

# Thermomechanical Cycling of Thin Liner High Fiber Fraction Cryogenic Pressure Vessels Rapidly Refueled by LH<sub>2</sub> pump to 700 bar

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

Project ID #  
ST111

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# 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

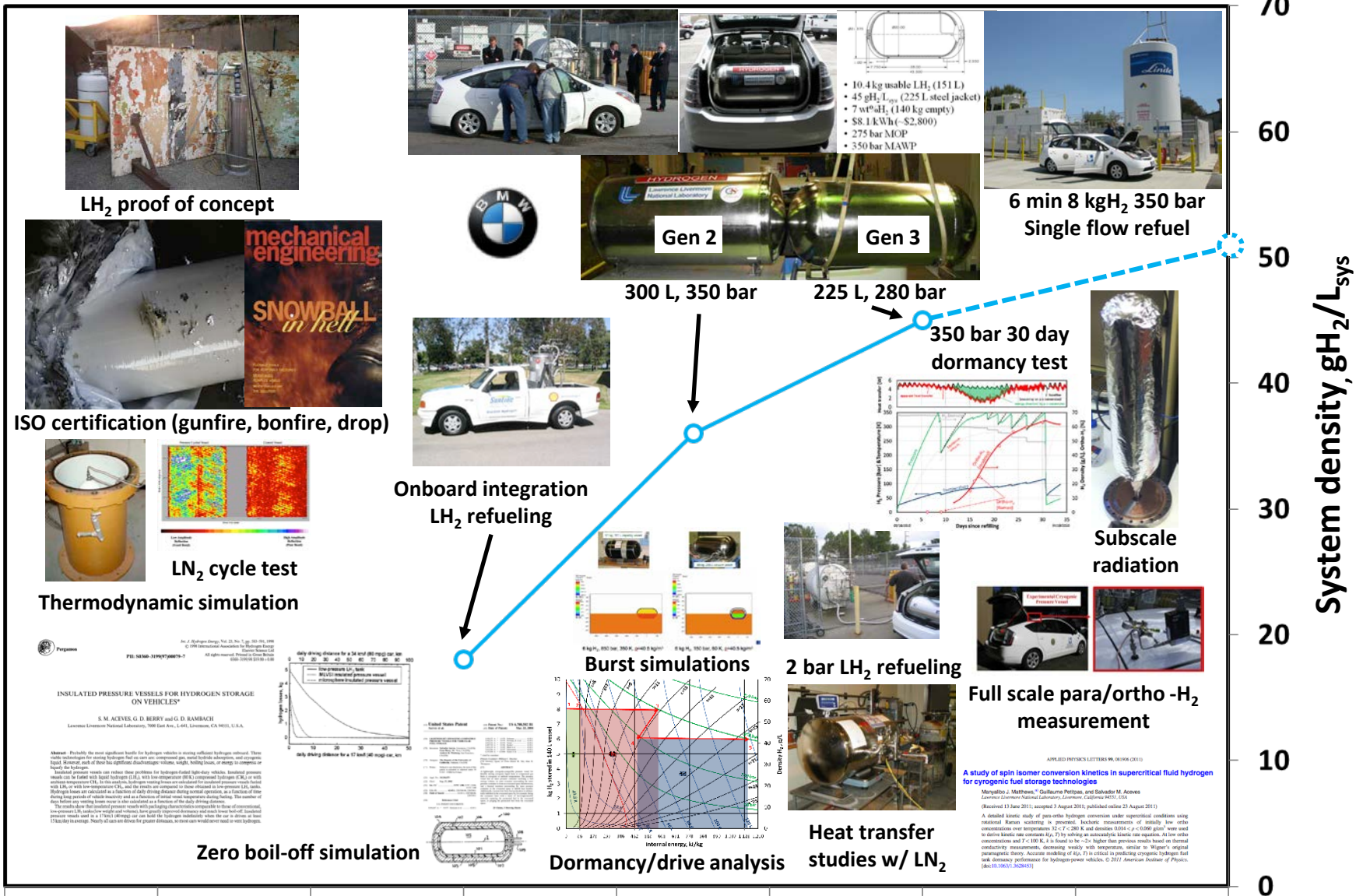
- **A. System weight and volume**
- **D. Durability/Operability**
- **N. Hydrogen venting**

## Partners

- **Spencer Composites**  
custom cryogenic pressure vessel
- **Linde** 875 bar LH<sub>2</sub> pump supply, operation & maintenance
- **BMW** thermal insulation, performance requirements, automotive perspective



