

Advancement of Systems Designs and Key Engineering Technologies for Materials Based Hydrogen Storage

**Bart A. van Hassel , J.M. Pasini, R.C. McGee,
J.R. Karra, A.M. Limarga, J. Holowczak,
I. Fedchenia, J. Khalil, J.C. Rampone and R. Brown**

United Technologies Research Center



DOE Hydrogen Program

Annual Merit Review

Washington, DC

May 15, 2012

Project ID: ST006



Overview

■ Timeline

- Start: February 2009
- End Phase 1: March 2011
- End Phase 2: June 2013
- End Phase 3 / Project: June 2014
- Percent complete: 55% (spending)

■ Budget

- \$5.91M Total Program
 - Reflects budget reduction with \$0.95M
 - \$4.58M DOE
 - \$1.33M (22.5%) UTRC
- FY09: \$600k DOE
- FY10: \$1,000k DOE
- FY11: \$750k DOE
- FY12: \$750k DOE

■ Barriers*

- A – J
- A. System Weight & Volume
- D. Durability/Operability
- J. Thermal Management

■ Targets*

- All

■ Partners



* DOE EERE HFCIT Program Multi-year Plan for Storage

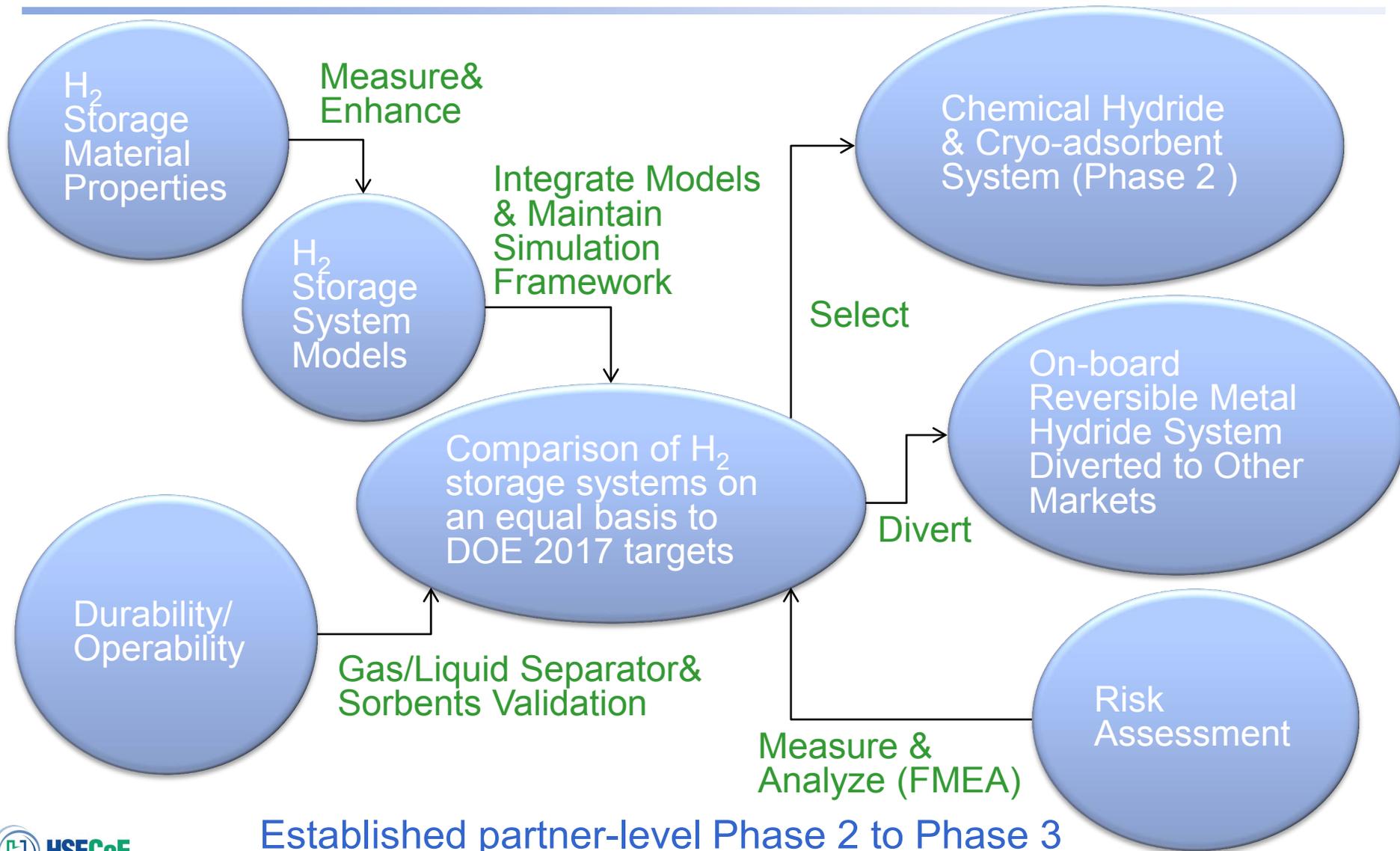
Objectives

- Design of materials based vehicular hydrogen storage systems that will allow for a driving range of greater than 300 miles

Performance Measure	Units	2010	2017	Ultimate
System Gravimetric Capacity	g H ₂ /kg system	45	55	75
System Volumetric Capacity	g H ₂ /L system	28	40	70
System fill time (for 5 kg H ₂)	minutes	4.2	3.3	2.5
Fuel Purity	% H ₂	SAE J2719 guideline (99.97% dry basis)		

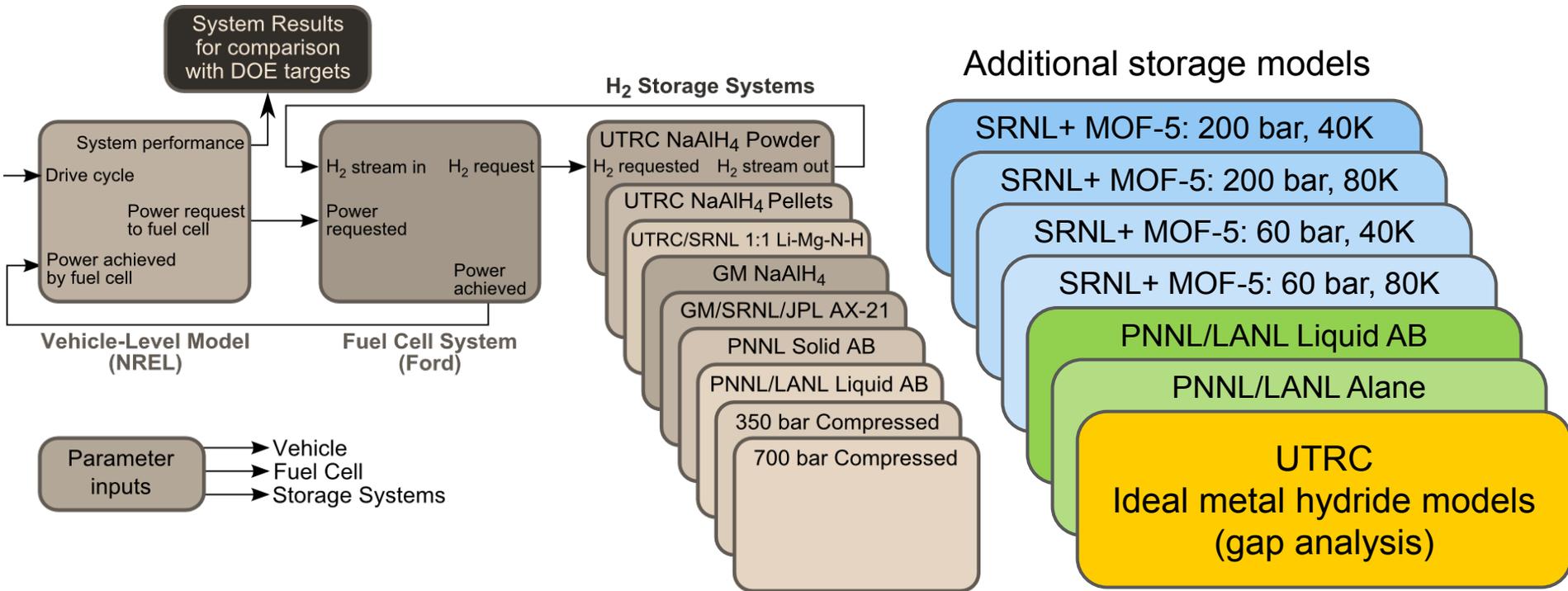
- Major project impact:
 - Integrated Power Plant Storage System Modeling:
 - Specified on-board reversible metal hydride material requirements. Diverted such a system to different markets.
 - UTRC oversees modeling framework on consistent platform
 - Gas/Liquid separation (GLS) of liquid chemical hydride
 - H₂ quality (NH₃ adsorbent, particulate filter)
 - Compaction/Materials thermal conductivity enhancement
 - Risk Analysis: Failure mode and effect analysis (FMEA)

