Cryogenic Pressure Vessels for $\text{H}_2$ Vehicles Rapidly Refueled by LH$_2$ pump to 700 bar

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The Road Ahead

• Cryogenic H$_2$ Onboard Storage
  • Temperature as a Degree of Freedom in H$_2$ storage
  • LLNL Cryocompressed Project History
  • 350 Bar Test Vehicle Park & Drive Results

• Current Project
  • 700 bar prototype (cryogenic) vessels
  • Refueling with LH$_2$ Pump
  • Test Vessel Cycling Facility

• System Considerations
  • Vacuum Jacketing
  • Vacuum, Temperature, Heat Transfer
  • Material properties at low temperatures

LLNL 350 bar cryogenic pressure vessel stores 10 kg LH$_2$ onboard a 2005 Prius
Onboard $\text{H}_2$ storage approaches face thermodynamic challenges

Cryogenic Liquid $\text{H}_2$ (28 Kelvin, 6 bar)  
*evaporation* when parked 3-4 days

Compressed Gas (350-700 bar)  
$\text{H}_2$ volume, fast fill *heating*

**Adsorbed $\text{H}_2$:** parasitic volume, *exothermic* refueling & cryogenics

**Hydrides:** parasitic mass, refuel *speed/temperature*
Thermodynamic limits of LH$_2$ & ambient H$_2$ storage can be overcome with H$_2$ pressure vessels operable across broad range of temperatures

- **Maximum Density, Minimum Mass**
- **Extended Thermal Endurance**
- **Superior Refuel Thermodynamics**
- **Thermal Isolation**
- **Low Internal Energy**

![Graph showing cryogenic H$_2$ gas and thermodynamic limits](image)
Thermodynamics of high pressure cryogenic H₂ refuel/storage can provide powerful automotive/driver characteristics

- **Maximum Density, Minimum Mass**
- **Extended Thermal Endurance**
- **Superior Refuel Thermodynamics**
- **Thermal Isolation**
- **Low Internal Energy**

- **Minimum Size/Cost**
- **Fuel Economy, Parking Time**
- **Low Energy Rapid Refueling**
- **High on-road Safety Factor (5-10)**
- **Low Burst Energy (3-5x)**
LLNL has pioneered cryogenic H₂ gas with a comprehensive approach while improving storage density, dormancy, safety, cost, & refueling.

1997-2003
Dormancy simulation
Subscale vessel testing

2003-2010
Onboard Commercial vessels
350 bar, 10 kg LH₂

2010-2013
Heat transfer
350 bar refuel w/ LH₂ pump

- LH₂ proof of concept
- ISO certification (gunfire, bonfire, drop)
- Thermodynamic simulation
- LN₂ cycle test
- Onboard integration LH₂ refueling
- Burst simulations
- 2 bar LH₂ refueling
- Full scale para/ortho-H₂ measurement
- Heat transfer studies w/ LN₂
- Dormancy/drive analysis
- 300 L, 350 bar
- 225 L, 280 bar
- 350 bar 30 day dormancy test
Key aspects of cryogenic H₂ onboard storage were explored during 200 lap LH₂ refuel/park/drive experiment of 350 bar H₂ Prius.

Temperature, H₂ Pressure and velocity (GPS) @ 1 Hz.

LLNL 3.6 mile outer loop: 25 mph maximum speed.

1 lap=3.6 miles

T~100 K

8 bar 100 kg LH₂ Dewar (3 bar 10 kg refueling)

875 bar LH₂ pump 800 kg Dewar

Elevation Profile. Delta: 60 ft
4 month refuel/park/drive demonstrated:
(A) 2 week dormancy @ 90% full (B) return to 20 K (400 miles)
(C) under 350 bar envelope for 7 mi/day (full)

- 2 wks park 90% full
- 250 mi/1 wk
- 130 mi/18 days
- 107 mi/15 days
- 50 mi/15 days
- 3 mi/wk

Driving Range @ 52 miles per kgH₂

<table>
<thead>
<tr>
<th>Temperature [Kelvin], Pressure [bar]</th>
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<tbody>
<tr>
<td>Outside temperature</td>
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Vented 8 kg (i.e. 400 mi)

