

# Compact (L)H<sub>2</sub> Storage with Extended Dormancy in Cryogenic Pressure Vessels

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ST\_34\_Berry**

This presentation does not contain any proprietary or confidential information



# Overview

## Timeline

- Start date: **October 2004**
- End date: **September 2011**
- Percent complete: **70%**

## Budget

- Total project funding
  - DOE: **\$4.5M**
- Funding for FY08:
  - **\$1.2M**
- Funding for FY09:
  - **\$2.25M**

## Barriers

- **A. Volume and weight**
- **O. Hydrogen boil-off**

## Targets

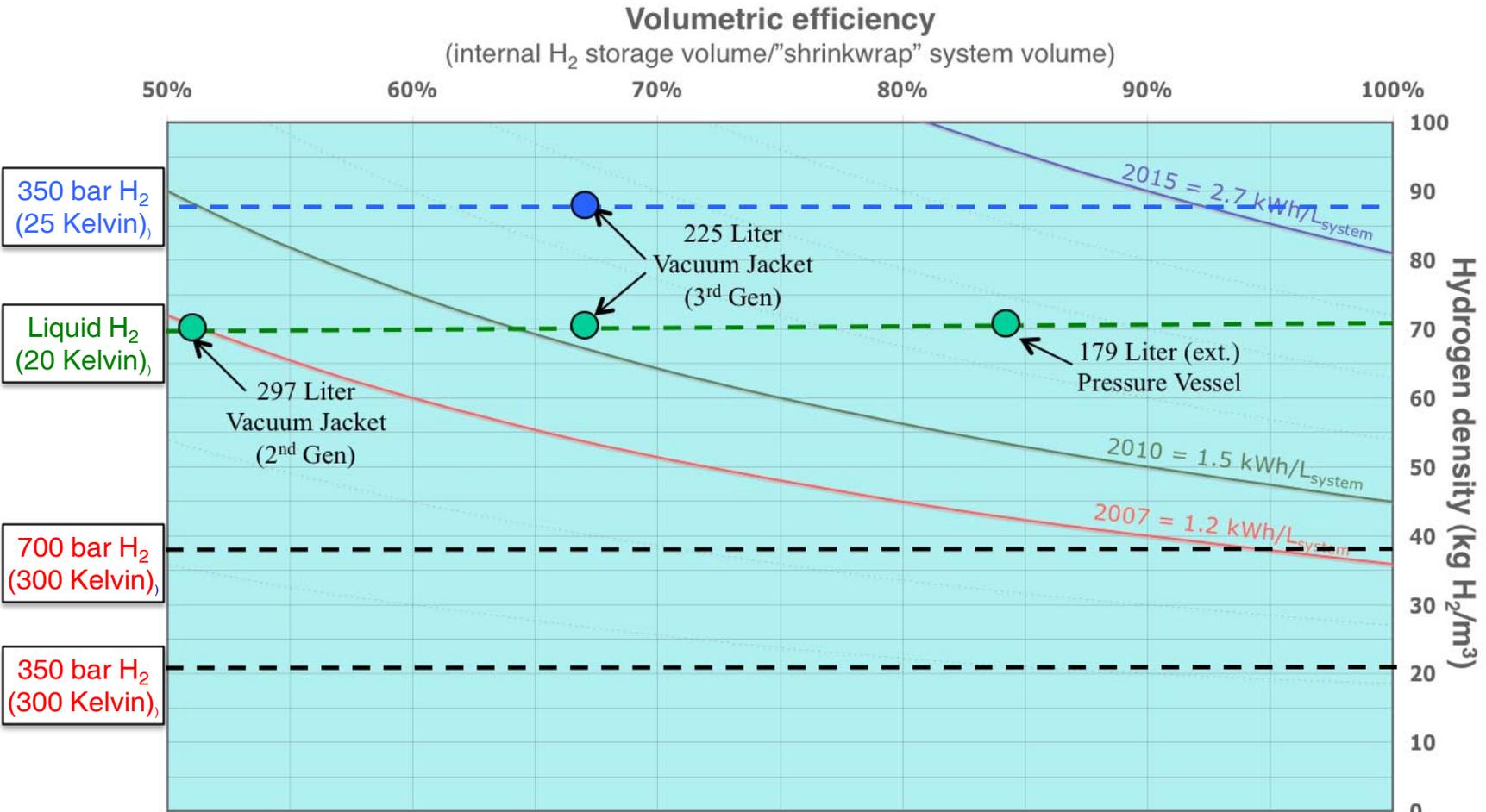
- **2010 DOE volume target**
- **2010 DOE weight target**

## Partners

- **CRADA** with BMW
- **CRADA** with Structural Composites Industries (SCI)



# Relevance: Cryogenic pressure vessels offer technical potential to exceed 2010 H<sub>2</sub> storage goals, and approach 2015



**Approach: Build systems exceeding 2010 volume/weight targets in collaboration with industrial partners understand fundamental potential of *both* system & H<sub>2</sub> behavior**



- *Fabricate third generation cryotank storing >45 kg H<sub>2</sub>/m<sup>3</sup><sub>system</sub>*
- *Achieve >1 week of dormancy*
- *Understand dormancy impacts of para-ortho conversion*
- *Investigate composite vessel impacts on vacuum quality*
- *Demonstrate adequate cycle life, (cryogenic shock, high pressure)*
- *Cryogenic vessel development and burst testing*
- *Explore **superliquid** H<sub>2</sub> ( $\rho > 70 \text{ kgH}_2/\text{m}^3$ )*