Approach

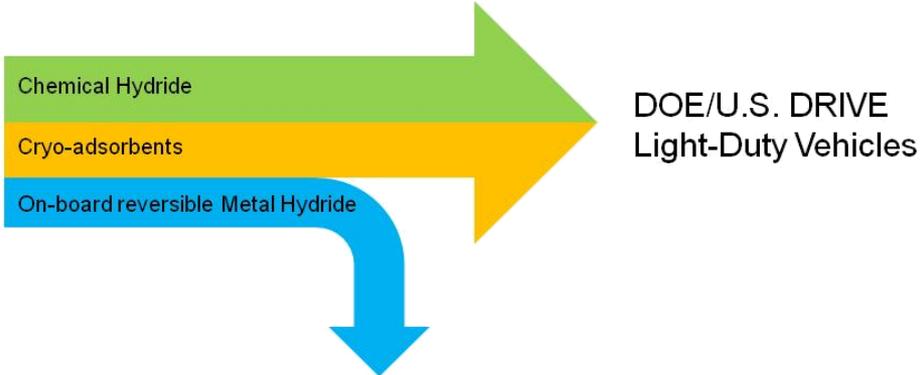


Established partner-level Phase 2 to Phase 3 transition criteria in updated SOPO

IPPSSM Framework Application



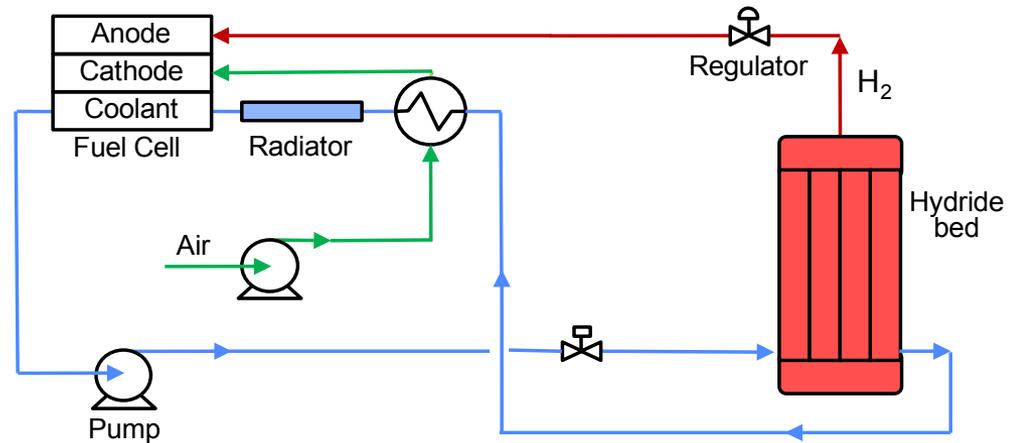
Quantitative comparison of H₂ storage systems on a common basis achieved by team effort



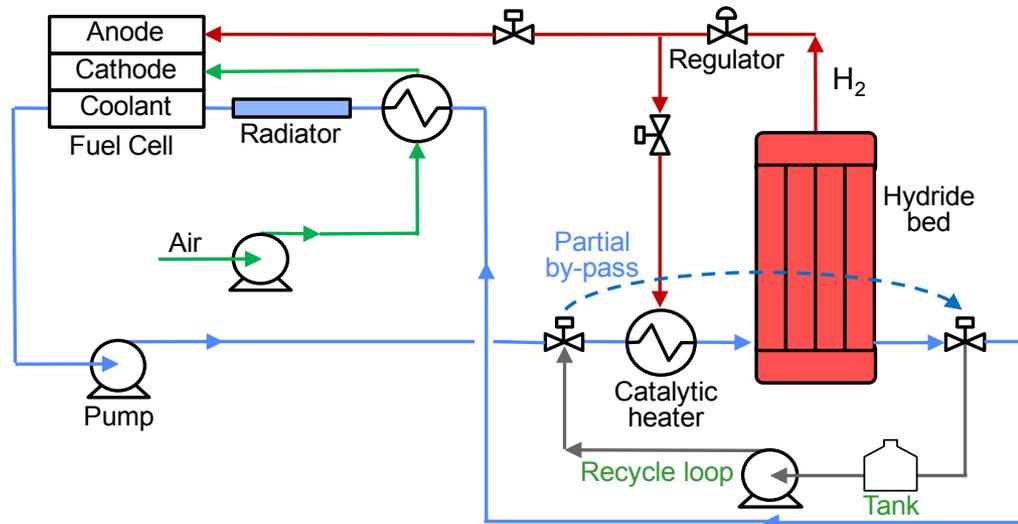
On-Board Reversible Metal Hydrides Diverted to Different Markets

Two qualitatively different systems:

- For higher H_2 pressure materials: use the **fuel cell waste heat** stream
- Very simple system: selected to determine the minimum material gravimetric capacity needed.
- No separate buffer tank: use H_2 in pores.

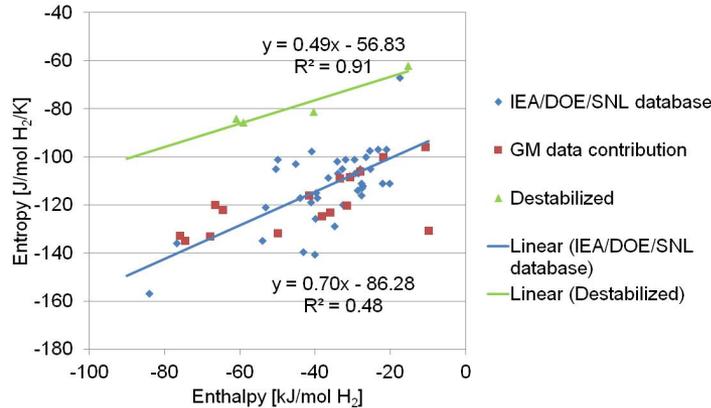


- For lower H_2 pressure materials: Mix of fuel cell coolant, **catalytic heater** and recycled fluid used for warm-up and to maintain T_{tank} .
- Increased material capacity to compensate for combusted H_2 and heavier BOP.
- No separate buffer tank: use H_2 in pores.



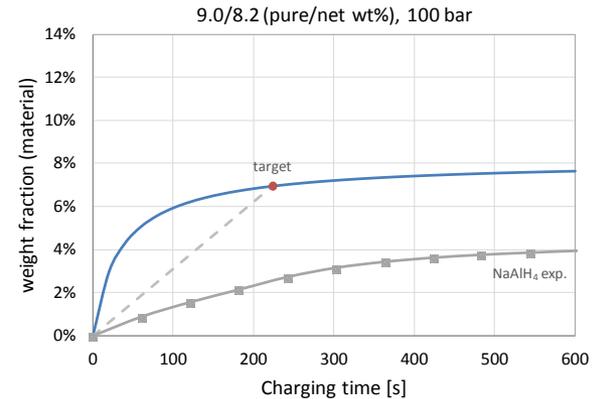
Analysis anchored in metal hydride databases

Thermodynamic Properties



Equilibrium pressure: fit ΔS vs ΔH

Kinetics



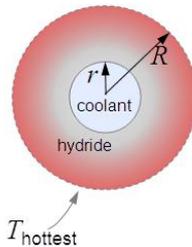
85% of capacity in 3.3 minutes

Heat Transfer (Acceptability Envelope)

heating rate per unit volume

$$\dot{Q} = \left(\frac{-\Delta H}{w_{H_2}} \right) \left(\frac{\Delta m_{H_2}}{\Delta t} \right) \left(\frac{M_{\text{hydride}}}{\rho_{\text{bed}}} \right)^{-1}$$

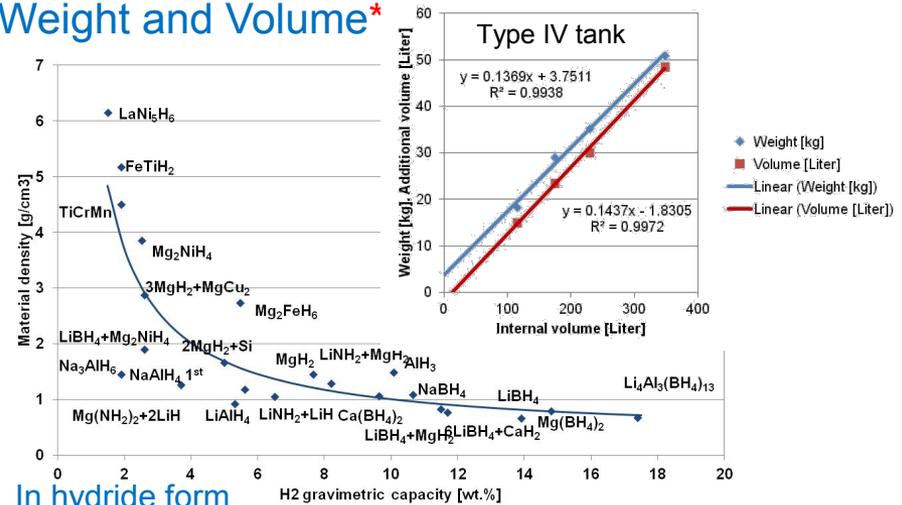
heat released per mass of H_2 absorbed
refueling rate
volume of hydride bed including voids



$$\Delta T = \frac{1}{8} \frac{\dot{Q}}{k} (R^2 - r^2) f(x) \quad 10 \text{ wt. \% ENG "worms", } \Delta T = 45^\circ\text{C}$$

