

# Cryogenic Pressure Vessels for H<sub>2</sub> Vehicles Rapidly Refueled by LH<sub>2</sub> pump to 700 bar

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*CAMX meeting*  
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# The Road Ahead

- Cryogenic H<sub>2</sub> Onboard Storage
  - Temperature as a Degree of Freedom in H<sub>2</sub> storage
  - LLNL Cryocompressed Project History
  - 350 Bar Test Vehicle Park & Drive Results
- Current Project
  - 700 bar prototype (cryogenic) vessels
  - Refueling with LH<sub>2</sub> 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<sub>2</sub> onboard a 2005 Prius*

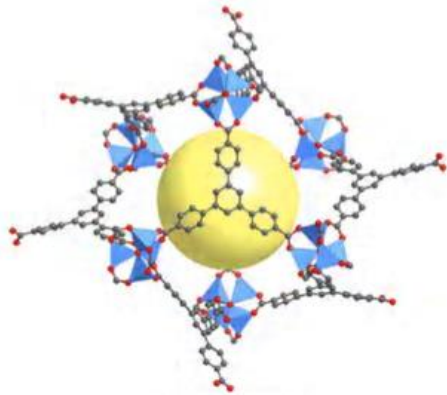
# Onboard H<sub>2</sub> storage approaches face thermodynamic challenges



Cryogenic Liquid H<sub>2</sub> (28 Kelvin, 6 bar)  
*evaporation* when parked 3-4 days



Compressed Gas (350-700 bar)  
H<sub>2</sub> *volume*, fast fill *heating*



MOF-177

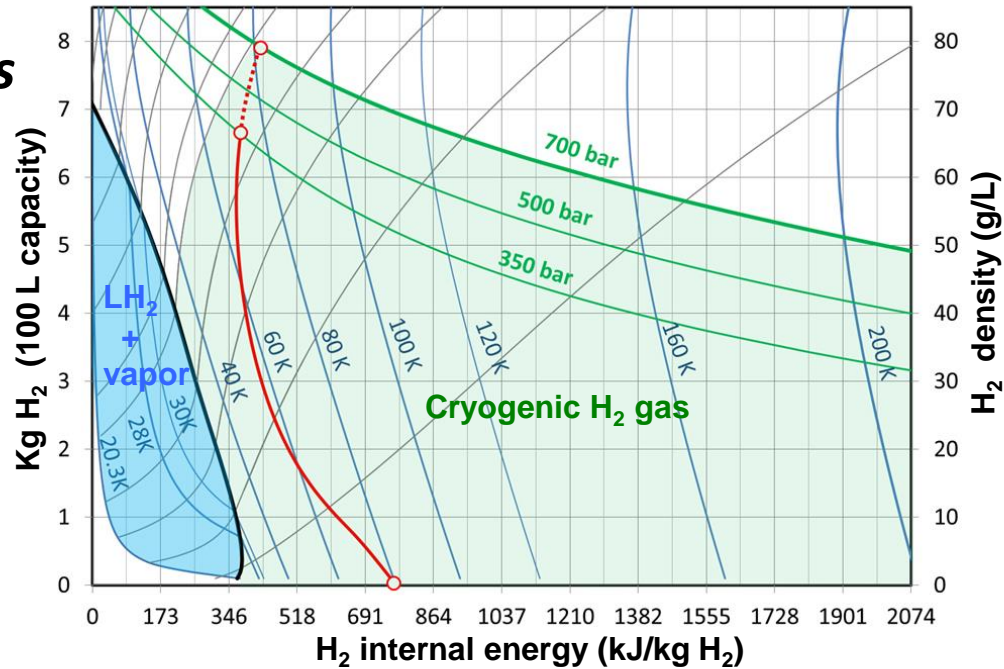
Adsorbed H<sub>2</sub>: parasitic volume,  
*exothermic* refueling & cryogenics



Hydrides: parasitic mass,  
refuel *speed/temperature*

# Thermodynamic limits of LH<sub>2</sub> & ambient H<sub>2</sub> storage can be overcome with H<sub>2</sub> pressure vessels operable across broad range of temperatures

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



# Thermodynamics of high pressure cryogenic H<sub>2</sub> 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 H<sub>2</sub> gas with a comprehensive approach while improving storage density, dormancy, safety, cost, & refueling