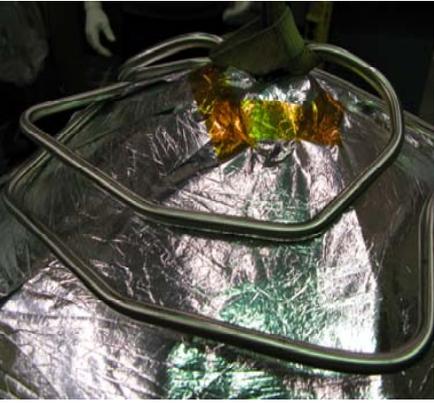
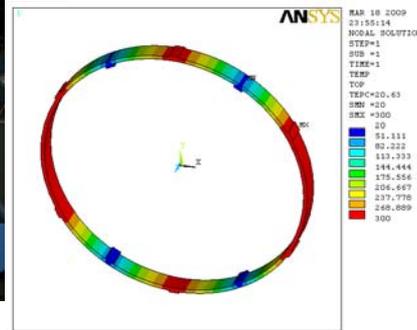
## Collaborations:

We have entered into cooperative research & development (CRADA) agreements with an automaker and pressure vessel manufacturer

- ***CRADA with BMW*** collaboration has been intensifying over 3 years. CRADA finalized June 2008 to investigate vacuum stability, conduct cryogenic pressure cycling, and study conversion to *ortho*-H<sub>2</sub>. BMW provides great automotive focus to our experimental and demonstration efforts.
- ***CRADA with Structural Composites Industries (SCI)***: Jan. 2009 CRADA formalized a longstanding relationship in high pressure and H<sub>2</sub> work of over two decades. Using LLNL's thermal/mechanical analysis capability and H<sub>2</sub> experience as well as SCI's in-depth composite cylinder design & manufacturing expertise to develop highly efficient and lower cost pressure vessels designed specifically for cryogenic H<sub>2</sub> storage.



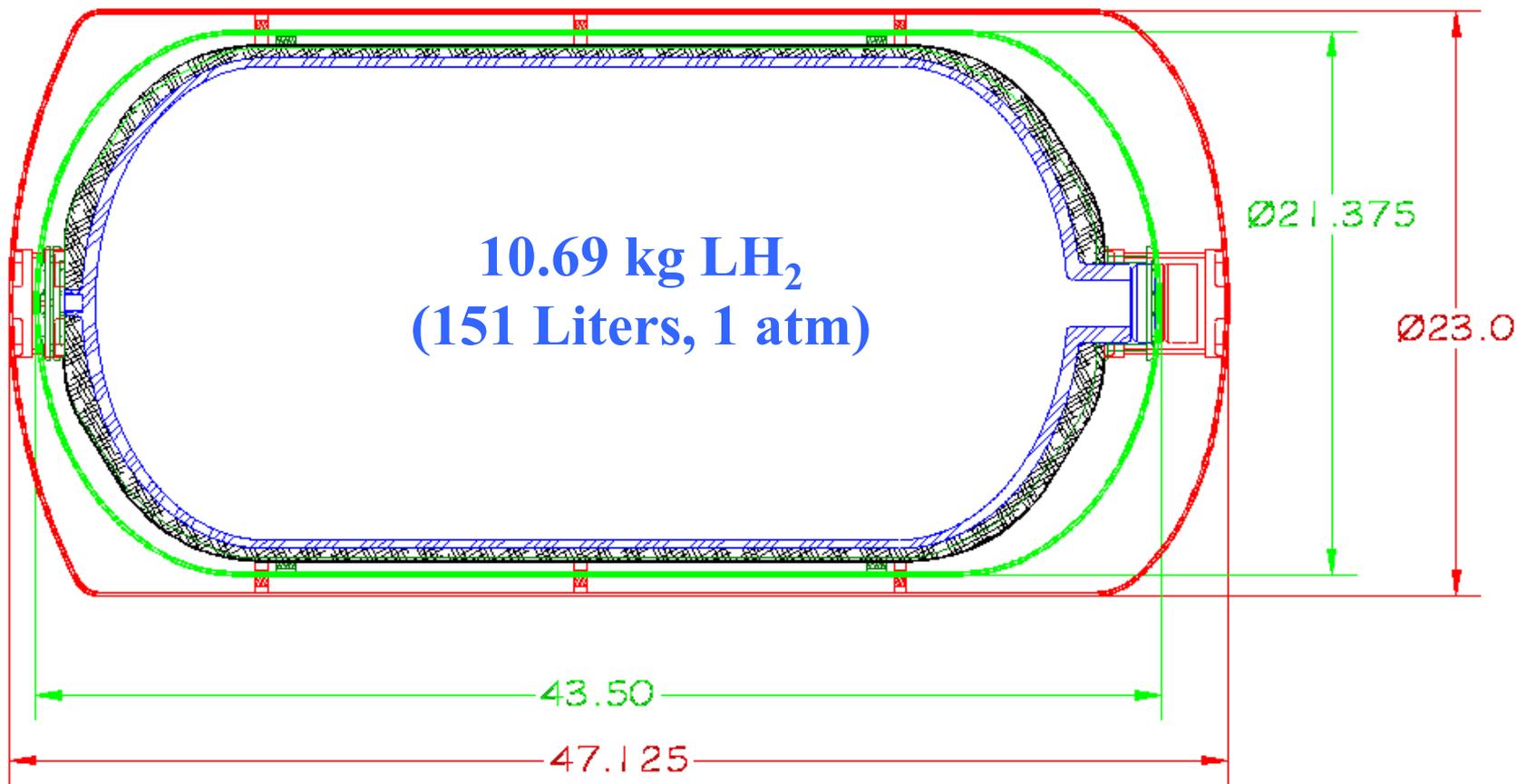
# We have refined our 3<sup>rd</sup> generation system to meet/exceed 2010 volume and weight targets