Short fill time (3.3. minutes)

Weight and Volume*



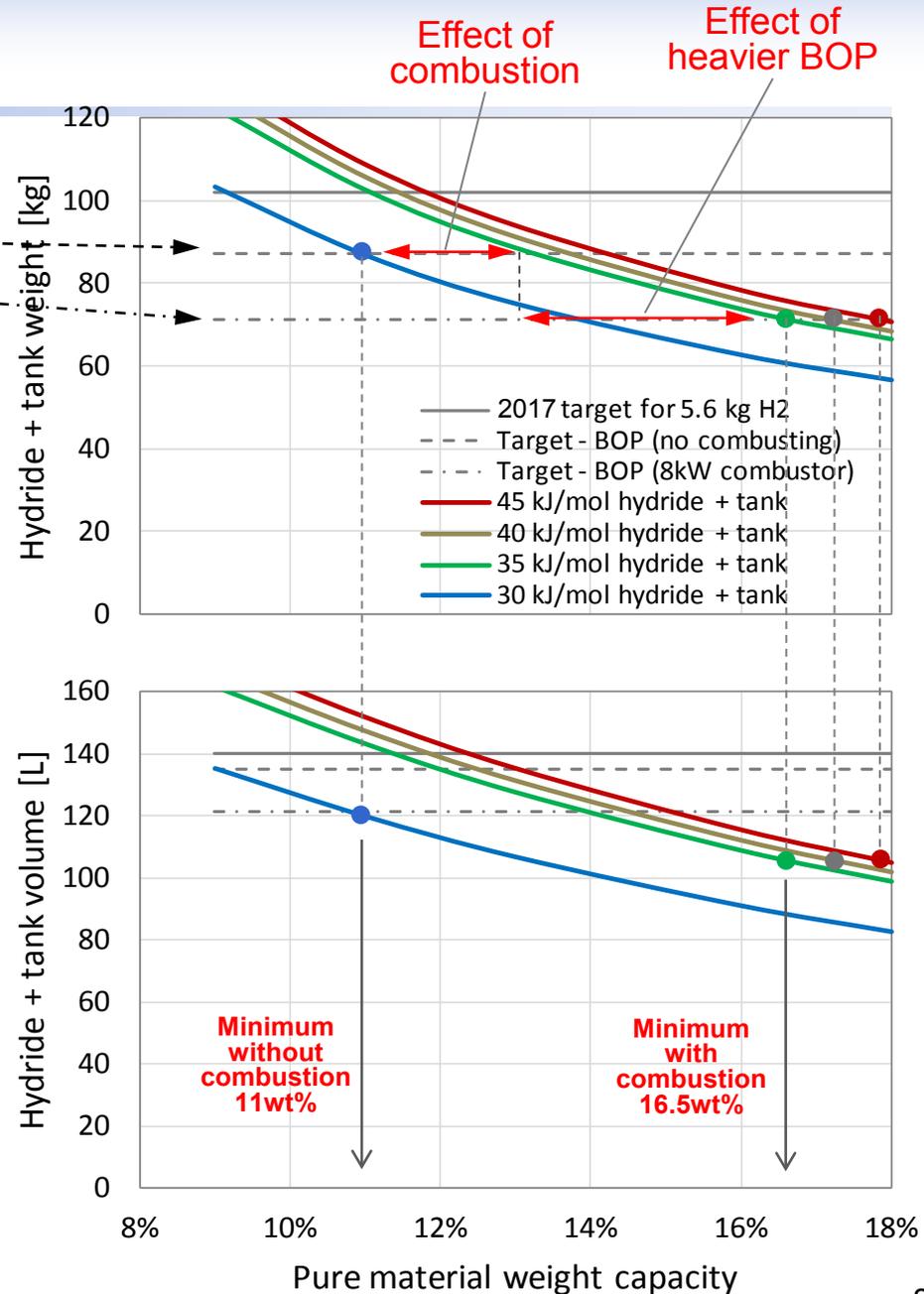
In hydride form

* Other parts from BOP Library (PNNL)

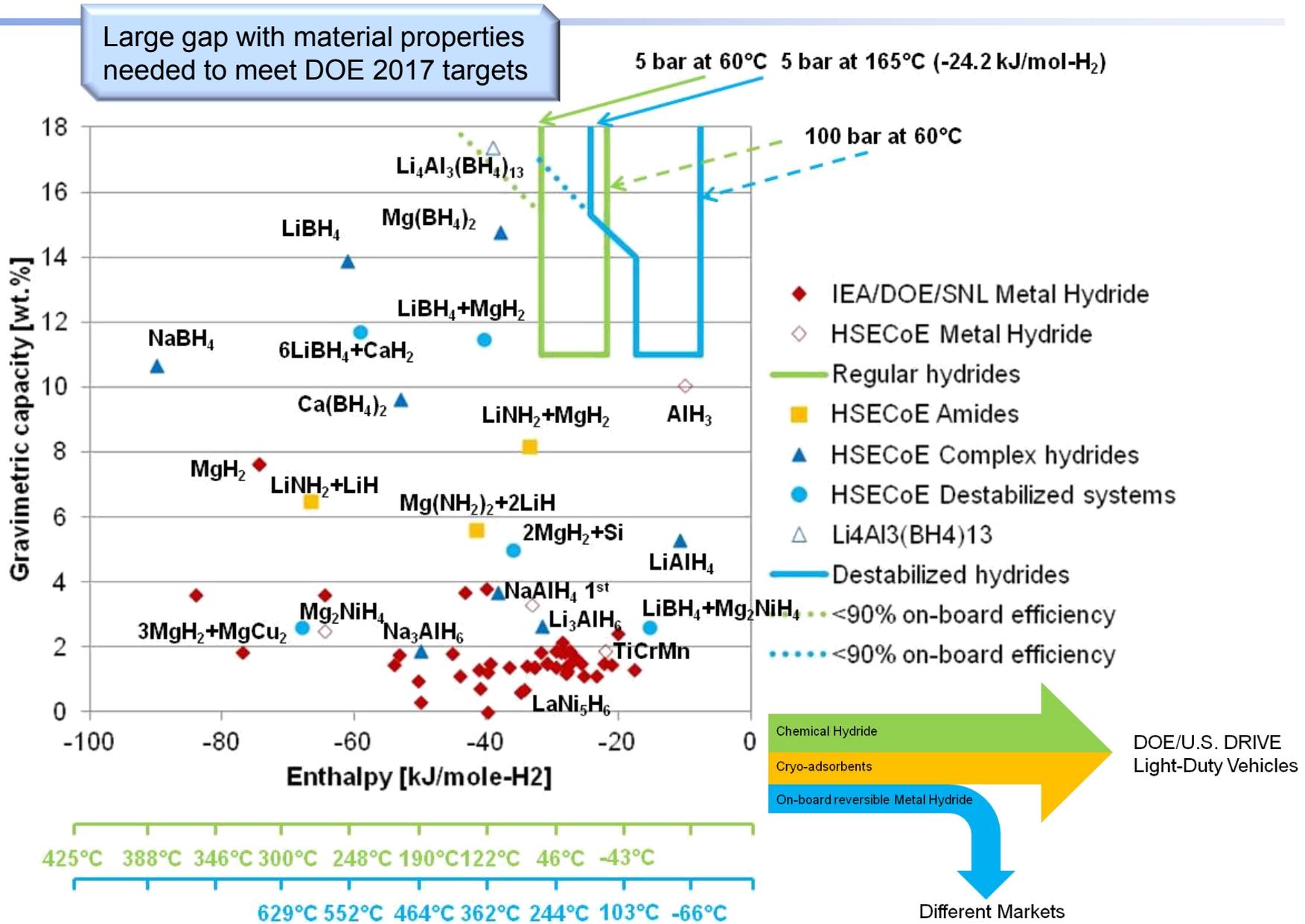
System weight and volume

- Allowable (hydride + tank) values
 - Using only waste heat
 - With a 8kW combustor loop

