • Followed by 1600 bar cryogenic H₂ testing

4. Demonstrate compact, lightweight system
   • Suspend best vessel in aluminum jacket
   • Characterize dormancy, rapid LH₂ refueling

Project goal: 60 L cryogenic H₂ storage system with 50gH₂/Lₜₚ & 9 wt% H₂ & 1500 cycles

<table>
<thead>
<tr>
<th>Storage Parameter</th>
<th>2017</th>
<th>Ultimate</th>
</tr>
</thead>
<tbody>
<tr>
<td>System Gravimetric Capacity, wt%</td>
<td>5.5</td>
<td>7.5</td>
</tr>
<tr>
<td>System Volumetric Capacity, g/L</td>
<td>40</td>
<td>70</td>
</tr>
<tr>
<td>System Cost, $/kWh</td>
<td>12</td>
<td>8</td>
</tr>
<tr>
<td>Operating ambient temperature, C</td>
<td>-40/60</td>
<td>-40/60</td>
</tr>
<tr>
<td>Min delivery temperature, C</td>
<td>-40</td>
<td>-40</td>
</tr>
<tr>
<td>Max delivery temperature, C</td>
<td>85</td>
<td>85</td>
</tr>
<tr>
<td>Operational cycle life</td>
<td>1500</td>
<td>1500</td>
</tr>
<tr>
<td>Min delivery pressure, bar</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Max delivery pressure, bar</td>
<td>12</td>
<td>12</td>
</tr>
<tr>
<td>Onboard efficiency, %</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>WTPP efficiency, %</td>
<td>60</td>
<td>60</td>
</tr>
<tr>
<td>System fill time (5 kg), min</td>
<td>3.3</td>
<td>2.5</td>
</tr>
<tr>
<td>Minimum full flow rate, (g/s)/kW</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>Start time to full flow (20 C), s</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Start time to full flow (-20 C), s</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>Transient response, s</td>
<td>0.75</td>
<td>0.75</td>
</tr>
<tr>
<td>Fuel quality %H₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Permeation &amp; leakage</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Toxicity</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Safety</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Loss of usable H₂, (g/h)/kg H₂</td>
<td>0.05</td>
<td>0.05</td>
</tr>
</tbody>
</table>

Green : measured
Yellow : potential/projected
Red : challenging
System densities of 40-52 gH₂/L_{sys} appear feasible for H₂ fill densities of 63-78 g/L.

Relevance: H₂ system density depends on vehicle usage, driver criteria for refueling, and auxiliary vacuum volume.

2017 DOE Target:
- Optimistic (89 L)
- Conservative (96 L)

System densities of 40-52 gH₂/L_{sys} appear feasible for H₂ fill densities of 63-78 g/L.
Approach (FY14): Extend LH$_2$ refueling to 700 bar
Measure H$_2$ density, refuel time, pump power for 163 L vessel

Up to 80g/L H$_2$ density possible at 700 bar
Approach (FY14) : Design, tooling, fabrication & test for small diameter, thin liner 60 L cryogenic prototype vessel

**LN₂ Tensile Testing**: Guide liner material choice and composite vessel fabrication to insure against failure in cryogenic tension

**Ambient Ring Rupture**: 18" apparatus testing compression due to autofrettage, composite strength in strain-scaled high fiber fraction wall, and cusp buckling limit

Ultrathin liner can resist buckling due to constraint from composite wall

Fabricate & Strength Test 700 bar 80% vol. efficient vessel: qualified by a 1600 bar cryogenic strength LN₂ test

A successful 1600 bar LN₂ strength test of the 60 L, thin liner, high fiber fraction prototype vessel is the FY14 Go/No-Go
**Approach:** 700 bar H$_2$ thermomechanical cycling of four 60 L prototypes 1250+ times to demonstrate final vessel durability