- Lighter, smaller vessel (4000 psi)
- Shorter, stronger boss (18,000+psi)
- Longer conduction paths (H<sub>2</sub> lines)
- Fewer support rings (3 to 2)
- Vacuum thickness cut by 2/3
- Less MLI layers in complex areas
- 3kW internal heat exchanger (BMW)
- LH<sub>2</sub> fill valve outside vacuum jacket
- Proof tested to 6600 psi
- Fabrication/integration complete
- System cryoshocked & leak tested
- Onboard dormancy test scheduled



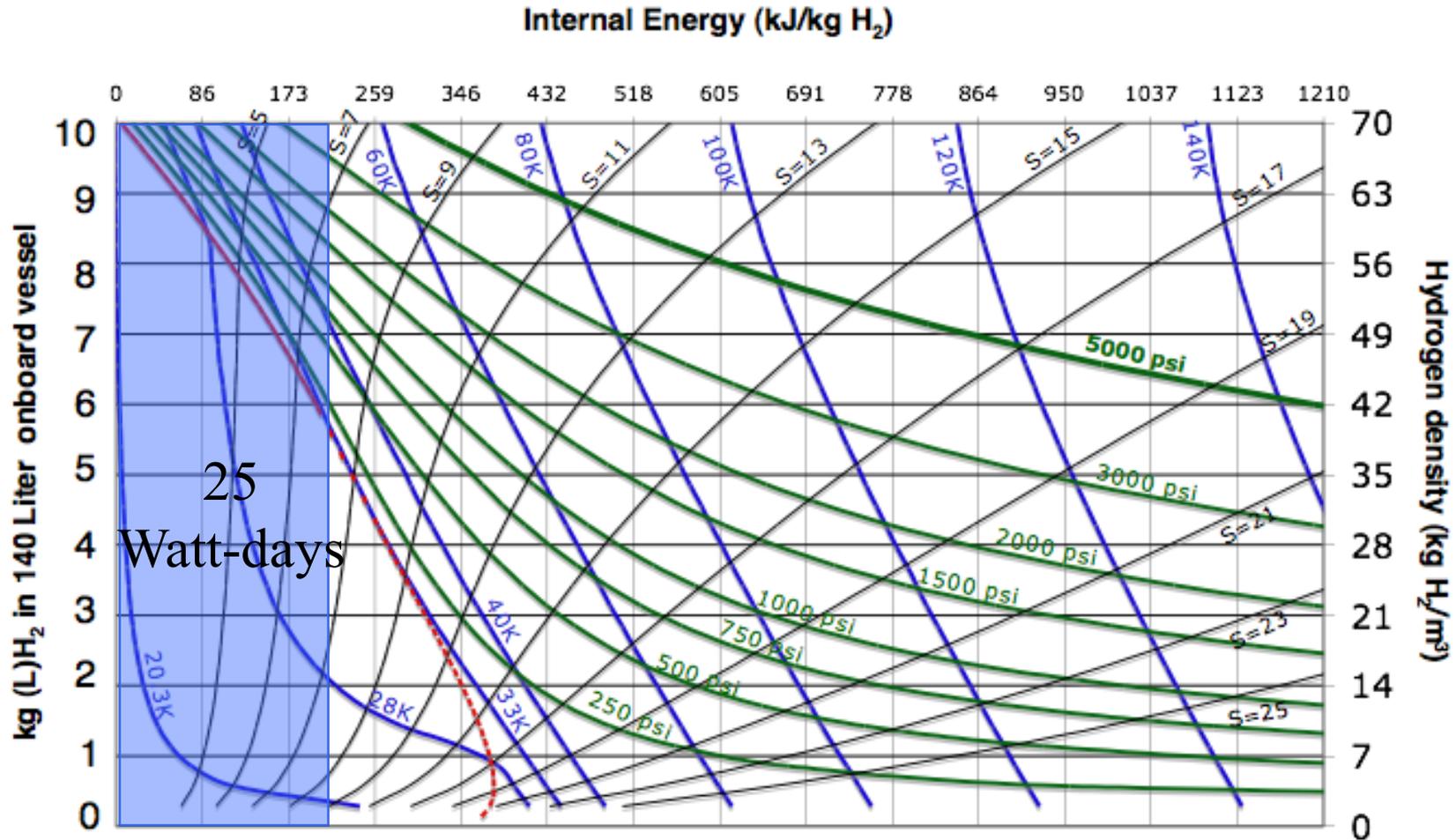
# 3<sup>rd</sup> generation cryotank & vacuum jacket saves 25 kg & 70 liters Storing 7.4 wt% H<sub>2</sub> at 45.2 kg H<sub>2</sub>/m<sup>3</sup>