- On-board reversible metal hydride:
 - Systems are limited by weight
 - Waste heat from fuel cell:
 - $\Delta H < 27$ to 32 kJ/mol (depends on drive cycle); >11 wt.%
 - Combustor loop:
 - $\Delta H > 27$ to 32 kJ/mol (depends on drive cycle); >16.5 wt.% due to BOP weight increase and H₂ combustion



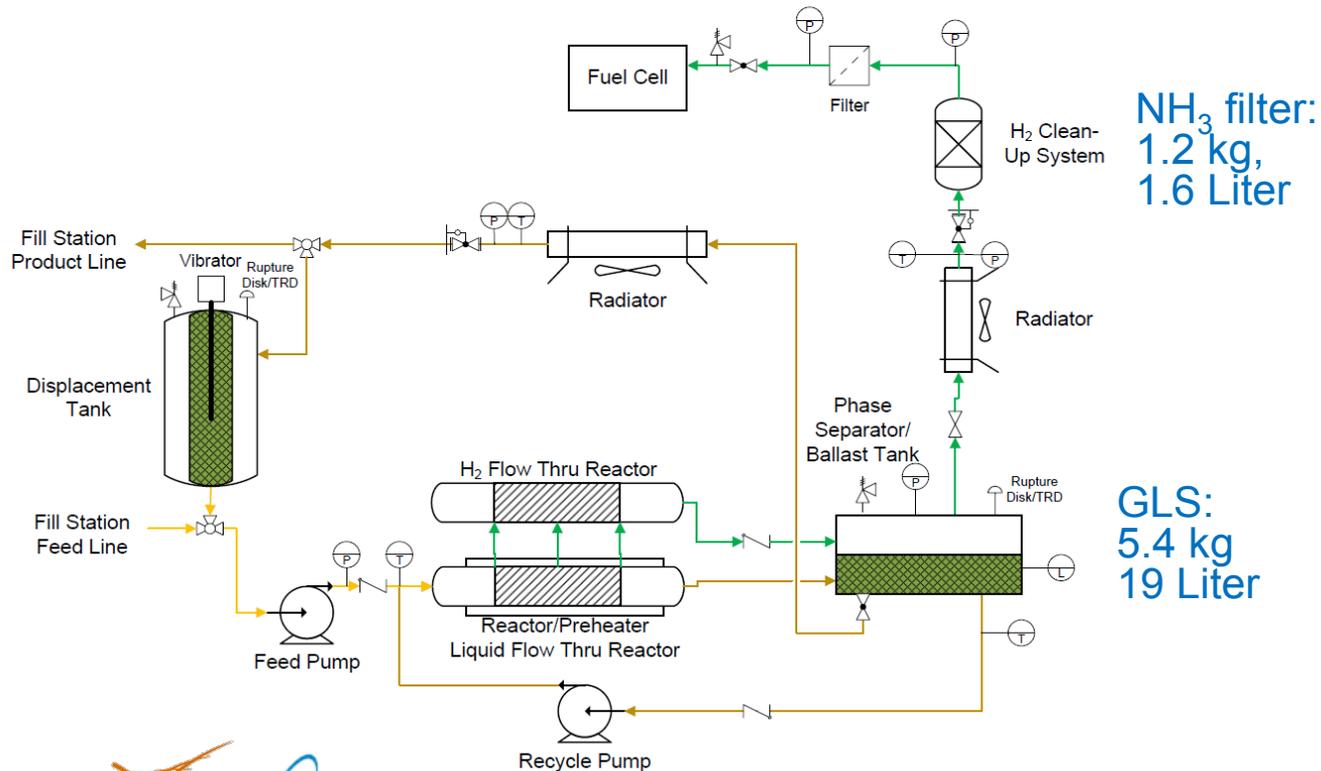
Available metal hydride materials vs. requirements



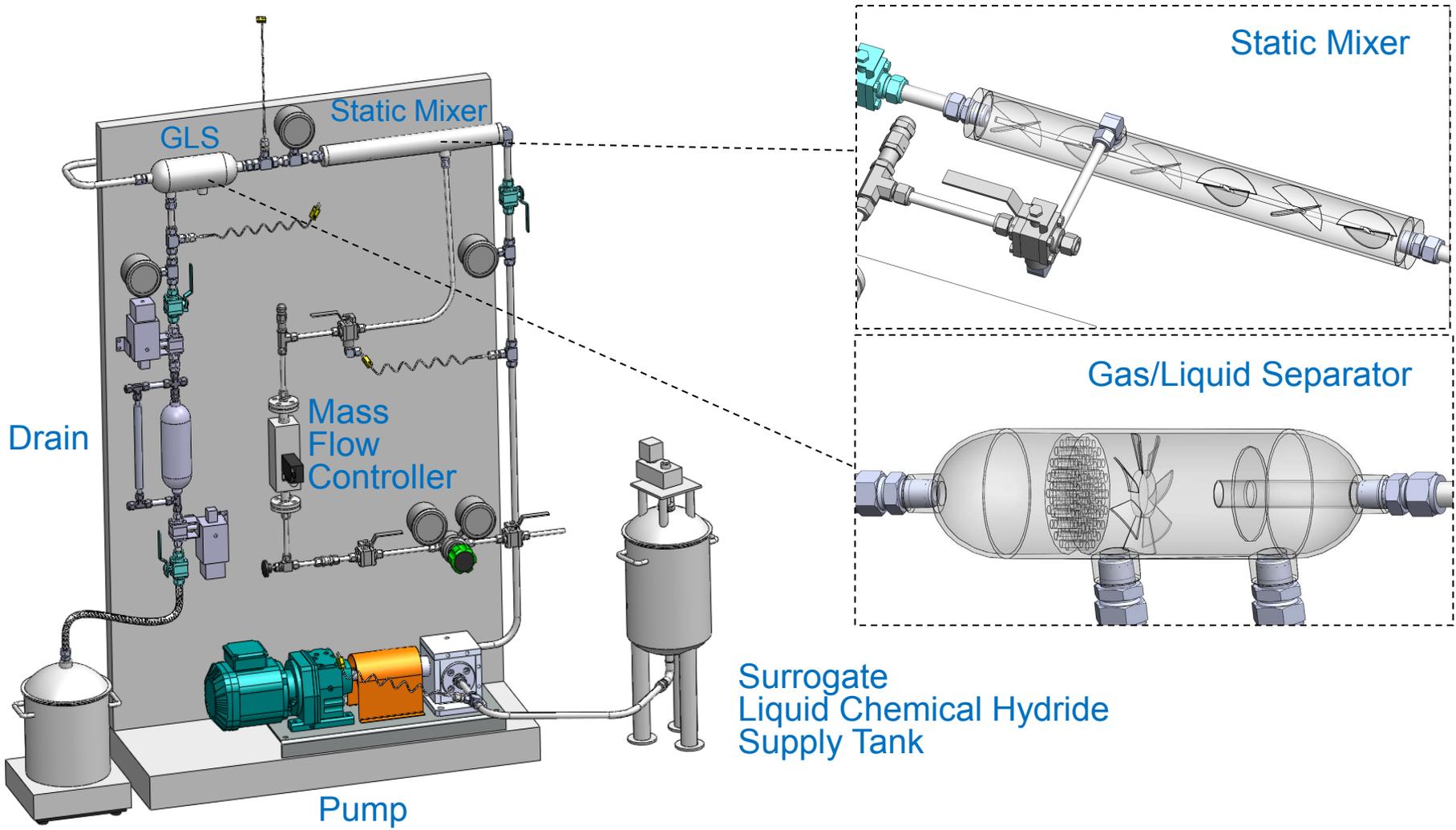
Liquid Chemical Hydride Operability (GLS Validation)

- Hydrogen gas must be separated from the liquid spent fuel following the exothermic thermolysis of ammonia borane.
- Designed gas-liquid separator (GLS) test system.
- UTRC: Surrogate fluid; LANL&PNNL: Engineering fluid form of AB