**1997-2003**

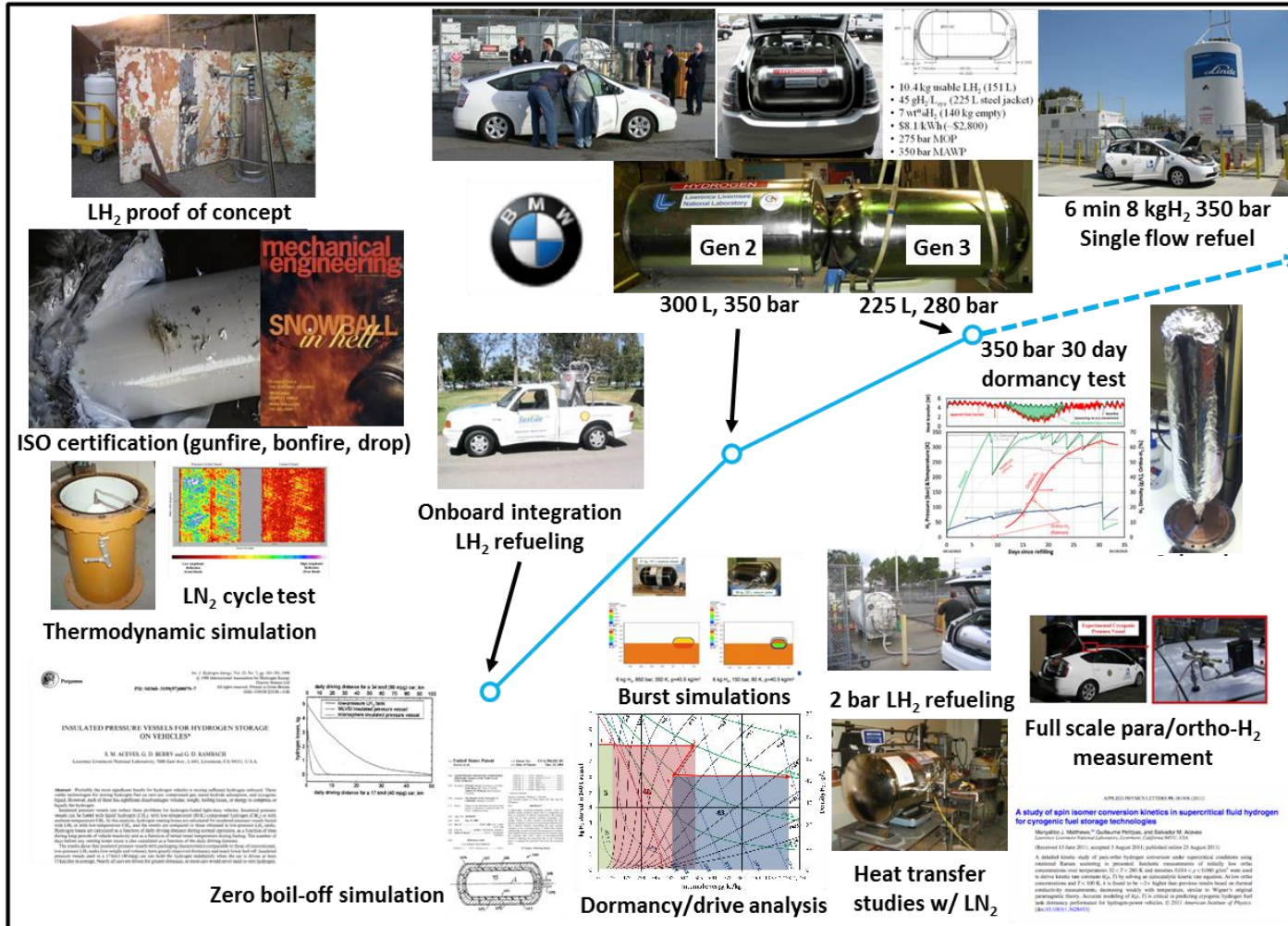
Dormancy simulation  
Subscale vessel testing

**2003-2010**

Onboard Commercial vessels  
350 bar, 10 kg LH<sub>2</sub>

**2010-2013**

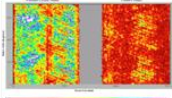
Heat transfer  
350 bar refuel w/ LH<sub>2</sub> pump



LH<sub>2</sub> proof of concept



ISO certification (gunfire, bonfire, drop)