# Project history: Increasingly compact H<sub>2</sub> storage



# Relevance: Chief objective of highest H<sub>2</sub> & system density with preferred diameter, capacity, cycle life & safety will simultaneously maximize progress toward other targets

## 1. Demonstrate 700 bar fueling with LH<sub>2</sub> pump

- Measure final density, time, electricity
- Use commercial 163 L 700 bar vessel

## 2. Develop 60 L H<sub>2</sub> 700 bar prototypes with thin liner, high fiber fraction, small diameter

- Custom design & fabrication for cryogenics
- Demonstrate 1600 bar strength with LN<sub>2</sub>

## 3. Cycle cryogenic vessels & LH<sub>2</sub> pump

- Long duration and accelerated testing
- Multiple vessels, 1250-1750 fuelings (each)
- Followed by 1600 bar cryogenic H<sub>2</sub> testing

## 4. Demonstrate compact, lightweight system

- Suspend best vessel in aluminum jacket
- Characterize dormancy, rapid LH<sub>2</sub> refueling

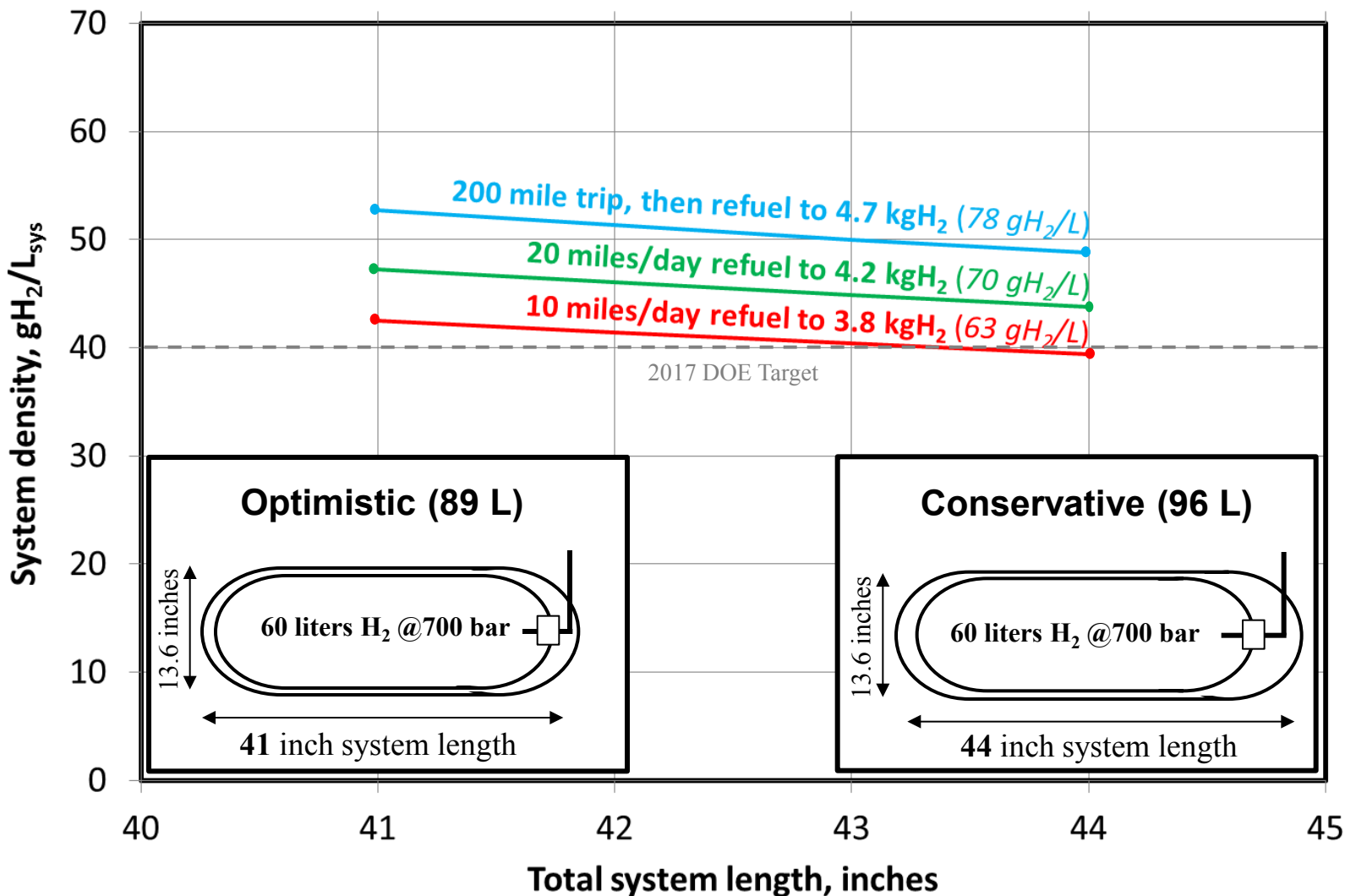
Technical System Targets: Onboard Hydrogen Storage for Light Duty Fuel Cell Vehicles		
Storage Parameter	2017	Ultimate
System Gravimetric Capacity, wt%	5.5	7.5
System Volumetric Capacity, g/L	40	70
System Cost, \$/kWh	12	8
Operating ambient temperature, C	-40/60	-40/60
Min delivery temperature, C	-40	-40
Max delivery temperature, C	85	85
Operational cycle life	1500	1500
Min delivery pressure, bar	5	3
Max delivery pressure, bar	12	12
Onboard efficiency, %	90	90
WTPP efficiency, %	60	60
System fill time (5 kg), min	3.3	2.5
Minimum full flow rate, (g/s)/kW	0.02	0.02
Start time to full flow (20 C), s	5	5
Start time to full flow (-20 C), s	15	15
Transient response, s	0.75	0.75
Fuel quality %H <sub>2</sub>	SAE J2719 and ISO/PDTS	
Permeation & leakage	Meet or exceeds standards	
Toxicity		
Safety		
Loss of usable H <sub>2</sub> , (g/h)/kg H <sub>2</sub>	0.05	0.05