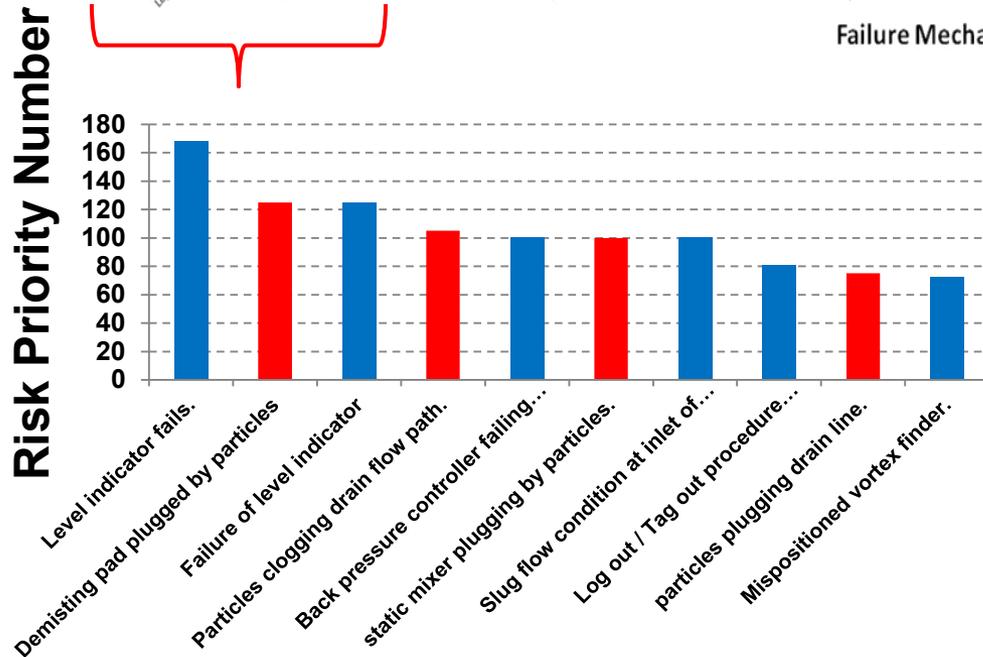
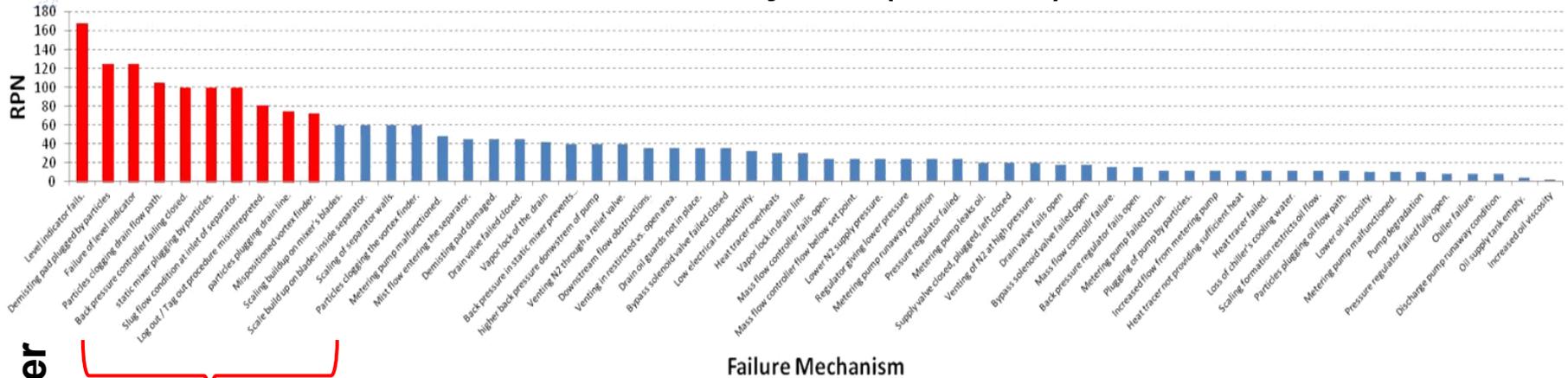
Chemical Hydride Storage and Reaction System
February 1, 2012



Gas-Liquid Separation Test Facility



Gas/Liquid Separator (GLS) Test Rig Failure Mode and Effect Analysis (FMEA)



Failure Mechanism

- Plugging related issues
- Other failure modes

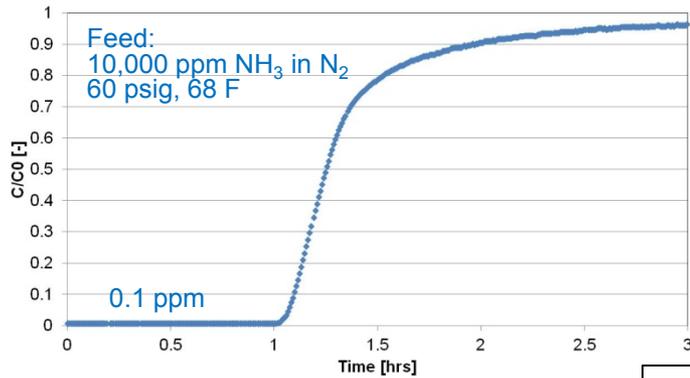
- Expected learnings from GLS tests:

- GLS risk factors
- Mitigation Strategies
- Efficiency
- Operability: Slurry pump, Heat exchanger, Gas Liquid Separator(s), Drain, Level Indicator, Plugging issues

- Supported FMEA of Cryo-adsorption and Chemical Hydride Systems in center wide team effort

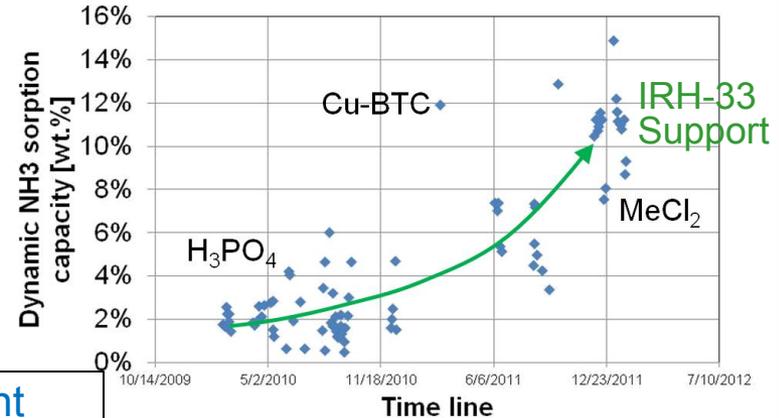
H₂ Quality (NH₃ Mitigation*)

Dynamic Breakthrough

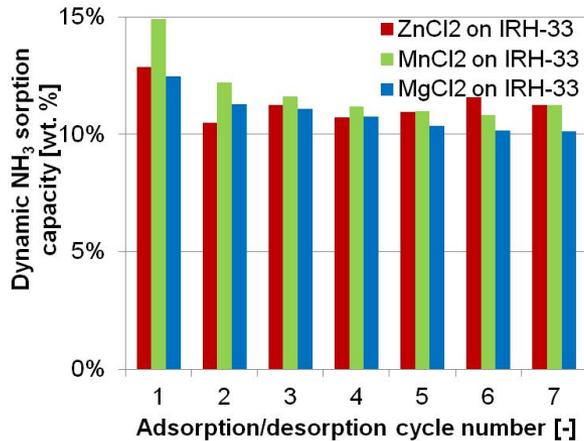


50 wt.% MnCl₂ on IRH-33

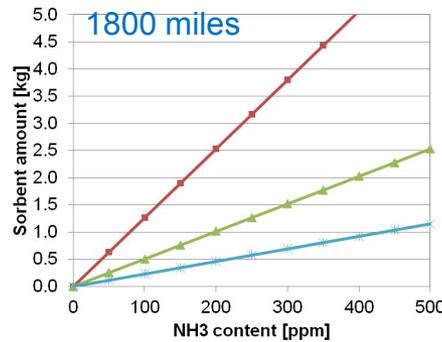
More Efficient Filter by Capacity Improvement



Regenerable

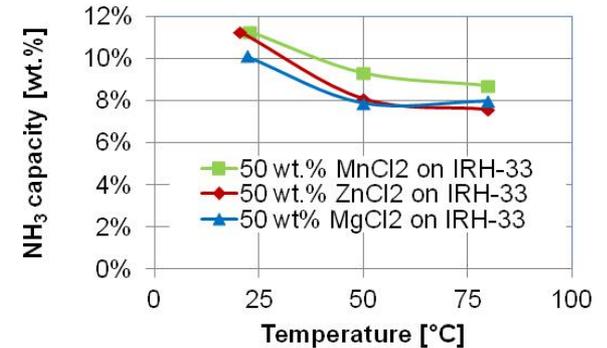


NH₃ Filter Weight



NH₃ filter: 1.2 kg, 1.6 Liter

Capacity over full ambient temperature range

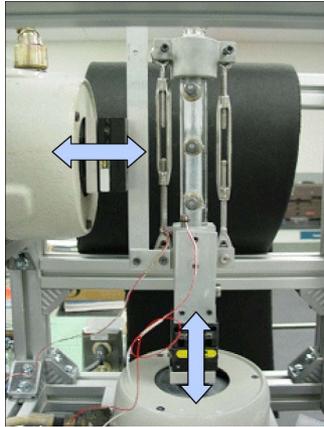


* LANL addresses Boron containing impurities

Cryo-Adsorption System Support: SAC Binderless Compaction

Vibration Packing

- Resulting density is equal to tap density (0.3 g/cm^3):
No density enhancement



Compressed Foam Enclosure

- Springback limits MaxSorb density to 0.3 g/cm^3 with high weight penalty for thermal conductivity enhancement



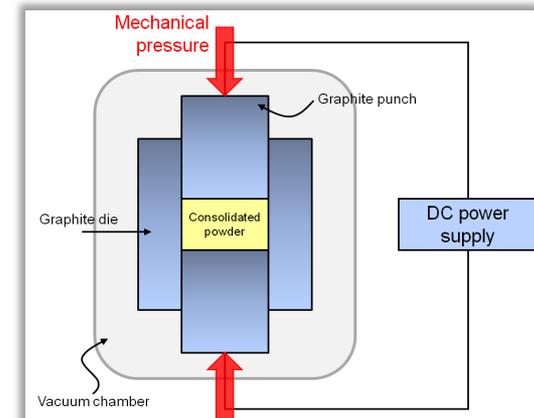
Filter Press

- Density limited to 0.3 g/cm^3 as only 35 psi pressure in absence of any vibration.