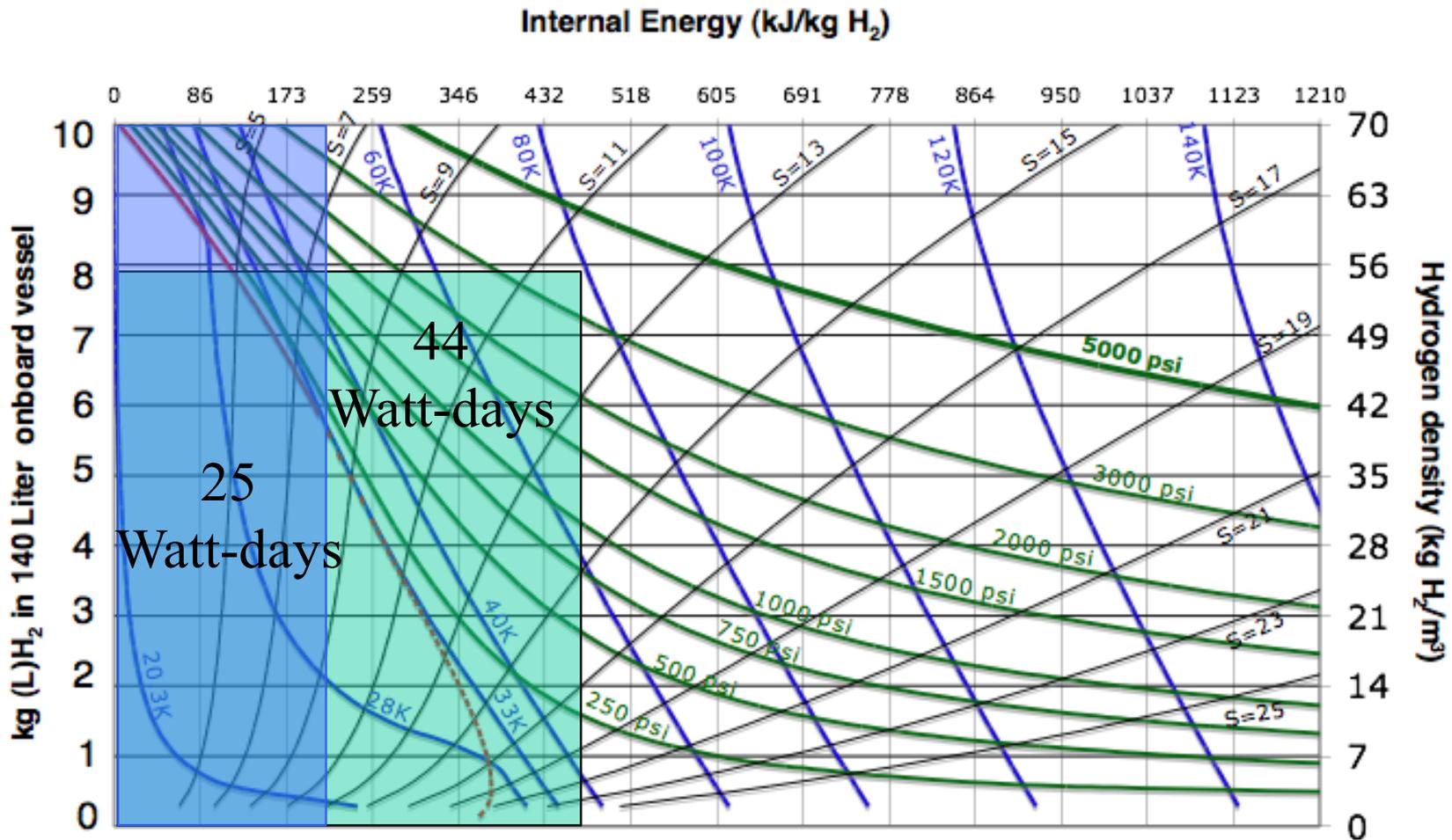
	<u>Weight (kg)</u>	<u>wt%<sub>H<sub>2</sub></sub></u>	<u>Volume (L)</u>	<u>kgH<sub>2</sub>/m<sup>3</sup></u>
4000 psi vessel+boss	60.9	14.9	179	59.7
Steel vacuum jacket	57.1	8.3	225.4	47.4
Ancillary components	16	<b>7.4</b>	11	<b>45.2</b>



# 3.5 day calculated dormancy of 10.7 kg LH<sub>2</sub> (full) in 3<sup>rd</sup> gen vessel (~7 watts, 4000 psi, H<sub>2</sub> heat capacity only)