<table>
<thead>
<tr>
<th>Vessel #</th>
<th>Liner material &amp; thickness</th>
<th>Fiber Fraction</th>
<th>Full Cryogenic tension excursions (60-120 K)</th>
<th>Empty Cryogenic compression excursions (60-120 K)</th>
<th>Full Warm tension excursions</th>
<th>Empty Warm compression excursions (240 K)</th>
<th>Empty Warm compression excursions (300 K)</th>
<th>Volume [L]</th>
<th>LH$_2$ Pump Throughput [tonnes H$_2$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Aluminum (~10 mm)</td>
<td>60%</td>
<td>625</td>
<td>500</td>
<td>&lt;5</td>
<td>0</td>
<td>125</td>
<td>163</td>
<td>6</td>
</tr>
<tr>
<td>1</td>
<td>A (&lt;1.5 mm)</td>
<td>70%</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>0</td>
<td>Autofrettage</td>
<td>1</td>
<td>60</td>
<td>N/A</td>
</tr>
<tr>
<td>2</td>
<td>A (&lt;1.5 mm)</td>
<td>70%</td>
<td>1250</td>
<td>1250</td>
<td>500</td>
<td>250</td>
<td>1</td>
<td>60</td>
<td>5 Accelerated Testing</td>
</tr>
<tr>
<td>3</td>
<td>B (&lt;1.5 mm)</td>
<td>70%</td>
<td>1250</td>
<td>1250</td>
<td>500</td>
<td>250</td>
<td>1</td>
<td>60</td>
<td>5 Long duration Testing</td>
</tr>
<tr>
<td>4</td>
<td>A or B (&lt;1.5 mm)</td>
<td>70%</td>
<td>1250</td>
<td>1000</td>
<td>0</td>
<td>125</td>
<td>125</td>
<td>60</td>
<td>4</td>
</tr>
<tr>
<td>5</td>
<td>A or B (&lt;1.5 mm)</td>
<td>80%</td>
<td>1250</td>
<td>1000</td>
<td>0</td>
<td>125</td>
<td>125</td>
<td>60</td>
<td>6</td>
</tr>
<tr>
<td>6</td>
<td>A or B (&lt;1.5 mm)</td>
<td>75%</td>
<td>20</td>
<td>20</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>60</td>
<td>&lt;1</td>
</tr>
</tbody>
</table>

Prototypes 2-5 will experience minimum 1250 peak tension (cold, full) and 250 peak compression (hot, empty) excursions. Duration & temperature differ.
Approach: Long duration & accelerated thermomechanical cycling of 60 L prototypes equivalent to 1250-1750 refuels

**Long Duration Cycling**

- 40 kW H₂ internal warming
- 40 kg LH₂ loop, 5/day <20% @ 700 bar
- 16 (P,T) points including warm & empty
- 50 days/10 tonnes LH₂ /3 months

**Accelerated Cycling**

- 500 W external warming
- 65 kg LH₂ daily loop, 80+% @ 700 bar
- 24 (P,T) points including warm & empty
- 125 days/8 tonnes LH₂ /6 months

Long duration testing uses vacuum degradation. Accelerated testing uses 875 bar H₂ heat exchanger. Simultaneous cycling of two 60 L prototypes
Accomplishment: Construction approval for LH$_2$ pump facility for simultaneous, remote cycling of uncertified 60 L vessels

- 875 bar H$_2$ Heat Exchanger (40 kW electric)
- Two ASME 50 bar 2m$^3$ Containment Vessels
- 900 ft$^2$ concrete test pad
- 875 bar H$_2$ line (Vacuum Jacketed)
- 875 bar LH$_2$ pump (75 kW$_{ave}$, 1.5kg H$_2$/min)
- 3000 gal Dewar (800 kg LH$_2$)
- Remote LH$_2$ pump operation, 2.5 kg/min vent stack, 25' pad exclusion zone
- Class 1 Division 1 electrical, air driven valves, 2 m$^3$ containment vessels

Existing
Planned construction

Compressed Air, Data
Transformer (500 kVA)
Compressor (Air)

NFP55 setback distances
Accomplishment: Preliminary hydrodynamic simulations for 1600 bar cryogenic H$_2$ test & 700 bar long duration cycling

1600 bar cryogenic expansion from 120 K (5.5 kg) has single, slower, impulse with 90 bar pressure peak comparable to 700 bar cycle test at 180 K (3.3 kg)
Collaborations with Industry Leaders

• **Spencer Composites (Sacramento, CA):** Long expertise in custom composite pressure vessel development. Collaborated previously with LLNL on cryogenic vessels for H$_2$ delivery.

• **Linde:** World class cryogenics experience. Manufactures maximum efficiency LH$_2$ pump. Delivered first commercial LH$_2$ pump to BMW in 2009 (300 bar). Very cooperative, sharing detailed information throughout pump development, construction, and installation.

• **BMW:** Long standing collaboration with LLNL through cryogenic pressure vessel CRADA. Contributing automotive perspective, technical information, and expertise. Advancing cryogenic pressure vessel technology & demonstration vehicles.
Challenges and barriers: Demonstrating technical performance elements to achieve onboard storage targets

- **Demonstrate high refuel density & durability of LH$_2$ pump:** Need 80+ gH$_2$/L cold refuel density and no degradation after pumping up to 24 tonnes LH$_2$ over ~ 2 years.

- **Demonstrate cryogenic strength and cyclability of thin-lined, high fiber fraction pressure vessels:** This is essential to meet very high system targets (50 gH$_2$/L, 9 wt % H$_2$, 1500 cycles).