LN<sub>2</sub> cycle test

Thermodynamic simulation



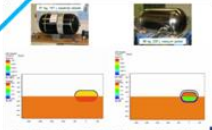
Zero boil-off simulation



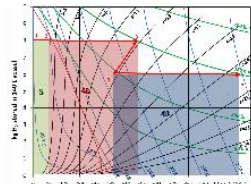
300 L, 350 bar      225 L, 280 bar



Onboard integration  
LH<sub>2</sub> refueling



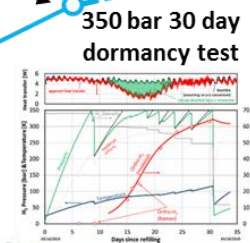
Burst simulations



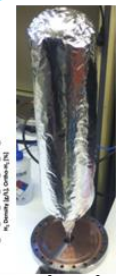
Dormancy/drive analysis



6 min 8 kgH<sub>2</sub> 350 bar  
Single flow refuel



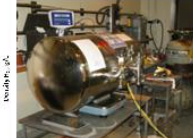
350 bar 30 day  
dormancy test



2 bar LH<sub>2</sub> refueling



Full scale para/ortho-H<sub>2</sub>  
measurement

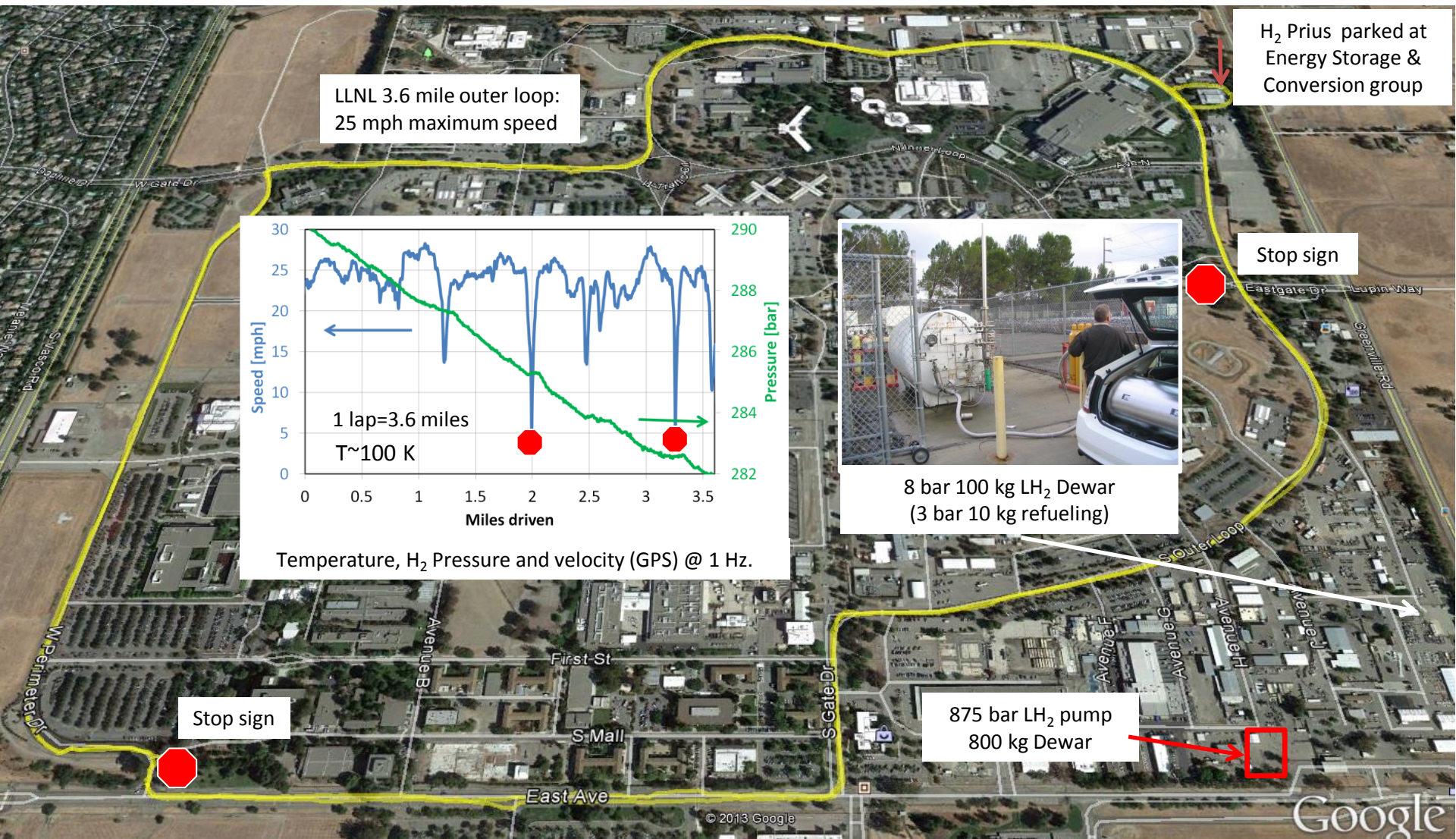


Heat transfer  
studies w/ LN<sub>2</sub>

H<sub>2</sub> storage density, gH<sub>2</sub>/L<sub>system</sub>

1997      1999      2001      2003      2005      2007      2009      2011      2013

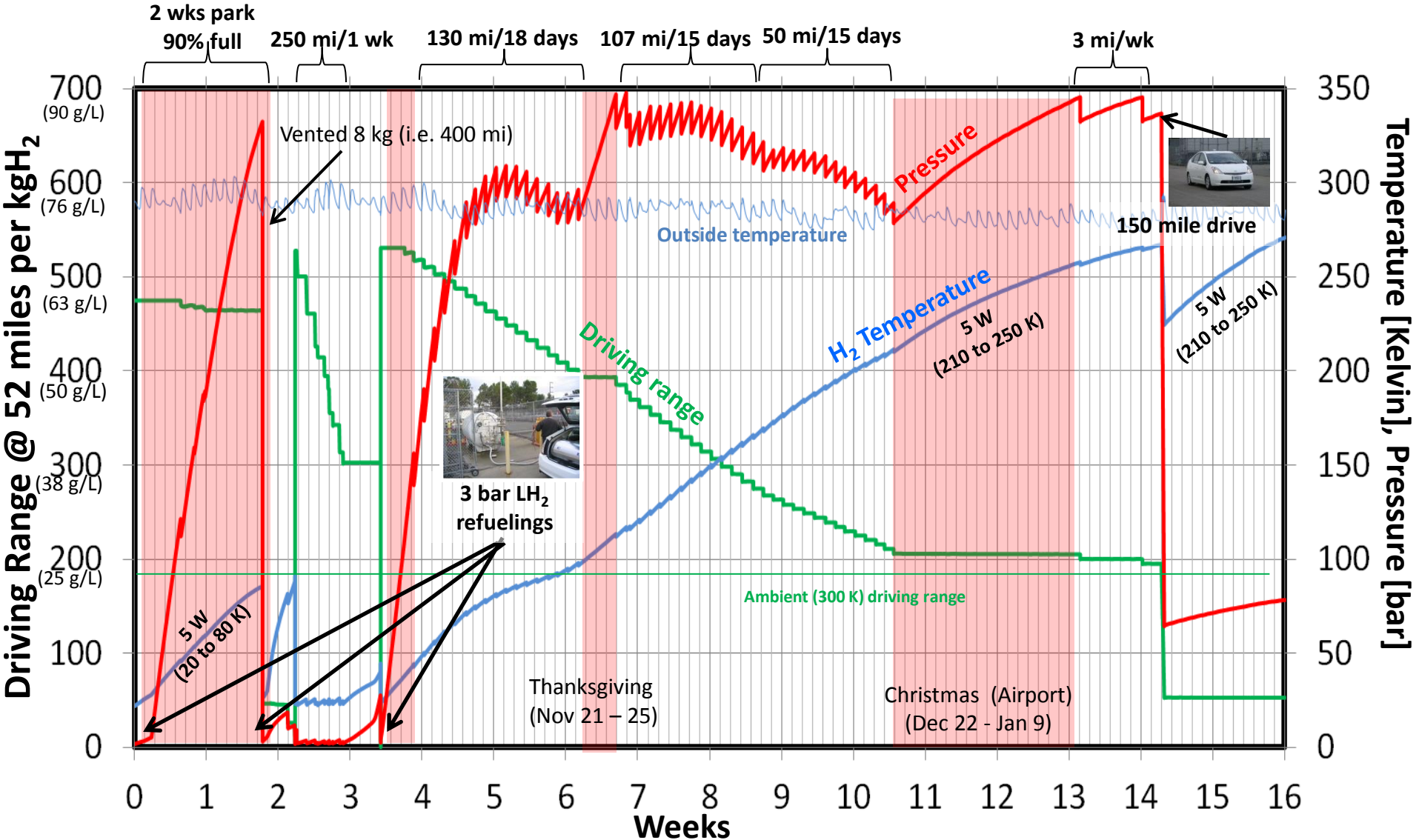
# Key aspects of cryogenic H<sub>2</sub> onboard storage were explored during 200 lap LH<sub>2</sub> refuel/park/drive experiment of 350 bar H<sub>2</sub> Prius