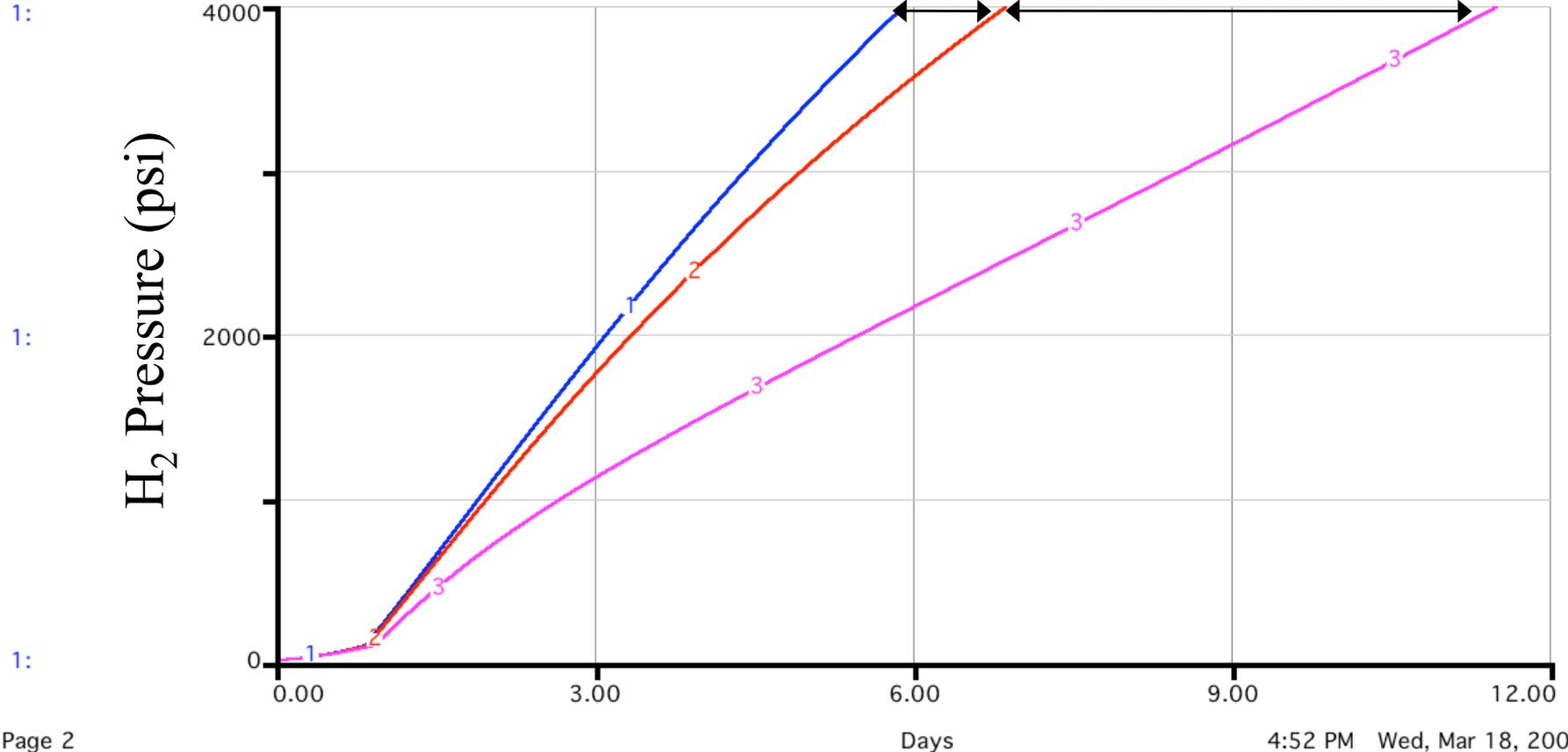


# 6.5 day calculated dormancy if 80% full w/LH<sub>2</sub> (7 Watts, 4000 psi, H<sub>2</sub> heat capacity only)



# Vessel warming combined with (theoretical) conversion to *ortho*-H<sub>2</sub> could extend dormancy of 8.55 kg LH<sub>2</sub> (80% full) to 11+ days

H2 Pressure: 1 - 2 - 3 -



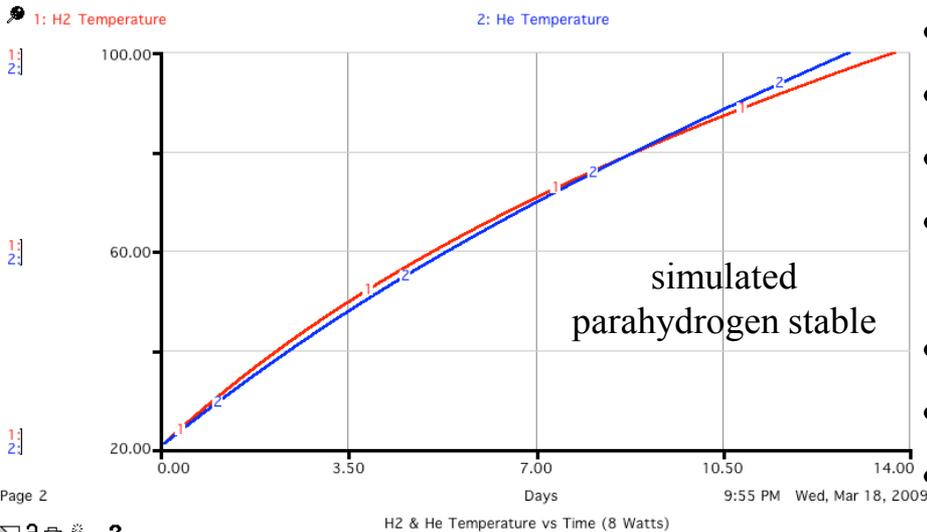
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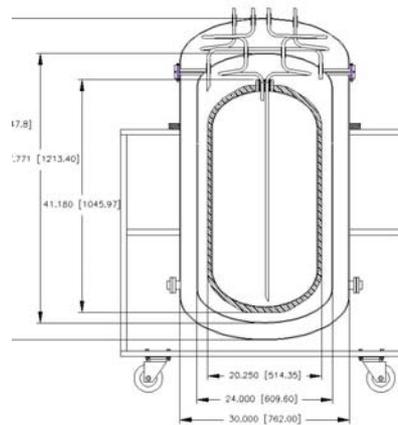
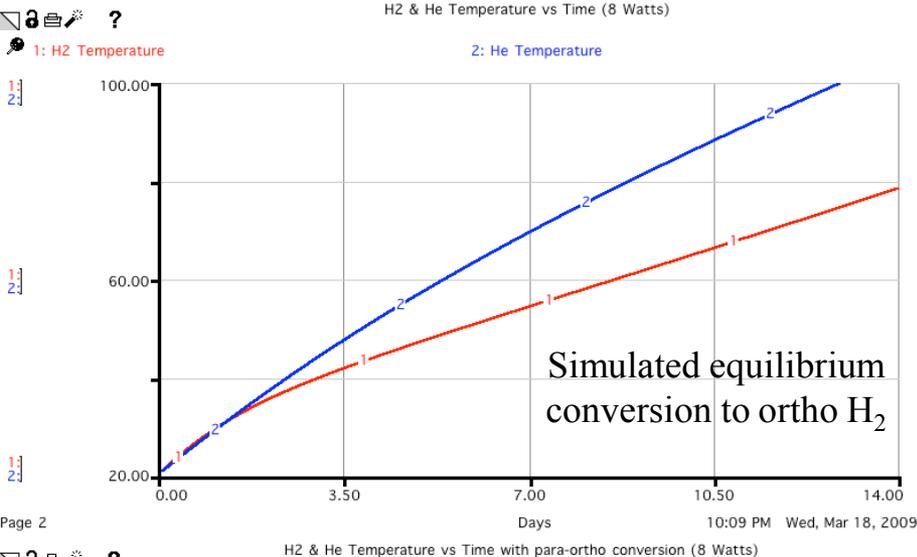
8.55 kg/7 Watt H<sub>2</sub> Pressure vs. Time with & without para-ortho conversion