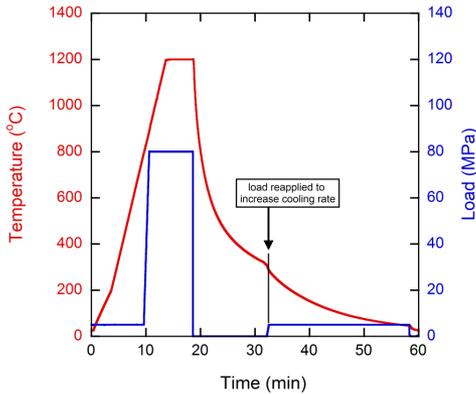
Spark Plasma Sintering (SPS)

- Rapid heat-up and cool down in graphite die to elevated temperatures ($1000\text{-}1200^\circ\text{C}$) results in densification to $0.5\text{-}0.625 \text{ g/cm}^3$: Some loss of SA BET but FAST!



Cryo-Adsorption System Support: Spark Plasma Sintering

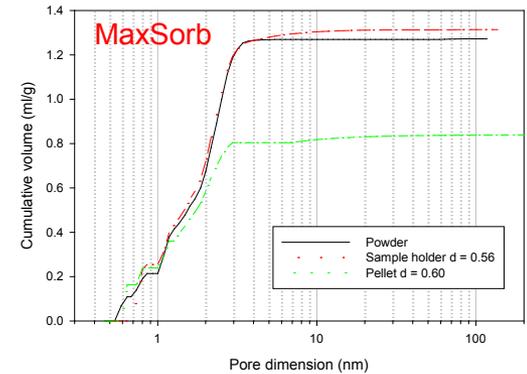
SPS technique



- Impurities reduce required operating temperature
- $\rho=0.6 \text{ g/cm}^3$ achieved

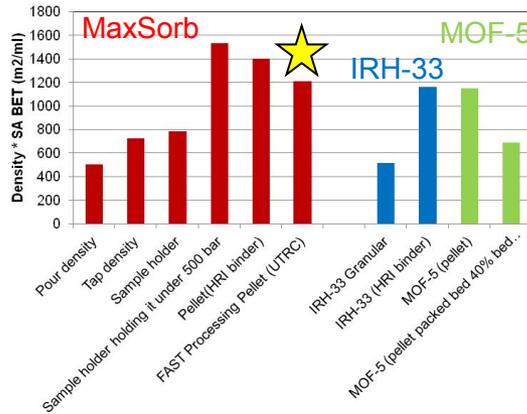
- Sintering reduces pore volume similar as use of binder

Pore volume loss



Volumetric specific surface area

- Comparable to values achieved with binder but faster processing



Scale-up

- Applicable to practical size of adsorbents ('hockey puck')

IRH-33

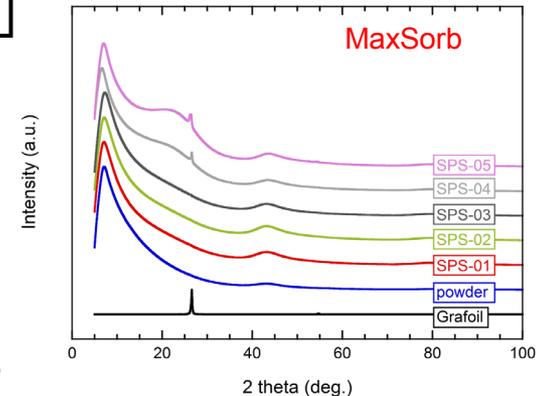


* IRH-33 and pore volume measurement kindly provided by UQTR

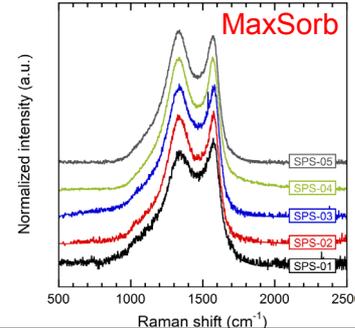
Characterization

SAC material remained highly disordered form of carbon

X-ray diffraction:

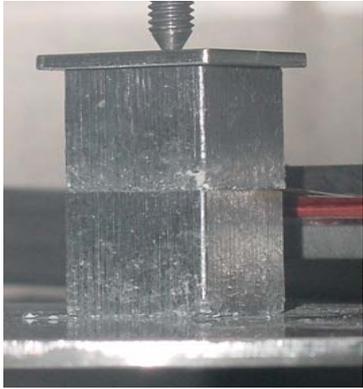


Raman:



Cryo-Adsorption System Support: Conductivity Enhancement

Compacted MOF-5



- MOF-5*+10wt.% ENG “worms”**
- Density: 0.6 g/cm³
- 25 MPa (3.53 kpsi)

Hot Disk thermal conductivity measurement

- Measurements in each orthogonal direction (x,y, and z(=axis of compaction))
- Parameters: 0.1W, 5s

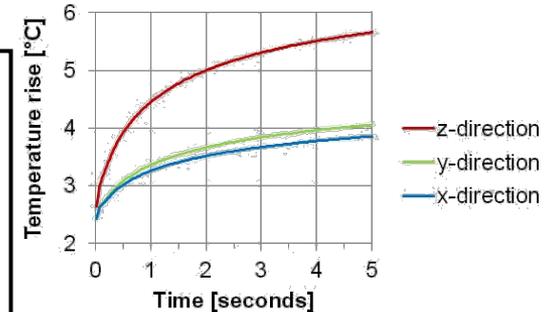
Thermal Conductivity Anisotropy

- Thermal conductivity in radial direction significant higher than in axial direction (5-10 x)

parameter	95% confidence interval	Unit
kX	3.32 < 3.45 < 3.58	W/m/K
kY	1.44 < 1.49 < 1.55	W/m/K
kZ	0.280 < 0.286 < 0.292	W/m/K
C _p	1395 < 1438 < 1484	J/kg/K

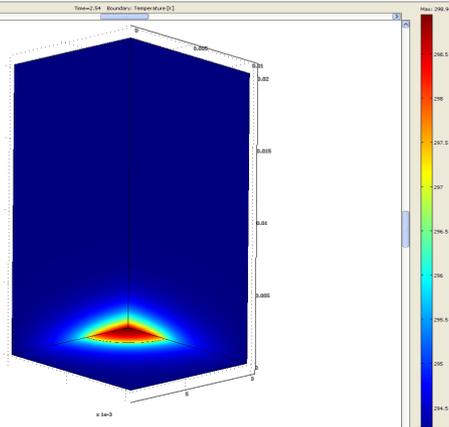
- High values of heat transfer coefficients

h _x	638 < 645 < 652	W/m ² /K
h _y	706 < 714 < 724	W/m ² /K
h _z	773 < 783 < 795	W/m ² /K



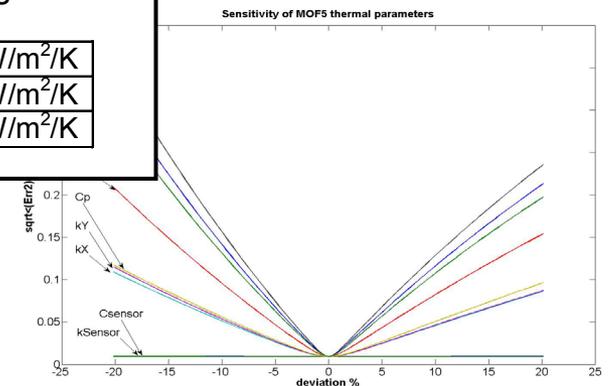
COMSOL Model

- Inverse problem solved with Matlab® optimizer



Dynamic COMSOL Multiphysics model of HotDisk thermal conductivity experiment. The predicted temperature rise with time is fitted to the experimental data with Matlab® optimizer