Elevation Profile. Delta: 60 ft

# 4 month refuel/park/drive demonstrated:

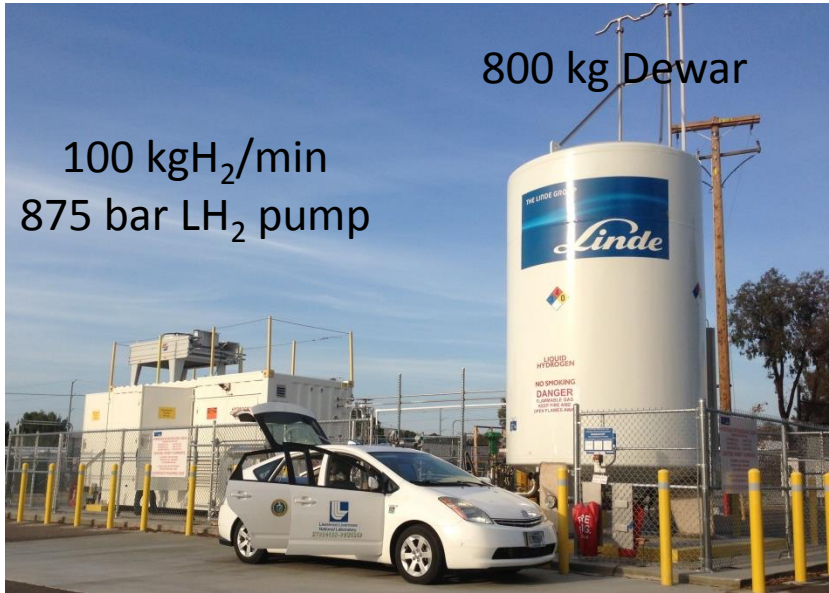
(A) 2 week dormancy @ 90% full (B) return to 20 K (400 miles)  
 (C) under 350 bar envelope for 7 mi/day (full)



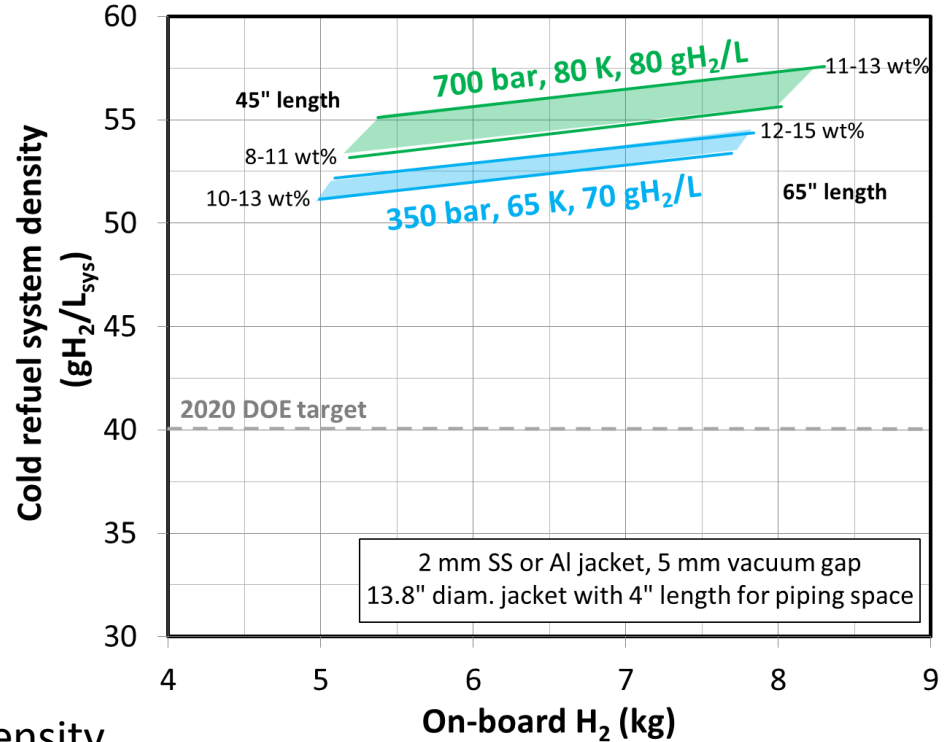


# 700 bar cryogenic H<sub>2</sub> refueling offers volume, capacity, & safety advantages balanced by increasing technical demands

- High density (cold) H<sub>2</sub> allows minimum vessel volume, mass, & cost with rapid refueling
- Large capacities improve cryogenic valve/vacuum jacket cost, mass, & volume per kg of H<sub>2</sub>
- Inert secondary containment, min burst energy @ max tension, on road safety factor of 5-10



7 minute 10 kgH<sub>2</sub> fill to 70 g/L (350 bar, 65 K)