# We will assess *para-H<sub>2</sub>* to *ortho-H<sub>2</sub>* conversion by experiments warming H<sub>2</sub> outside two-phase LH<sub>2</sub> region complemented by a surrogate test with He if warranted



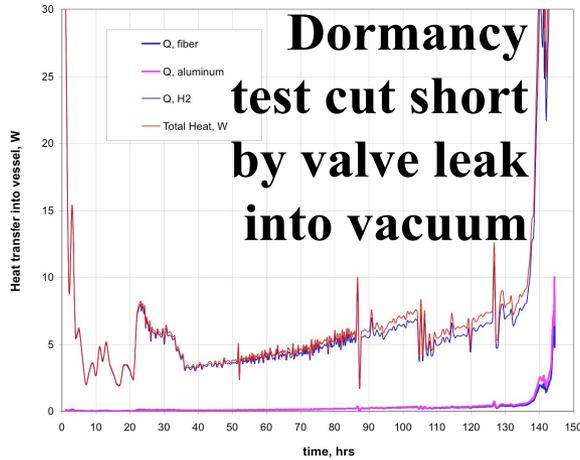
- Measure Weight, Pressure, & Temperature
- Integrated (20-100K) test and/or fixed T
- Results interpretable w/o vessel corrections
- Aggregate *para-ortho* conversion impact directly measured by He surrogate test
- Full scale (163 L) test & expt. range (T,P, ρ)
- 10 ksi vessel w/ coolant & vacuum jacket
- Hardware capability to confirm/reverse *para-ortho* conversion at automotive scale



- Collaborating with BMW on experimental strategy, methodology
- Exp't simulations use real properties of all L(H<sub>2</sub>) states, phases



# Outgassing experiments on as received 1 liter composite vessel: H<sub>2</sub>O majority component, hydrocarbons not improved by baking



**Dormancy test cut short by valve leak into vacuum**

Compound (and boiling point)	Concentration in parts per billion by vol.					
	Ambient		60°C		82°C	
	First test No cycling	2 <sup>nd</sup> test 10 cycles	First test No cycling	2 <sup>nd</sup> test 10 cycles	First test No cycling	2 <sup>nd</sup> test 10 cycles
Water (100°C)	80,000	4,000	350,000	4,500	300,000	5,500
Acetaldehyde (20.2°C)		23	230	22,000	1500	11,000
Acetone, (56.5°C)	85	74	1100	23,000	8300	19,000
Ethanol, (78.4°C)	87	29	800	97	4500	3000
Isopropyl alcohol (83.6°C)	23	17	110		690	
Trichloroethylene (87.2°C)	6.2	9.2	4.1			
1-propanol (97.1°C)			360	120	2400	
Toluene (110.6°C)			2.7		14	
Acetic acid butyl ester (126°C)	47	260	2900	2900	8200	9500
Ethyl benzene (136°C)	4.7	6.5	120	52	700	210
Xylenes, total (140°C)	20	30	430	240	2500	1000
Styrene (145°C)	5.9	8.7	110	70	630	290
2-heptanone (151°C)	39	530	4800	2900	12,000	25,000
1, 3, 5 trimethylbenzene (164°C)	1.7	1.1	20	8.5	91	120
1, 2, 4 trimethylbenzene (169°C)	1.9	1.6	39	11	180	130
<b>Total hydrocarbons</b>	<b>321</b>	<b>990</b>	<b>11,026</b>	<b>51,490</b>	<b>41,705</b>	<b>69,250</b>
<b>Total</b>	<b>80,321</b>	<b>4990</b>	<b>361,026</b>	<b>55,890</b>	<b>341,705</b>	<b>74,750</b>