**Project goal: 60 L cryogenic H<sub>2</sub> storage system with 50gH<sub>2</sub>/L<sub>sys</sub> & 9 wt% H<sub>2</sub> & 1500 cycles**

Green : measured  
 Yellow : potential/projected  
 Red : challenging



# Relevance: H<sub>2</sub> system density depends on vehicle usage, driver criteria for refueling, and auxiliary vacuum volume

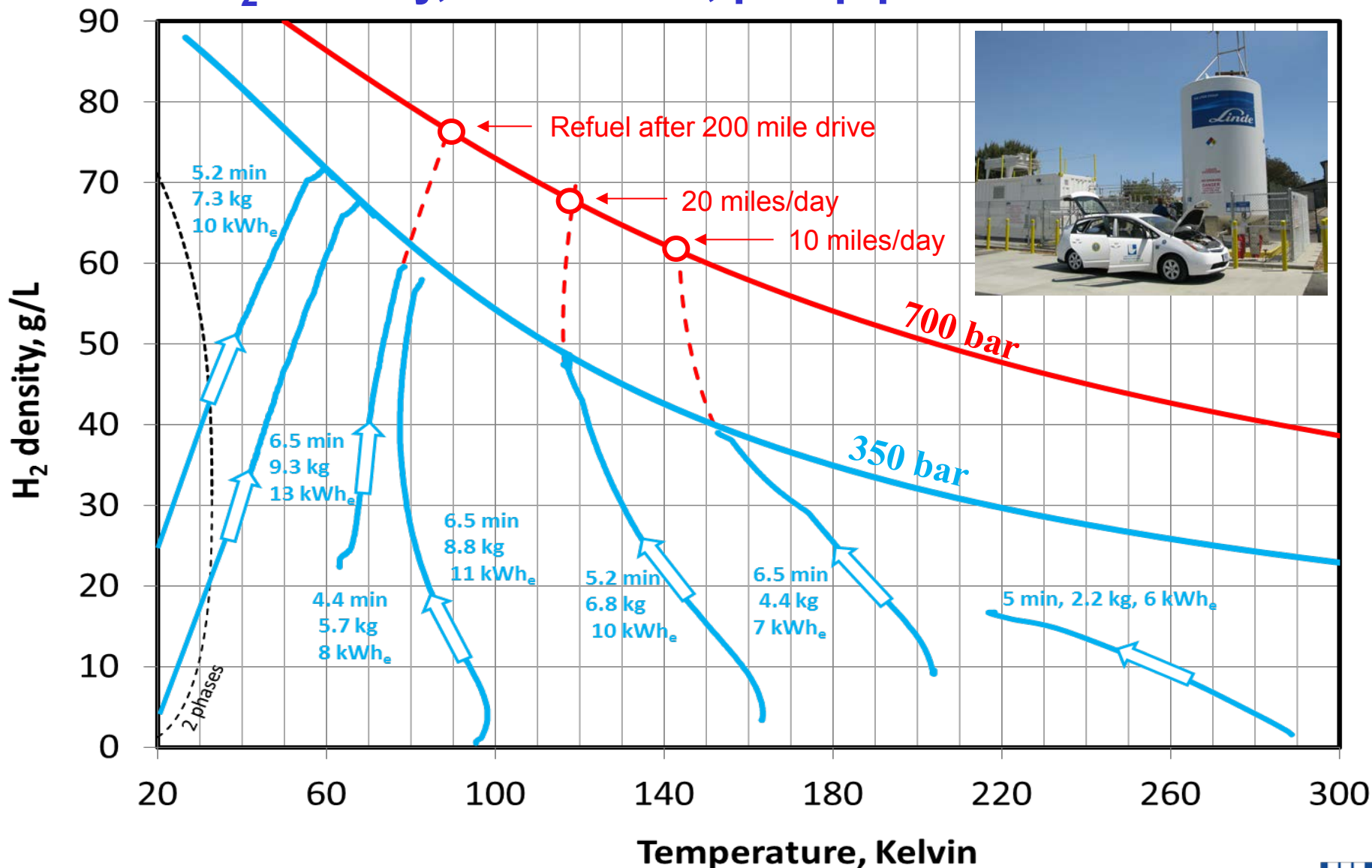


**System densities of 40-52 gH<sub>2</sub>/L<sub>sys</sub> appear feasible for H<sub>2</sub> fill densities of 63-78 g/L**



# Approach (FY14): Extend LH<sub>2</sub> refueling to 700 bar

Measure H<sub>2</sub> density, refuel time, pump power for 163 L vessel



**Up to 80g/L H<sub>2</sub> density possible at 700 bar**



# Approach (FY14) : Design, tooling, fabrication & test for small diameter, thin liner 60 L cryogenic prototype vessel

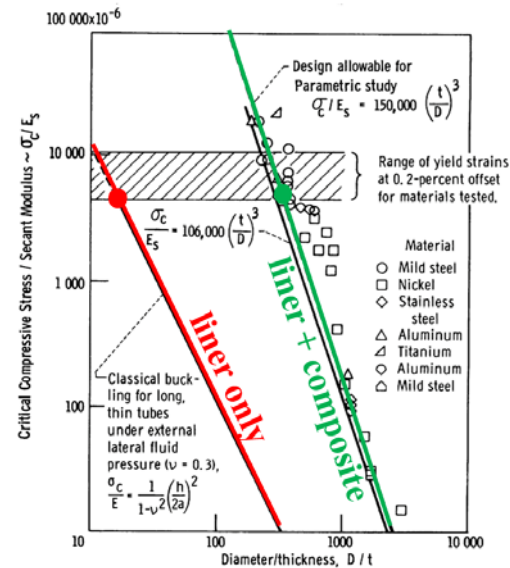
**LN<sub>2</sub> Tensile Testing** : Guide liner material choice and composite vessel fabrication to insure against failure in cryogenic tension



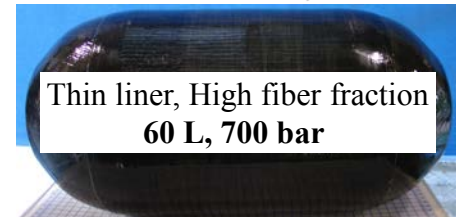
**Ambient Ring Rupture: 18" apparatus testing compression** due to autofrettage, composite strength in strain-scaled high fiber fraction wall, and cusp buckling limit



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 LN<sub>2</sub> test



**A successful 1600 bar LN<sub>2</sub> strength test of the 60 L, thin liner, high fiber fraction prototype vessel is the FY14 Go/No-Go**



# Approach: 700 bar H<sub>2</sub> thermomechanical cycling of four 60 L prototypes 1250+ times to demonstrate final vessel durability