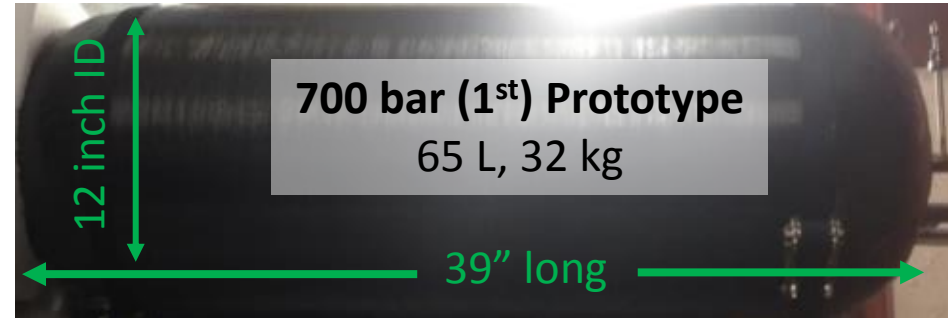
- Small vacuum space necessary for system density
- Temperature *variations* alter system/material behavior, density, dormancy, H<sub>2</sub> burst energy
- Competing design objectives: *acceleration* (strong suspension) vs. *parking* (thermal isolation)

**We will demonstrate 5 kg H<sub>2</sub> storage at 700 bar (50 g/L, 9+ wt%)**

# Our objective is to explore thermomechanical limits of 12 inch vessels designed specifically for cryogenic H<sub>2</sub> storage



*70% volumetric efficiency*  
*9 mm Al liner*



*81% volumetric efficiency*  
*1.8 mm non-Al liner*

**Ultra Thin liner (1.3-1.5 mm):** necessary for small diameters

**Non-Al liner:** liner, piping, and weld durability under cryogenic H<sub>2</sub> cycling

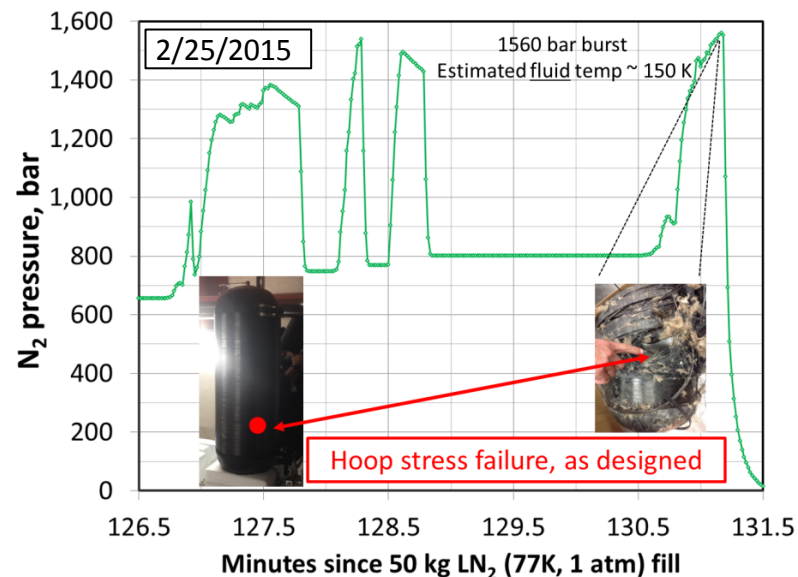
**Maximum fiber fraction:** minimum wall volume & thermal inertia

**We are demonstrating 700 bar prototype cryogenic vessels designed for 80+% volumetric efficiency**

# 1<sup>st</sup> go/no-go (LN<sub>2</sub>) test demonstrated vessel cryogenic strength Cryogenic durability (1,500 LH<sub>2</sub> refuels) to be shown in 2<sup>nd</sup> test

## FY15 Go/No-Go milestone

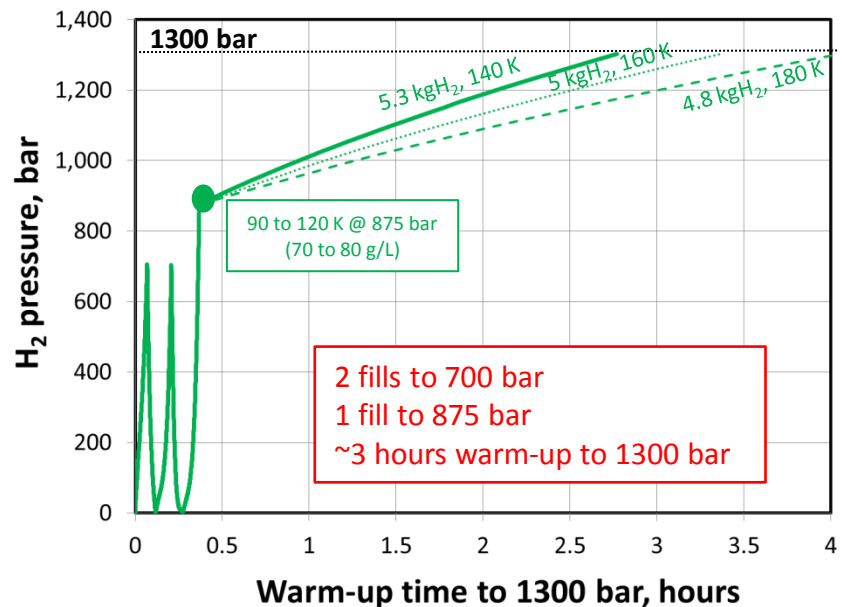
Demonstrated cryogenic 2.23 safety factor (1560 bar)  
32 kg vessel, 1.8 mm liner with 81% volumetric efficiency  
4 rapid pressurizations of 50 kg LN<sub>2</sub> with warm N<sub>2</sub> gas