**Oven in pressure cell**



**1 liter vessel under vacuum in oven**

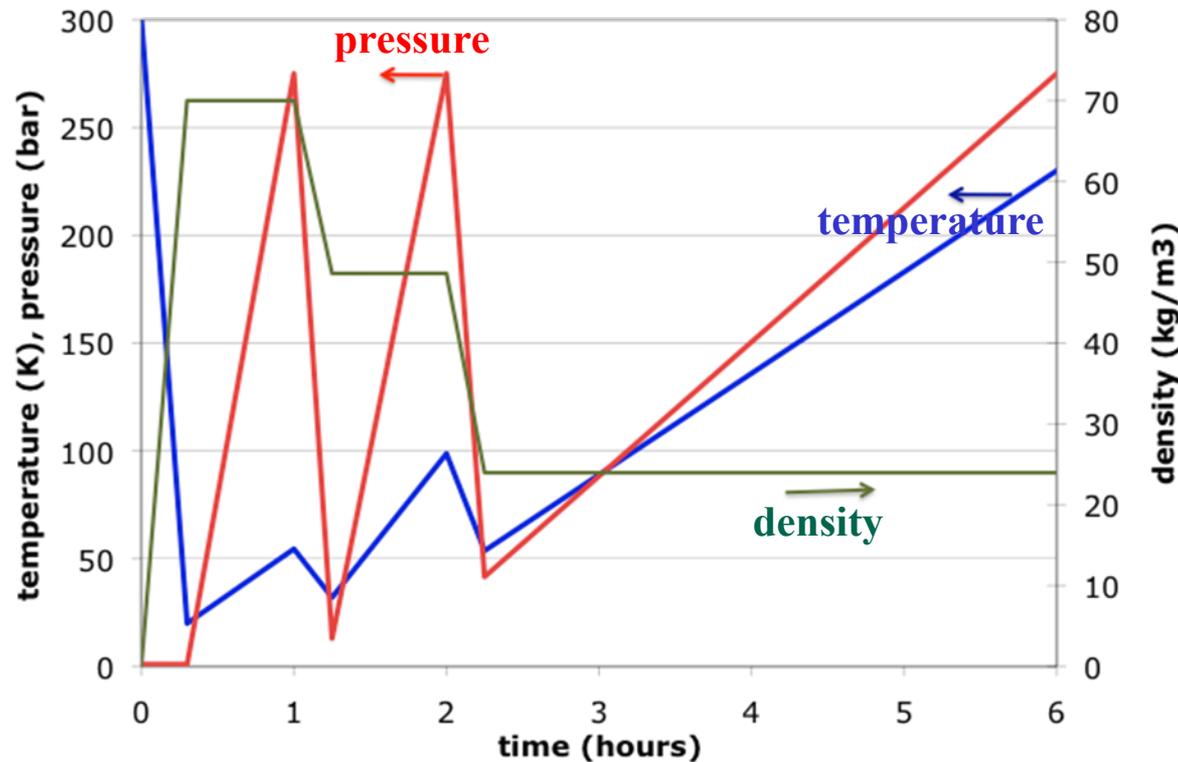


# Outgassing experiments have been planned in collaboration with BMW to separate pressure cycling (Ar) from thermal effects and investigate vessel processing and surface treatments

- *Pre-bake vessels to 100°C:* Determine if H<sub>2</sub>O can be essentially eliminated.
- *Cycle vessels slowly or with cooled gas:* Keeping vessels at ambient temperature (or below) better represents expected onboard conditions.  
Measurements after 10 & 100 pressure cycles
- *Outgassing from vacuum cured vessels with/without UV coating:* Investigate processing effects on outgassing, and potential cycling effects on coatings



# A 4000 psi vessel identical to the 3<sup>rd</sup> generation storage system will be cryogenically cycle tested



- High & Low Pressure at Cryogenic T (20-100 Kelvin)
- Vacuum jacketed vessel warmed internally (2-5 kW)
- Ultrasound characterization after hundreds of cycles



# We will acquire a high pressure cryogenic H<sub>2</sub> fueling capability



- *We currently fill at low pressure* from a conventional LH<sub>2</sub> storage vessel
- *A high pressure LH<sub>2</sub> pump* offers rapid single phase refueling without boiloff
- *Site Permission and Utilities granted*  
Will also serve for high pressure cryogenic H<sub>2</sub> testing (e.g. *para-ortho*)
- *We plan to explore densities beyond LH<sub>2</sub>* to meet DOE's ultimate storage goals. Pressurized LH<sub>2</sub> is up to ~25% more compact and needs to be studied, tested, and ultimately demonstrated onboard



## Pressure vessel designs can be improved by accounting for vessel usage

**6250 psi H<sub>2</sub>, 350 K**

**Safety factor = 2.25**

***Fill* safety factor = 1.8**

### **Current automotive H<sub>2</sub> vessel**

- Filled with H<sub>2</sub> at up to 80°C
- Service pressure: 5000 psi
- Fill pressure: 6250 psi
- Burst pressure: 11,250 psi