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

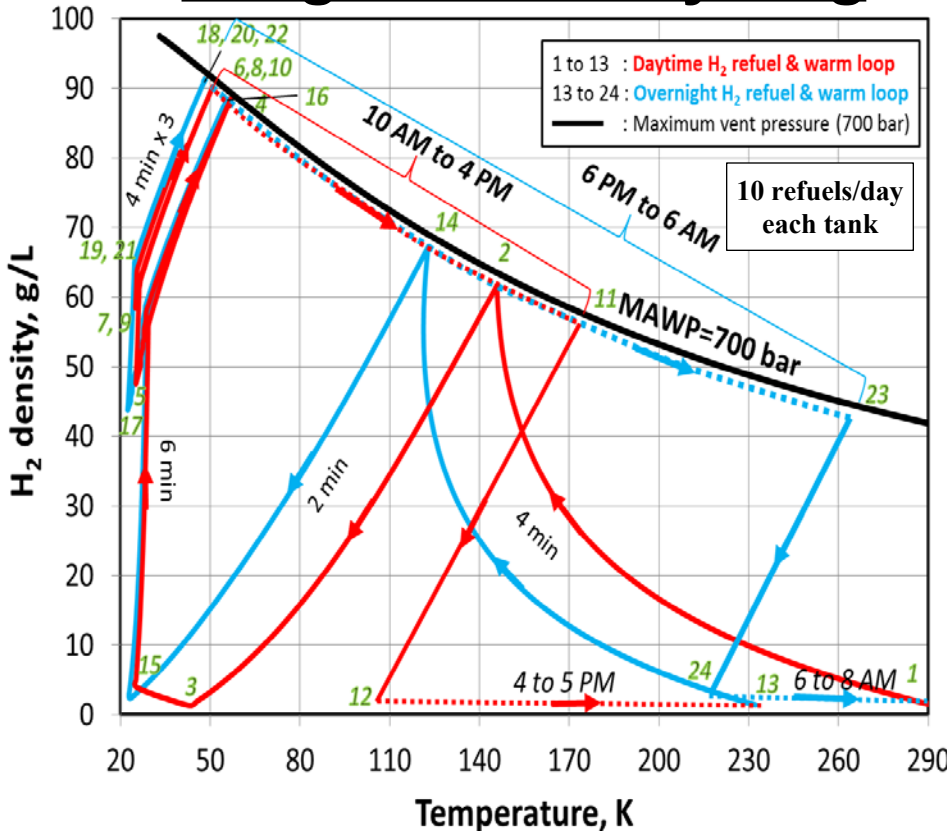
**Prototypes 2-5 will experience minimum 1250 peak tension (cold, full) and 250 peak compression (hot, empty) excursions. Duration & temperature differ**





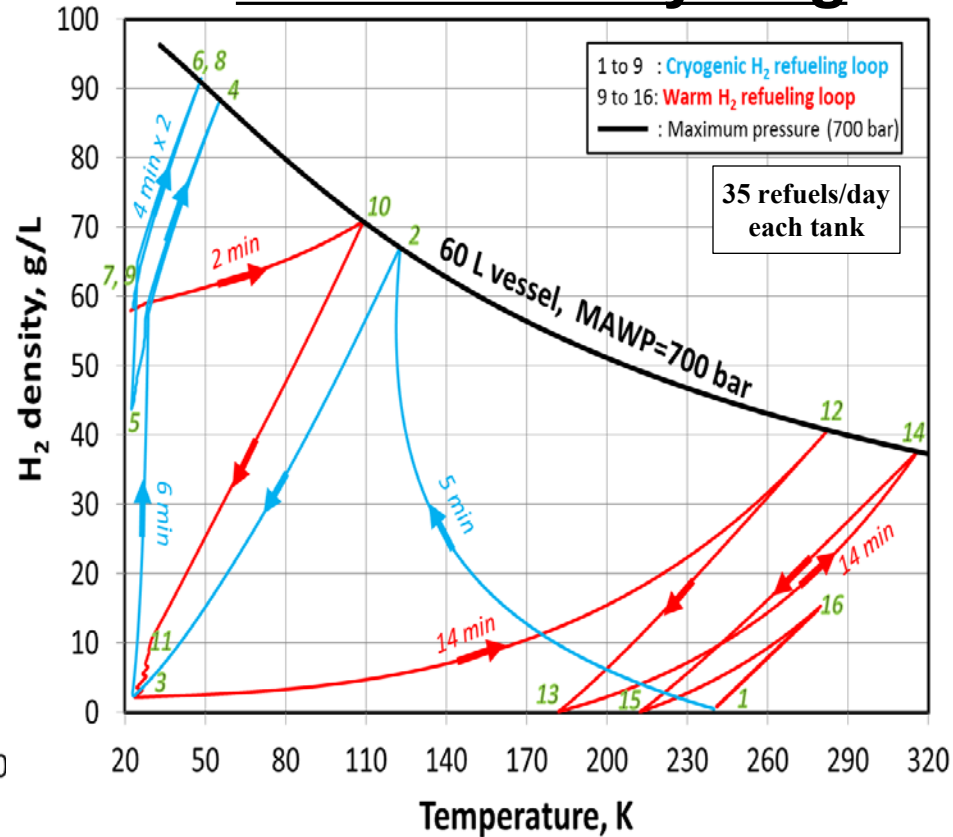
# Approach: Long duration & accelerated thermomechanical cycling of 60 L prototypes equivalent to 1250-1750 refuels