## FY16 Go/No-Go milestone

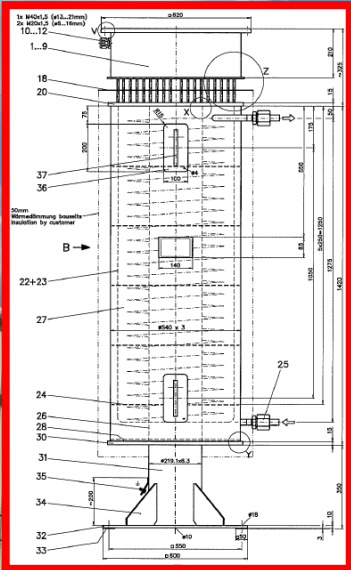
Demonstrate EOL cryogenic safety factor > 1.85  
after 1,500 LH<sub>2</sub> fuelings

1,300 bar test from 875 bar H<sub>2</sub> at 90-120 K  
Slow (~3 hr) temperature rise to 140-180 K



# 100 kg H<sub>2</sub>/hr, 800 kg LH<sub>2</sub> facility for cycling (120-200 fills/day) of full-scale prototype vessels

Vent stack  
(6 kgH<sub>2</sub>/min)



Flow meter installed  
250 kgH<sub>2</sub>/day  
+/- 0.2%

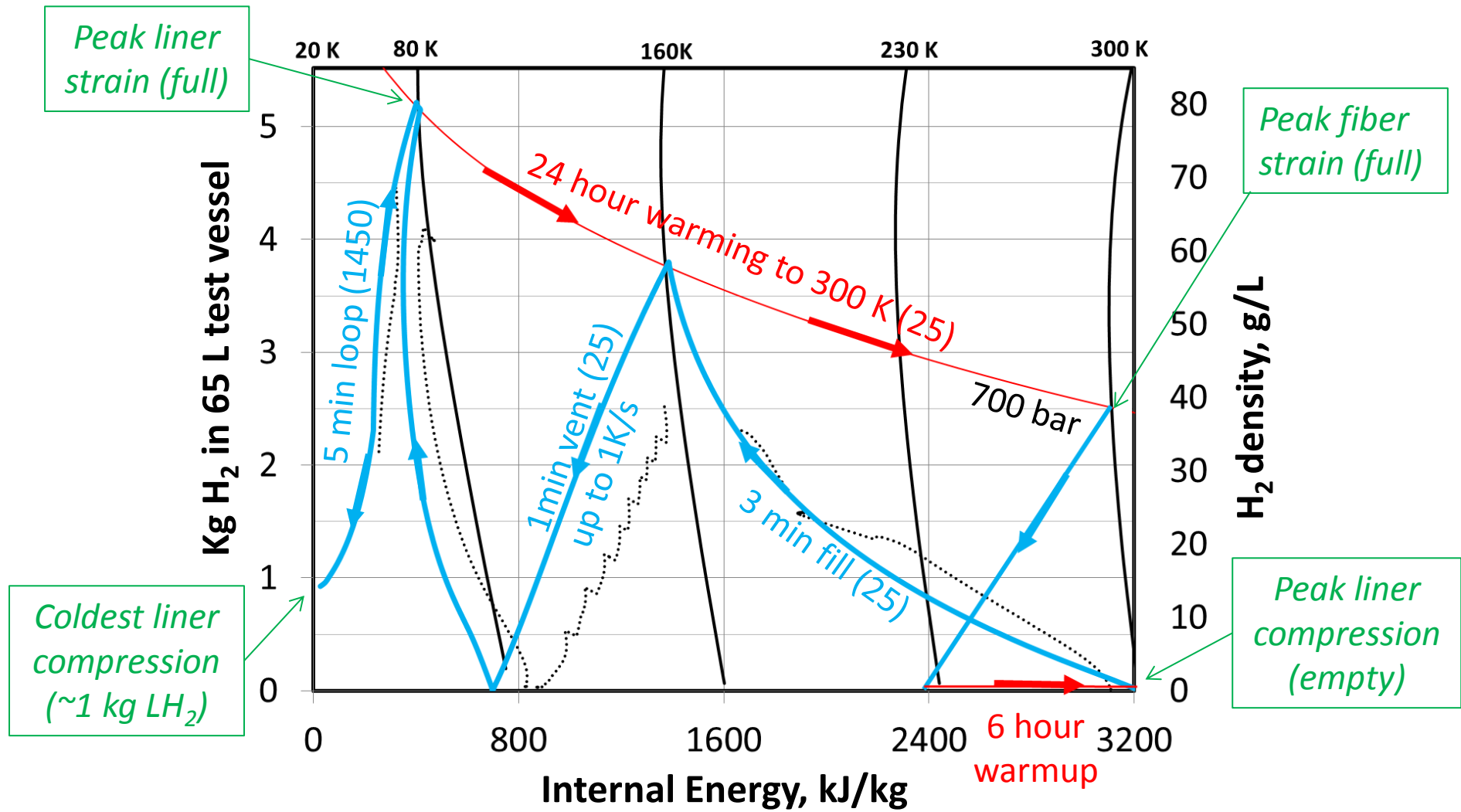
800 kg LH<sub>2</sub> Dewar  
(650 kg actual)