**5000 psi H<sub>2</sub>, 25-50 K**

**Safety factor = 1.8**

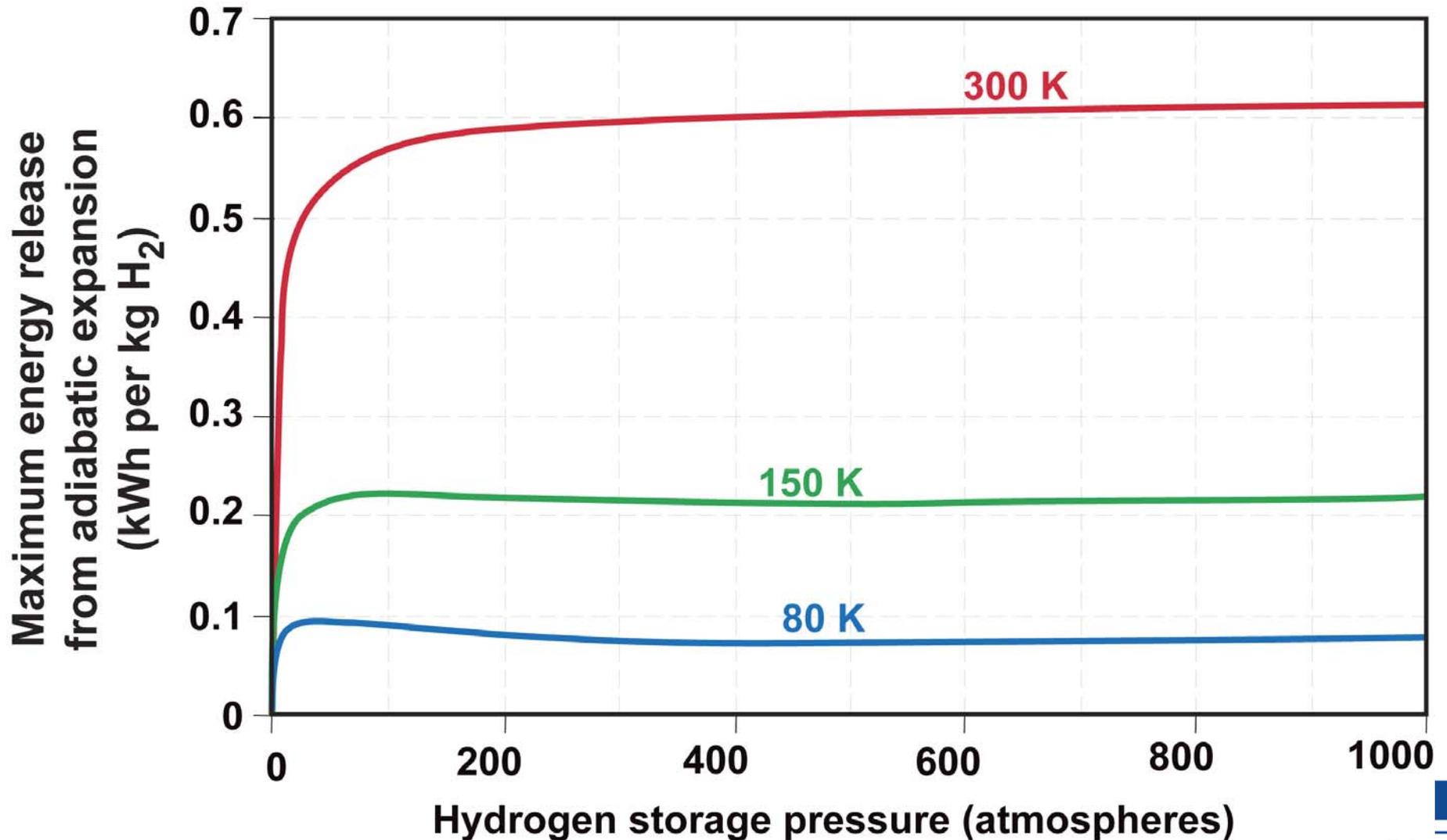
***Fill* safety factor = 1.8**

### **Future automotive cryo-H<sub>2</sub> vessel**

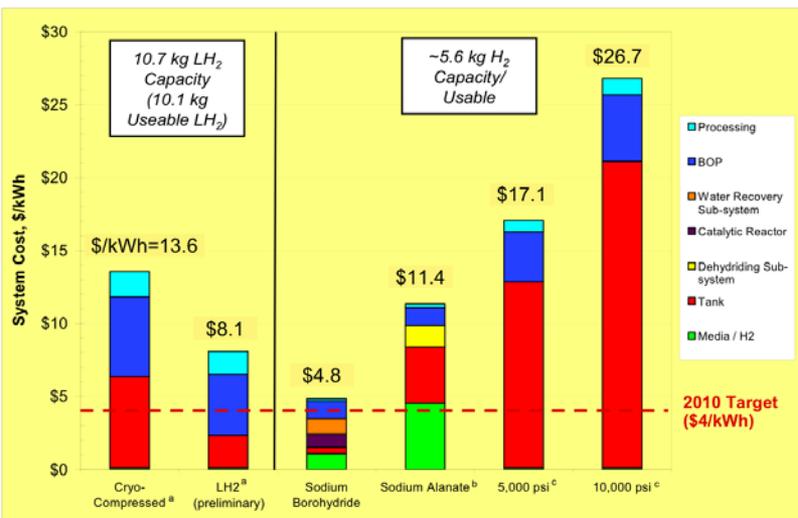
- Filled only with cold H<sub>2</sub>
- Service pressure: 5000 psi
- Fill pressure: 5000 psi
- Burst pressure: 9,000 psi



# Cryogenics offers dramatic safety opportunities: cooling H<sub>2</sub> *removes* far more burst energy than reducing pressure



# Cryogenic pressure vessel systems will be less expensive than ambient compressed H<sub>2</sub> storage for fundamental reasons



Source: TIAX

- *Compact LH<sub>2</sub> (71 vs. 23-39 kgH<sub>2</sub>/m<sup>3</sup>) cuts carbon fiber (per kg H<sub>2</sub> stored)*
- *Pressurized LH<sub>2</sub> even more compact ('top off' potential up to 88 kgH<sub>2</sub>/m<sup>3</sup>)*
- *Cryogenic H<sub>2</sub> in protective vacuum jacket may enable glass fibers to provide more value than carbon*
- *Very low burst energy, no fast fill overpressure, secondary containment of vacuum jacket could justify lower burst pressure ratio ( $P_{burst}/P_{dormancy}$ ), improving pressure vessel mass, volume, and structural efficiency*

- SCI cryotank (350 bar) cost estimates (per kgH<sub>2</sub> stored):
- 30% less vs. ambient 350 bar
- 60% less than 700 bar



## Future work: after demonstrating superior weight and volume of cryogenic pressure vessels and adequate cycle life, study a spectrum of H<sub>2</sub> states and flexible pressure vessel systems

- ***Pressurized LH<sub>2</sub>*** offers fertile ground for achieving ultimate DOE storage goals but requires new refueling strategies.
- ***Normal LH<sub>2</sub>*** if our *para-ortho* transition experiments measure slow kinetics then we plan to investigate “normal” LH<sub>2</sub> (25% *para*) in cryotanks, anticipating liquefaction capital cost & energy savings.
- ***Multiple Volume Vessels*** offer flexible blend of capacity, weight, cost, shape, and dormancy over a single state H<sub>2</sub> storage vessel, but multiple states of onboard H<sub>2</sub> adds complexity.



## Summary

- *Cryogenic pressure vessels can exceed 2010 DOE storage targets* for weight and volume, with promising dormancy & cost relative to conventional LH<sub>2</sub> tanks and ambient pressure vessels
- *In collaboration with industrial partners, we are addressing interactions between pressure, temperature, and materials.* Outgassing, cryogenic cycling, and cryogenic burst tests
- *We are investigating fundamental operational aspects at full scale:* internal heat exchange, dormancy and dormancy recovery, *para-ortho* conversion, higher density (pressurized) refueling
- *Safety advantages of cryogenic pressure vessels are yet to be assessed.* Very low burst energy, fill vs. dormancy safety factor, protective vacuum jacket, material strength at cryogenic temps