## Long Duration Cycling



- 500 W external warming
- 65 kg LH<sub>2</sub> daily loop, 80+% @ 700 bar
- 24 (P,T) points including warm & empty
- 125 days/8 tonnes LH<sub>2</sub>/6 months

## Accelerated Cycling

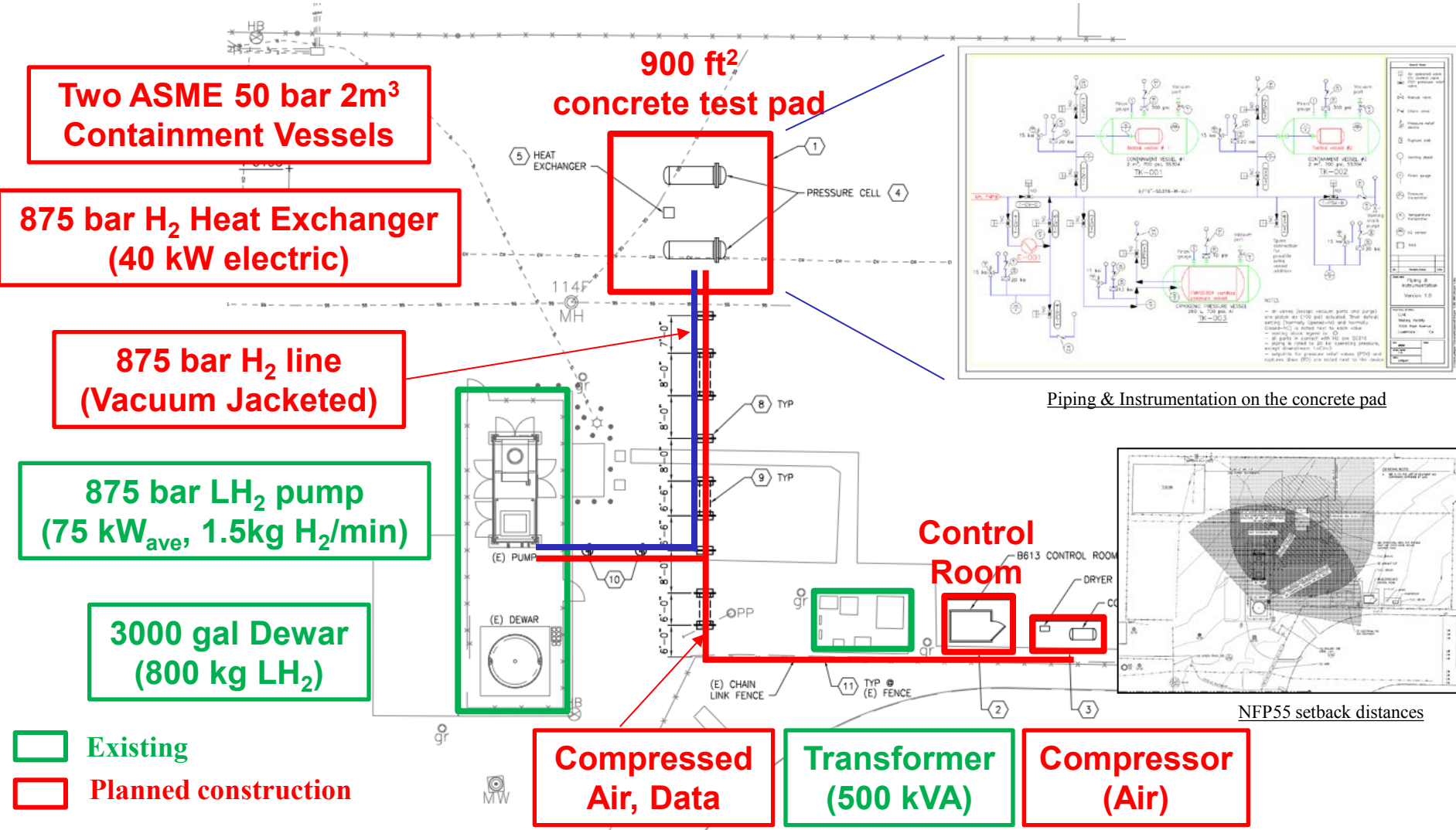


- 40 kW H<sub>2</sub> internal warming
- 40 kg LH<sub>2</sub> loop, 5/day <20% @ 700 bar
- 16 (P,T) points including warm & full
- 50 days/10 tonnes LH<sub>2</sub>/3 months