- **Demonstrate compact, lightweight system with adequate dormancy:** thin (<1cm) vacuum space with volumetrically efficient vacuum jacket necessary for small diameter onboard storage.
Planned FY14/F15 work

Future work includes:
- construction of the testing facility
- vacuum insulation of a conventional 700 bar (163 L) pressure vessel using more compact and lightweight designs, for baseline testing
- Development of thin lined high fraction 60 L 700 bar pressure vessel

First Go/No Go (successful cryogenic 1600 bar strength test of prototype vessel) will enable second phase of the project: thermomechanical testing

<table>
<thead>
<tr>
<th>Milestones</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q3/FY14</td>
<td>Complete construction of test facility concrete pad</td>
</tr>
<tr>
<td>Q4/FY14</td>
<td>Deliver custom 60 L 700 bar pressure vessel with 80% volumetric efficiency</td>
</tr>
<tr>
<td>Q1/FY15</td>
<td>Demonstrate 1600 bar inert cryogenic burst strength of 60 L custom composite vessel</td>
</tr>
<tr>
<td>1st Go/No-Go</td>
<td></td>
</tr>
<tr>
<td>Q2/FY15</td>
<td>Determine pump performance at 700 bar using 163 L conventional vessel (40 gH₂/Lsys, 6 wt%H₂)</td>
</tr>
<tr>
<td>Q3/FY15</td>
<td>Complete 1500 accelerated thermomechanical cycles on two 60 L 700 bar, 80% volume efficient vessels</td>
</tr>
</tbody>
</table>
Planned work: 3 year project will demonstrate rapid refueling of 700 bar cryogenic H₂ vessels with high system density, small diameter (~35 cm), & cryogenic durability (1500 refuels)

Rapid pressurized LH₂ refuel from any condition
- 100 kg/hr, up to 875 bar
- Refueled H₂ density 63-80 g/L (up to 700 bar)
- Potential for low LH₂ evaporation (1-3%)

Volumetric efficiency at 60 L capacity
- Up to 4.8 kg H₂ peak H₂ storage
- Thin metallic liner (<2 mm)
- High fiber fraction (70+%)
- Thin vacuum gap (<1 cm)
- Final system demo: 50 +gH₂/Lsys, 9 wt%H₂
- Characterize heat transfer, vacuum, & dormancy

700 bar vessel durability and cryogenic cycling
- Initial pump performance measurement
  - Use 163 L vessel for baseline pump behavior (refuel time, fill density, electricity, evaporation)
- Cryogenically cycle up to five 60 L vessels
  - Spectrum of liner/composite combinations
  - Long duration vs. accelerated cycling
**Project Summary**

**Relevance**
Cryo-compressed storage has the potential to meet challenging DOE goals. Critical issues such as maximum system density, scalability, vessel and pump durability are being addressed.

**Approach**
Small diameter thin lined high fiber fraction 700 bar cryogenic pressure vessels are being developed then tested for strength & durability using LH₂ pump.

**Accomplishments**
Project just started. Testing facility has been designed. First prototype vessel design and facility safety analysis are underway.

**Future work**
Fabrication then cryogenic strength test of first prototype vessel by the end of FY14. Construction of testing facility. Static test on the first year (Go/No Go) If successful, prototype vessels cycling will follow.
Responses to reviewers’ comments

The project too closely replicates the work of BMW: BMW is producing a commercial product that may succeed in the market due to longer driving range, improved safety, and rapid refueling. LLNL is researching (1) The thermodynamics and behavior of H₂ at superliquid (70+ g/L) densities, (2) The viability of improvements to high pressure (>350 bar) cryogenic H₂ storage, (3) Thermomechanical lifecycle & strength testing with cryogenic H₂, and (4) High pressure (875 bar) cryogenic refueling station performance and durability.

This project should add specific technology gaps and a cost model. Analysis of technology gaps and potential led to the proposed project. Argonne has conducted extensive cost modeling revealing that cryogenic pressurized storage has lowest cost of ownership. We have worked with Argonne to develop accurate cost models.

The project should add a variety of other FCEV manufacturers. Other OEMs have expressed interest in conducting experiments at LLNL and/or joining the project.
Responses to reviewers’ comments

The Linde LH$_2$ pump has the potential of 1–3% hydrogen boil-off loss and additional boil-off from the LH$_2$ storage tank. A 3% loss has a significant detrimental impact on WTW energy efficiency and cost: Pump evaporation does not result in Dewar boil-off. Pump extracts LH$_2$ from Dewar, and returns a fraction of evaporated LH$_2$ back into Dewar. Dewar typically depressurizes when running at these conditions. Boil-off from Dewar is due to environmental heat transfer or LH$_2$ transfer during Dewar fill. This approach to hydrogen refueling also results in a variable amount of hydrogen in the fuel tank at the end of refueling, depending on the temperature, pressure, and amount of hydrogen in the tank at the start of refueling. Vehicle owners may not accept this. H$_2$ density in cryogenic pressurized storage is self-regulated: Frequent drivers keep vessel cold and refuel to high density while infrequent drivers’ warm vessel reduces storage density. Self-regulated density minimizes H$_2$ venting for all users. Two cold refuels are sufficient to transition from minimum to maximum range during continuous driving.