40 kW<sub>e</sub> Heat Exchanger  
20 to 273 K @ 60 kg/hr

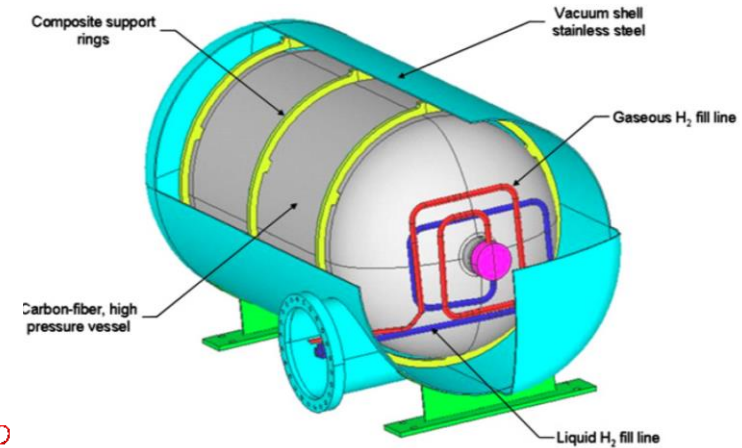
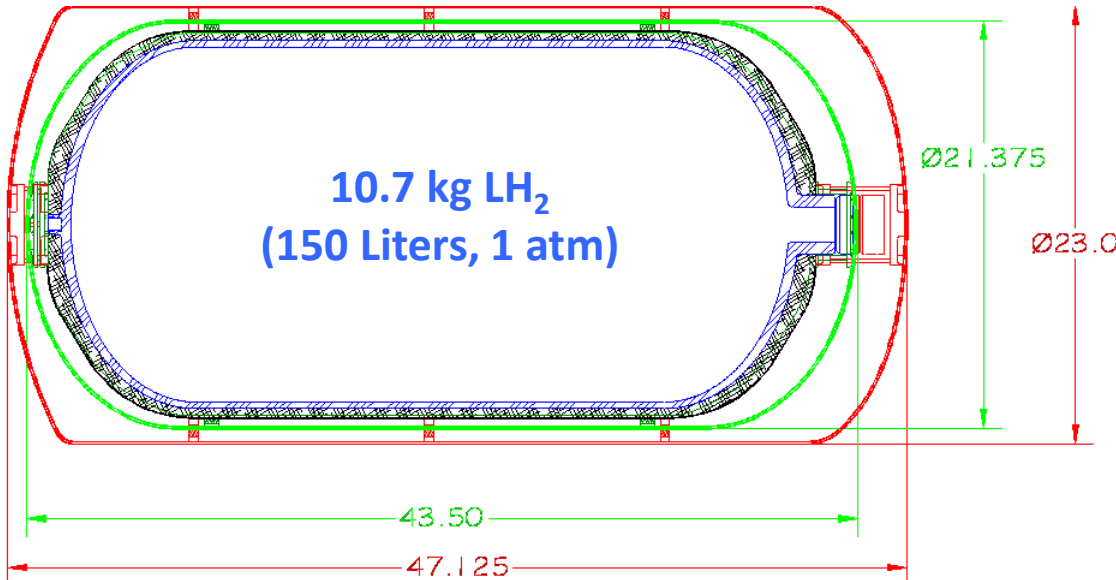
65 bar ASME Containment  
65 Liters H<sub>2</sub> at 360 K, 875 bar  
125 Liters H<sub>2</sub> at 160 K, 700 bar

875 bar LH<sub>2</sub> pump  
130 kW<sub>e</sub>  
(100 kgH<sub>2</sub>/hr)

# Ideal cryogenic H<sub>2</sub> cycling covers full pressure & temperature range, emphasizing maximum thermomechanical stress and time at pressure