**Long duration testing uses vacuum degradation. Accelerated testing uses 875 bar H<sub>2</sub> heat exchanger. Simultaneous cycling of two 60 L prototypes**



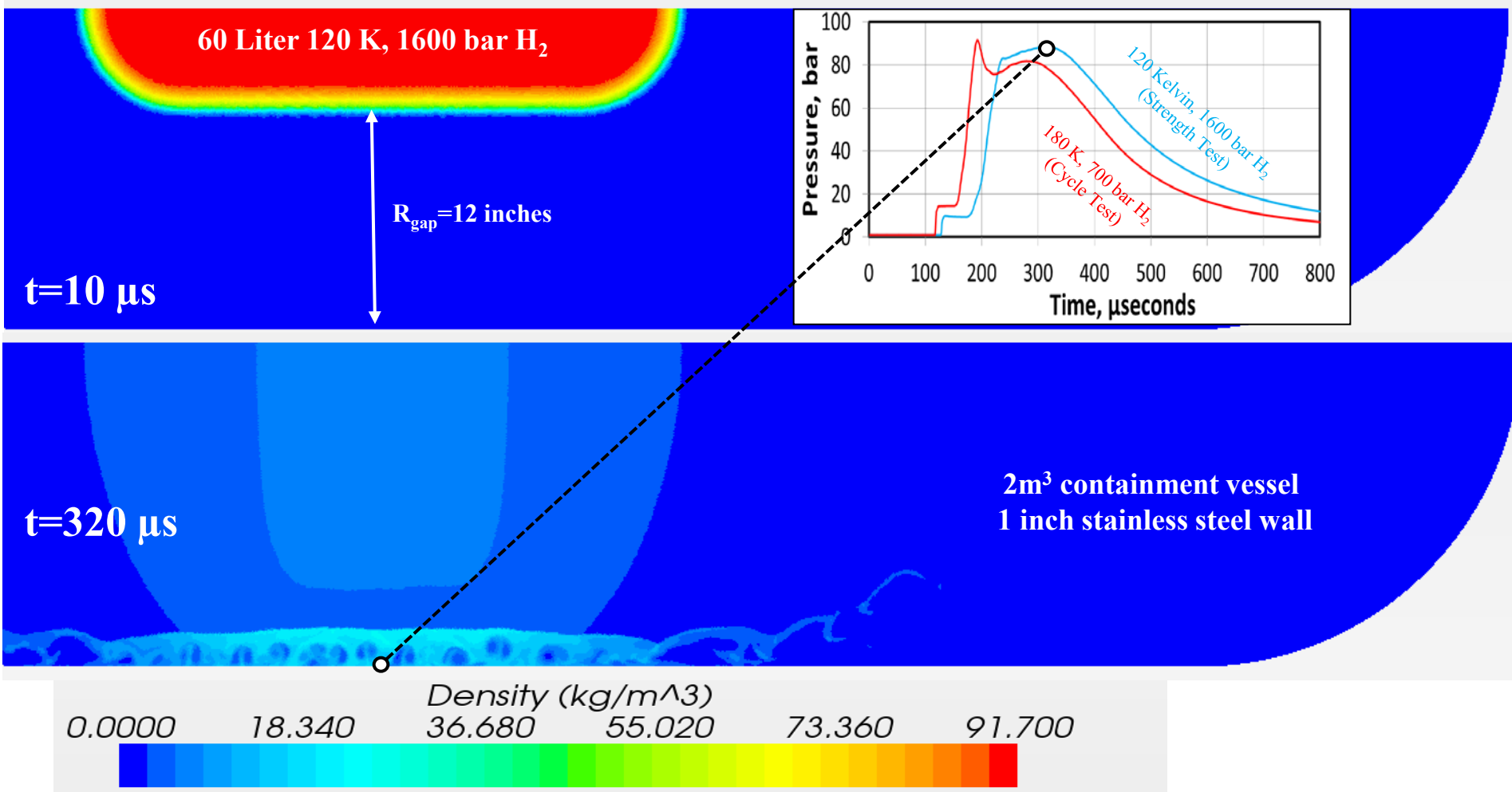
# Accomplishment: Construction approval for LH<sub>2</sub> pump facility for simultaneous, remote cycling of uncertified 60 L vessels



**Remote LH<sub>2</sub> pump operation, 2.5 kg/min vent stack, 25' pad exclusion zone  
 Class 1 Division 1 electrical, air driven valves, 2 m<sup>3</sup> containment vessels**