3 bar LH₂ refuelings

2 bar refuelings

Driving range

H₂ Temperature

5 W
(210 to 250 K)

150 mile drive

Ambient (300 K) driving range

5 W
(210 to 250 K)

5 W
(20 to 80 K)

Thanksgiving (Nov 21 – 25)

Christmas (Airport) (Dec 22 - Jan 9)
700 bar cryogenic H$_2$ refueling offers volume, capacity, & safety advantages balanced by increasing technical demands

- High density (cold) H$_2$ allows minimum vessel volume, mass, & cost with rapid refueling
- Large capacities improve cryogenic valve/vacuum jacket cost, mass, & volume per kg of H$_2$
- Inert secondary containment, min burst energy @ max tension, on road safety factor of 5-10
- Small vacuum space necessary for system density
- Temperature variations alter system/material behavior, density, dormancy, H$_2$ burst energy
- Competing design objectives: acceleration (strong suspension) vs. parking (thermal isolation)

We will demonstrate 5 kg H$_2$ storage at 700 bar (50 g/L, 9+ wt%)
Our objective is to explore thermomechanical limits of 12 inch vessels designed specifically for cryogenic H₂ storage.

Ultra Thin liner (1.3-1.5 mm): necessary for small diameters
Non-Al liner: liner, piping, and weld durability under cryogenic H₂ cycling
Maximum fiber fraction: minimum wall volume & thermal inertia

We are demonstrating 700 bar prototype cryogenic vessels designed for 80+% volumetric efficiency.
1st go/no-go (LN₂) test demonstrated vessel cryogenic strength
Cryogenic durability (1,500 LH₂ refuels) to be shown in 2nd test

FY15 Go/No-Go milestone

Demonstrated cryogenic 2.23 safety factor (1560 bar)
32 kg vessel, 1.8 mm liner with 81% volumetric efficiency
4 rapid pressurizations of 50 kg LN₂ with warm N₂ gas

FY16 Go/No-Go milestone

Demonstrate EOL cryogenic safety factor > 1.85
after 1,500 LH₂ fuelings

1,300 bar test from 875 bar H₂ at 90-120 K
Slow (~3 hr) temperature rise to 140-180 K
100 kg H₂/hr, 800 kg LH₂ facility for cycling (120-200 fills/day) of full-scale prototype vessels

- **Vent stack (6 kgH₂/min)**
- **Flow meter installed**
  - 250 kgH₂/day
  - +/- 0.2%
- **800 kg LH₂ Dewar**
  - (650 kg actual)

**40 kW_e Heat Exchanger**
20 to 273 K @ 60 kg/hr

**65 bar ASME Containment**
- 65 Liters H₂ at 360 K, 875 bar
- 125 Liters H₂ at 160 K, 700 bar

**875 bar LH₂ pump**
- 130 kW_e
  - (100 kgH₂/hr)
Ideal cryogenic H₂ cycling covers full pressure & temperature range, emphasizing maximum thermomechanical stress and time at pressure.
LLNL developed two vacuum jacket generations for 150 L cryogenic H₂. The smallest 3mm steel jacket was 225 L, 60 kg with <1” vacuum gap.
Preliminary long term vacuum pressure data did not indicate increased heat transfer below \( \sim 250 \text{ K} \).
Multiple month experiments indicated vacuum pressure followed vessel temperature.
Low temperature material properties offer opportunity and challenge for cryogenic pressure vessels

Opportunities greatest at **coldest** temperatures (typically <100 Kelvin)

- Increased composite fatigue life
- Increased composite stiffness
- Increased metal strength, cycle life
- Declining thermal conductivity
- Asymptotic heat capacity
- Asymptotic thermal contraction coefficient

Challenges due to temperature **change and variation**

- Aluminum minimizes gradients but high CTE
- Stainless steel sustains gradients but medium CTE
- Composites sustain highest gradients with small CTE

- Majority of thermal contraction typically occurs between 300 K and 200 K
- 10% of thermal contraction at T < 100 Kelvin

Focus on gradients at moderate temperatures & dissimilar materials

**Extreme cold can maximize thermomechanical properties**