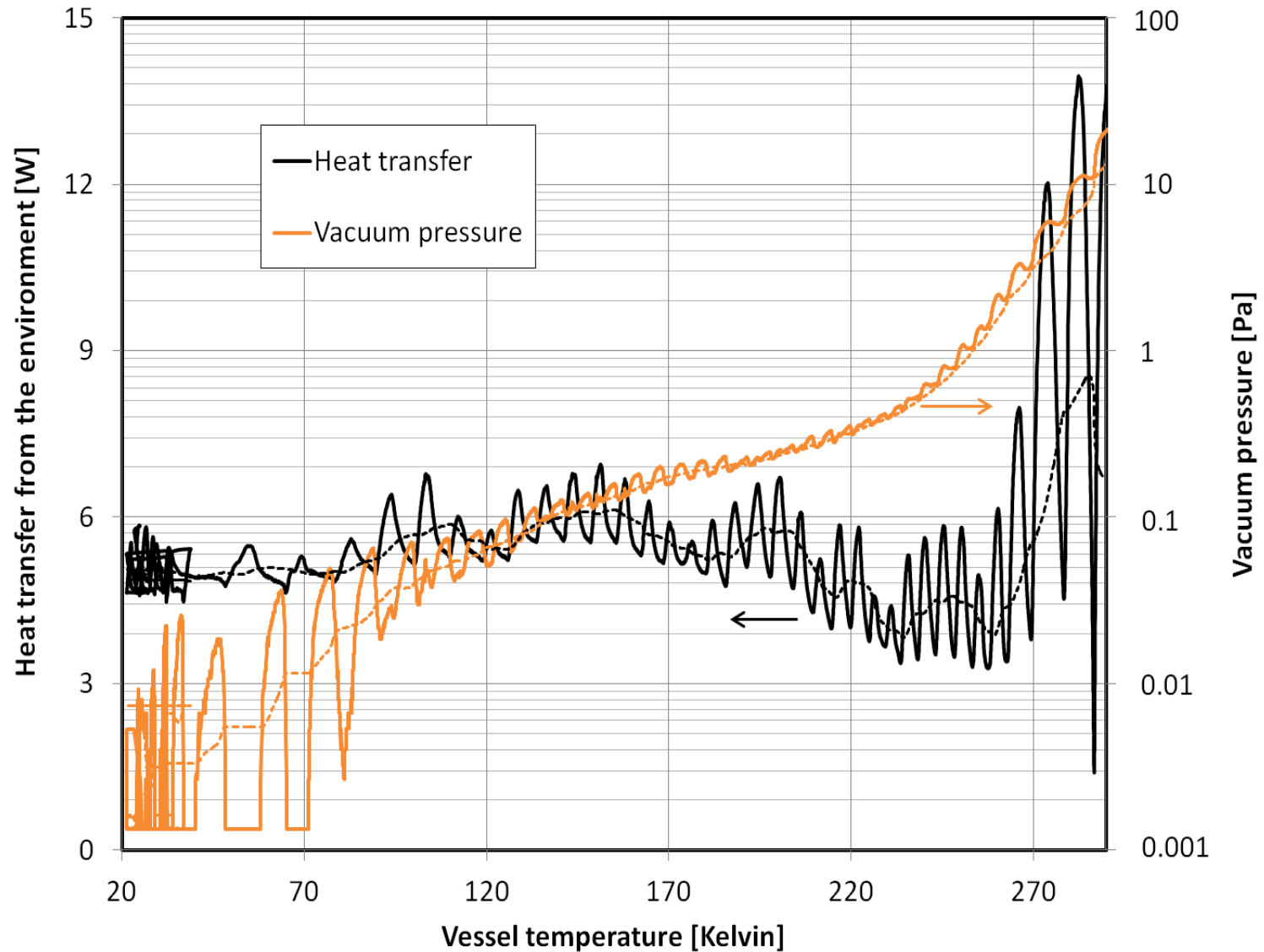


LLNL developed two vacuum jacket generations for 150 L cryogenic H<sub>2</sub> the smallest 3mm steel jacket was 225 L, 60 kg with <1" vacuum gap

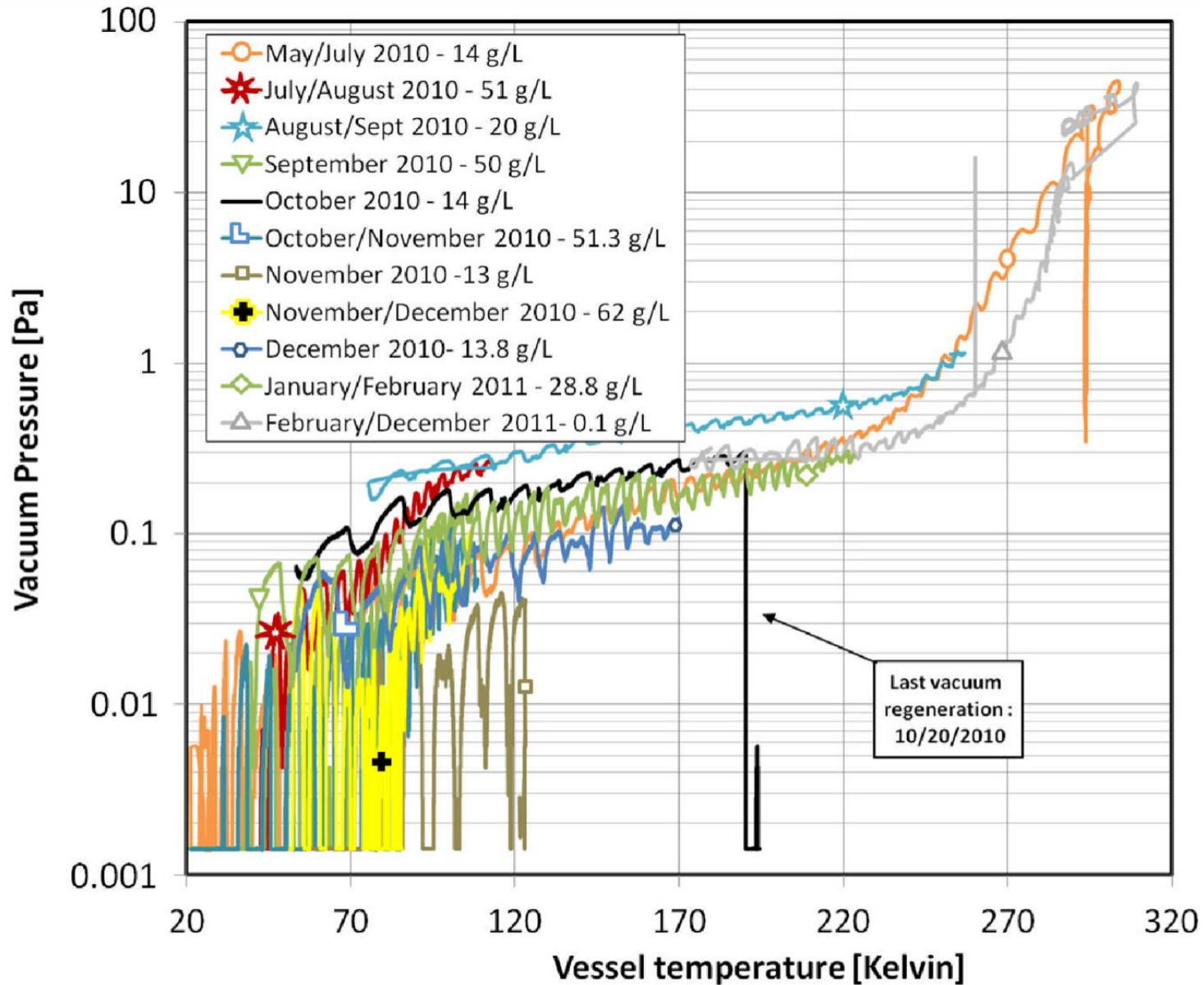


	<u>Weight (kg)</u>	<u>wt%H<sub>2</sub></u>	<u>Volume (L)</u>	<u>kgH<sub>2</sub>/m<sup>3</sup></u>
4,000 psi vessel+boss	60.9	14.9	179	59.7
Steel vacuum jacket	57.1	8.3	225	47.4
Ancillary components	16	<b>7.4</b>	11	<b>45.2</b>

# Preliminary long term vacuum pressure data did not indicate increased heat transfer below ~250 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**