# Accomplishment: Preliminary hydrodynamic simulations for 1600 bar cryogenic H<sub>2</sub> 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<sub>2</sub> delivery
- ***Linde***: World class cryogenics experience. Manufactures maximum efficiency LH<sub>2</sub> pump. Delivered first commercial LH<sub>2</sub> 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<sub>2</sub> pump:*** Need 80+ gH<sub>2</sub>/L cold refuel density and no degradation after pumping up to 24 tonnes LH<sub>2</sub> 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<sub>2</sub>/L, 9 wt % H<sub>2</sub>, 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:

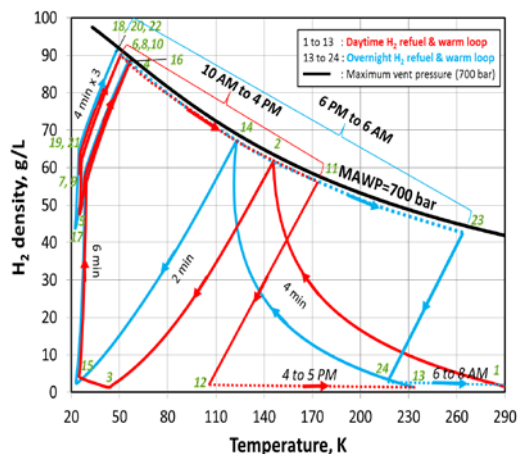
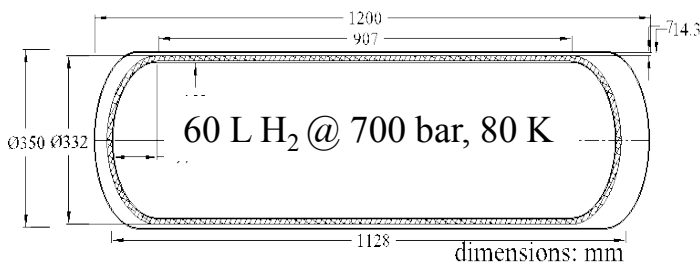
- construction of the testing facility
- vacuum insulation of a conventional 700 bar (163 L) pressure vessel using more compact and lightweight designs, for baseline testing
- Development of thin lined high fraction 60 L 700 bar pressure vessel

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

Milestones	Description
Q3/FY14	Complete construction of test facility concrete pad
Q4/FY14	Deliver custom 60 L 700 bar pressure vessel with 80% volumetric efficiency
Q1/FY15 <i>1<sup>st</sup> Go/No-Go</i>	Demonstrate 1600 bar inert cryogenic burst strength of 60 L custom composite vessel
Q2/FY15	Determine pump performance at 700 bar using 163 L conventional vessel (40 gH <sub>2</sub> /L <sub>sys</sub> , 6 wt%H <sub>2</sub> )
Q3/FY15	Complete 1500 accelerated thermomechanical cycles on two 60 L 700 bar, 80% volume efficient vessels



# Planned work: 3 year project will demonstrate rapid refueling of 700 bar cryogenic H<sub>2</sub> vessels with high system density, small diameter (~35 cm), & cryogenic durability (1500 refuels)



## Rapid pressurized LH<sub>2</sub> refuel from any condition

- 100 kg/hr, up to 875 bar
- Refueled H<sub>2</sub> density 63-80 g/L (up to 700 bar)
- Potential for low LH<sub>2</sub> evaporation (1-3%)

## Volumetric efficiency at 60 L capacity

- Up to 4.8 kg H<sub>2</sub> peak H<sub>2</sub> storage
- Thin metallic liner (<2 mm)
- High fiber fraction (70+%)
- Thin vacuum gap (<1 cm)
- Final system demo : 50 +gH<sub>2</sub>/L<sub>sys</sub>, 9 wt%H<sub>2</sub>
- 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 LH<sub>2</sub> 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 H<sub>2</sub> at superliquid (70+ g/L) densities, (2) The viability of improvements to high pressure (>350 bar) cryogenic H<sub>2</sub> storage, (3) Thermomechanical lifecycle & strength testing with cryogenic H<sub>2</sub>, 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<sub>2</sub> pump has the potential of 1–3% hydrogen boil-off loss and additional boil-off from the LH<sub>2</sub> 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<sub>2</sub> from Dewar, and returns a fraction of evaporated LH<sub>2</sub> back into Dewar. Dewar typically *depressurizes* when running at these conditions. Boil-off from Dewar is due to environmental heat transfer or LH<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> venting for all users. Two cold refuels are sufficient to transition from minimum to maximum range during continuous driving