Error analysis



- High sensitivity of error measure to the sample thermal conductivity parameters results in narrow confidence interval

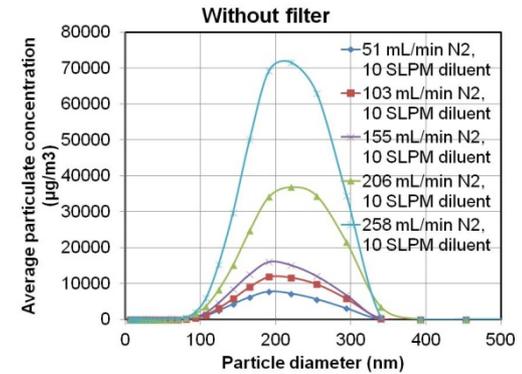
H₂ Quality: Particulate Mitigation

Test Setup



- Particulate analyzer ($d_p < 0.5 \mu\text{m}$)

Concentration & Particulate size without filter



Conclusion:

- Porous SS metal filters are effective (even $10\mu\text{m}$); Need guidance on longevity.:



- Filter needs to be inside bed
- SAE J2719 April 2008 standard

Parameter	Value
Maximum particulate size	< $10 \mu\text{m}$
Particulate concentration:	< $1000 \mu\text{g}/\text{m}^3$

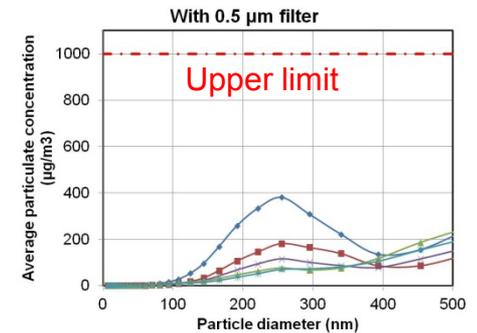
Porous SS Metal Filters

- Determine required filter area for longevity of cryo-adsorption system



Pore Diameter: 0.2 0.5 1 2 5 10 μm

Concentration & Particulate size with filter



- Particulate concentration well below SAE J2719 guideline even when recorded with $10\mu\text{m}$ filter

Summary

Relevance: Design of materials based vehicular hydrogen storage systems that will allow for a driving range of greater than 300 miles

Approach: Leverage in-house expertise in various engineering disciplines and prior experience with metal hydride system prototyping to advance materials based H₂ storage for automotive applications

Technical Accomplishments and Progress:

- IPPSSM: Completed assessment of on-board reversible metal hydride system and diverted it to different markets.
- Developed on-board reversible metal hydride materials requirements in order for a system to meet the DOE/U.S.Drive 2017 targets.
- Supported FMEA of cryo-adsorption and chemical hydride systems.
- Designed Gas/Liquid Separator (GLS) setup for chemical hydride system.
- Performed FMEA of GLS setup.
- Developed and demonstrated more efficient and regenerable NH₃ filter with high capacity over a wide range of operating temperature.
- Demonstrated binderless compaction of super activated carbon.
- Characterized thermal conductivity anisotropy of MOF-5 + ENG 'worms'.
- Tested performance of SS particulate filters.

Acknowledgements

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Technical Back-Up Slides

Partner level Phase 2 to Phase 3 Go/No-Go Criteria

Month/Year	Partner-Level Go/No-Go
March/2013	Report on ability to develop a gas liquid separator capable of handling 720 mL/min liquid phase and 600 L/min of H ₂ @ STP (40 wt% AB @ 2.35 Eq H ₂ and max H ₂ flow of 0.8 g/s H ₂) fluid having a viscosity less than 1500cp resulting in a gas with less than 100ppm aerosol having a mass less than 5.4 kg and volume less than 19 liters.
	Report on ability to develop an ammonia scrubber with a minimum replacement interval of 1800 miles of driving resulting in a maximum ammonia outlet concentration of 0.1ppm (inlet concentration = 500ppm) having a maximum mass of 1.2 kg and a maximum volume of 1.6 liters.

All targets are equal

Parameter	Unit	2017 Target	System +5.6 kg H ₂	Compressed*	
				350 bar	700 bar
System gravimetric capacity	[wt.%]	5.5	102 kg	117 kg	119 kg
System volumetric capacity	g-H ₂ /L	40	140 L	329 L	224 L
Refueling time [5 kg-H ₂]	minutes	3.3			
On-board energy efficiency	%	90			
Purity		SAE J2719			
Operating ambient T	°C	-40 to +60			
Operational cycle life	#	1500			
Minimum delivery pressure (abs.)	bar	5			
Etc.					

*5.6 kg usable H₂: 5 kpsi: 4.8 wt.%, 17 g/L; 10 kpsi: 4.7 wt.%, 25 g/L

Minimum balance of plant requirements

- Using waste heat
Use the TIAX 350 bar system BOP

	Mass	Volume
	kg	L
Check valve	0.2	0.1
Manual valve	0.2	0.1
Solenoid valve	0.6	0.4
Relief valve	0.3	0.1
Pressure transducer	0.1	0.0
Temperature transducer	0.1	0.0
Pressure regulator	2.1	0.7
Pressure relief device	0.5	0.3
Piping	5.0	1.0
Boss	0.4	0.1
Vehicle interface bracket	2.0	0.5
Fill system control module	1.0	1.0
Miscellaneous	2.0	0.5
Total	14.5	4.8

- Combusting H₂
Add a combustion loop to the 350 bar BOP
8 kW microchannel HX/combustor sized by OSU

	Mass	Volume
	kg	L
Coolant valve	1.0	0.4
Coolant fluid	3.0	0.0
Coolant pump	3.0	2.4
Coolant lines	4.0	2.6
System insulation	1.0	5.0
Oil tank	0.7	2.6
Catalytic heater	2.5	0.8
Blower	0.4	0.2
Headers & fittings	0.5	0.1
Sub-Total	16.0	14.1
	14.5	4.8
Total	30.5	18.9

T.Q. Hua, R.K. Ahluwalia, J.K. Peng, et al., "Technical assessment of compressed hydrogen storage tank systems for automotive applications," *Int. J. Hydrogen Energy* **36**, 3037–3049 (2011).

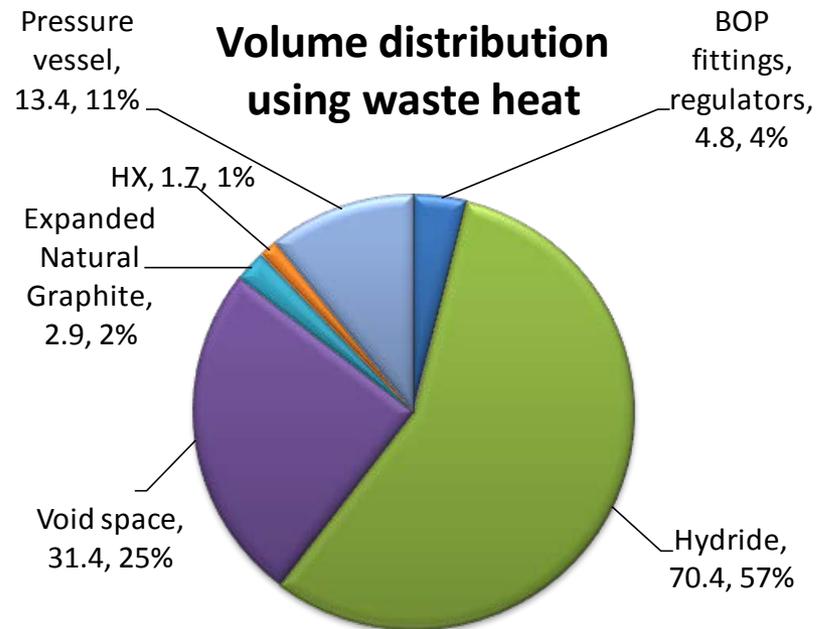
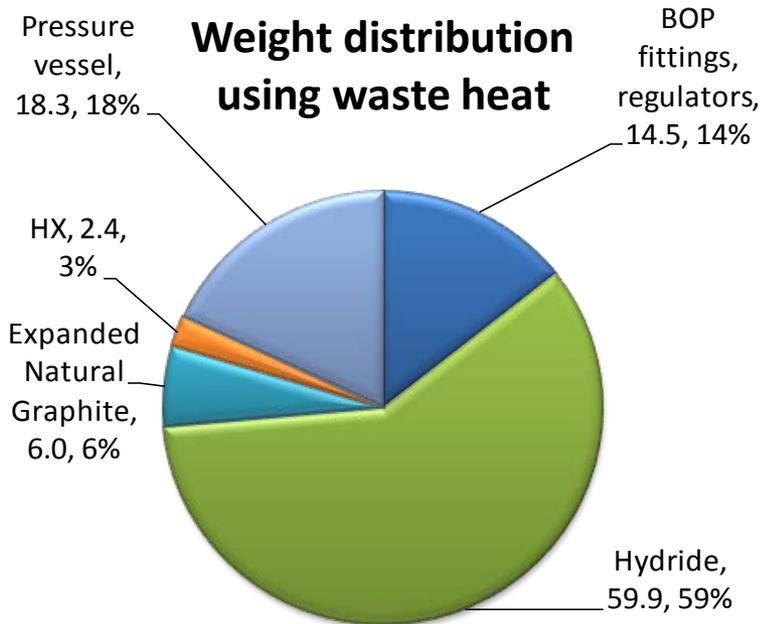
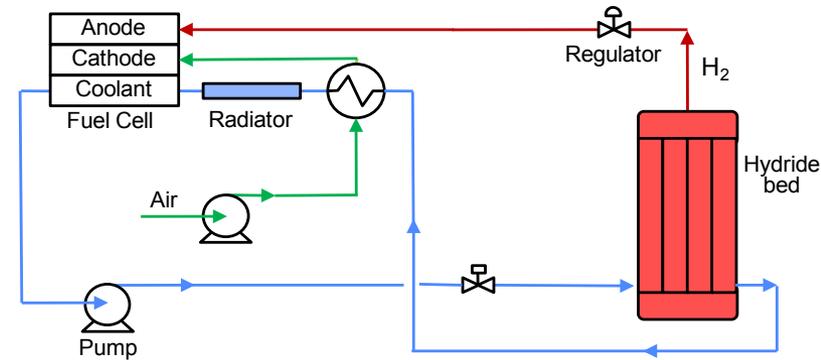
Drive cycles & test conditions for use in the framework

Case	Test Schedule	Cycles	Description	Test Temp (°F)	Distance per cycle (miles)	Duration per cycle (minutes)	Top Speed (mph)	Average Speed (mph)	Max. Acc. (mph /sec)	Stops	Idle	Avg. H2 Flow (g/s)*	Peak H2 Flow (g/s)*	Expected Usage
1	Ambient Drive Cycle - Repeat the EPA FE cycles from full to empty and adjust for 5 cycle post-2008	UDDS	Low speeds in stop-and-go urban traffic	75 (24 C)	7.5	22.8	56.7	19.6	3.3	17	19%	0.09	0.69	1. Establish baseline fuel economy (adjust for the 5 cycle based on the average from the cycles) 2. Establish vehicle attributes 3. Utilize for storage sizing
		HWFET	Free-flow traffic at highway speeds	75 (24 C)	10.26	12.75	60	48.3	3.2	0	0%	0.15	0.56	
2	Aggressive Drive Cycle - Repeat from full to empty	US06	Higher speeds; harder acceleration & braking	75 (24 C)	8	9.9	80	48.4	8.46	4	7%	0.20	1.60	Confirm fast transient response capability – adjust if system does not perform function
3	Cold Drive Cycle - Repeat from full to empty	FTP-75 (cold)	FTP-75 at colder ambient temperature	-4 (-20 C)	11.04	31.2	56	21.1	3.3	23	18%	0.07	0.66	1. Cold start criteria 2. Confirm cold ambient capability – adjust if system does not perform function
4	Hot Drive Cycle - Repeat from full to empty	SC03	AC use under hot ambient conditions	95 (35 C)	3.6	9.9	54.8	21.2	5.1	5	19%	0.09	0.97	Confirm hot ambient capability - adjust if system does not perform function
5	Dormancy Test	n/a	Static test to evaluate the stability of the storage system	95 (35 C)	0	31 days	0	0	0	100%	100%			Confirm loss of useable H2 target

*Based on NREL simulation with compact vehicle, 5.6 kg usable H2, 80 kW fuel cell with a 20 kW battery

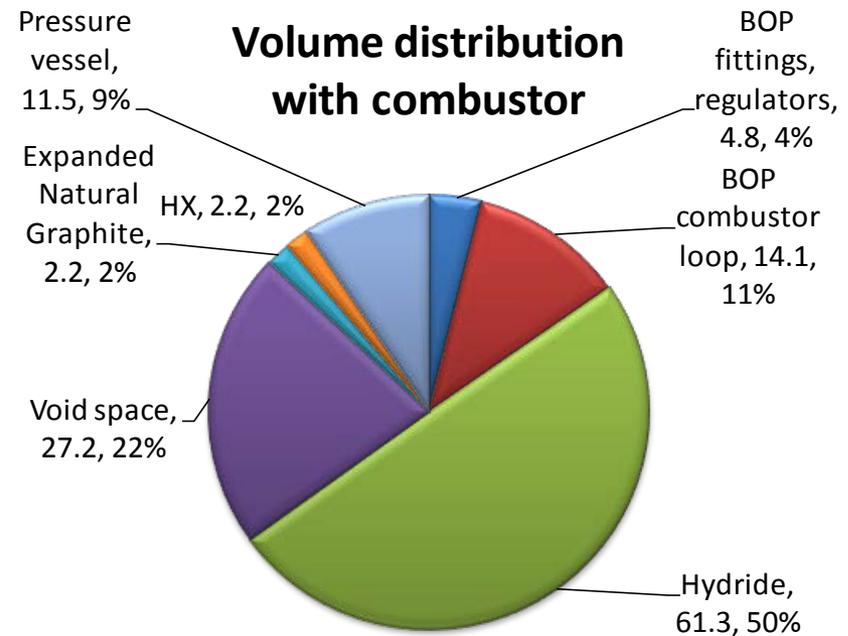
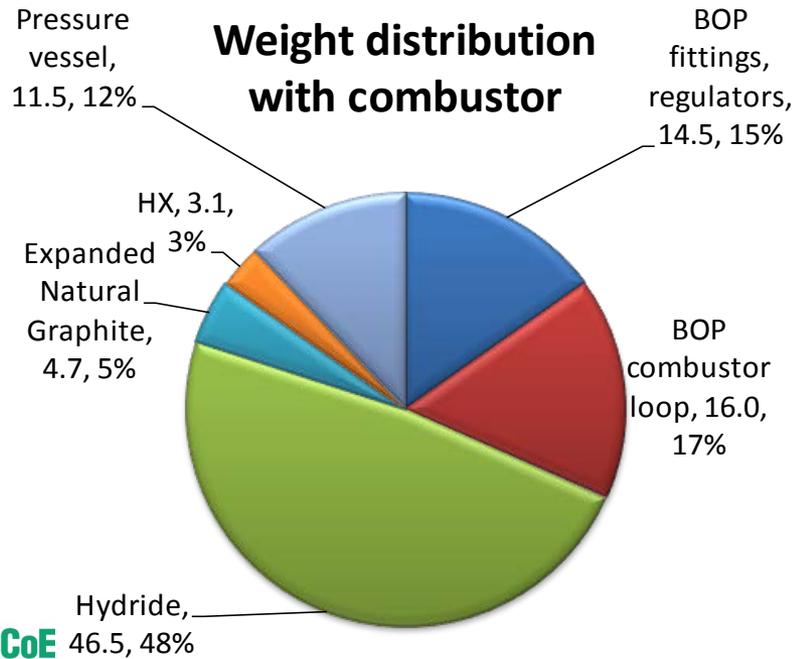
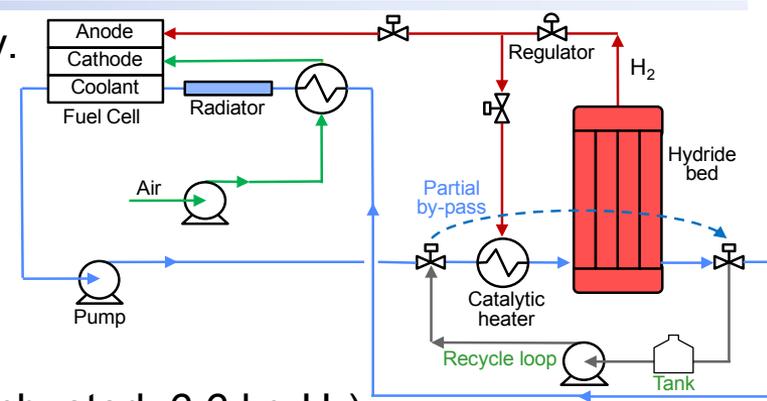
Complete system using waste heat only

- Satisfies all targets.
- $\Delta H = -27 \text{ kJ/mol-H}_2$, $\Delta S = -105 \text{ J/mol-H}_2/\text{K}$
- 11 wt% pure material capacity
- $T (5 \text{ bar}) = 20.7 \text{ C}$
- On-board efficiency: $\sim 100\%$
- System: 101 kg (5.8 wt%), 124 liters (48 g-H₂/L)
- 66 kg of hydride delivers 5.9 kg-H₂.



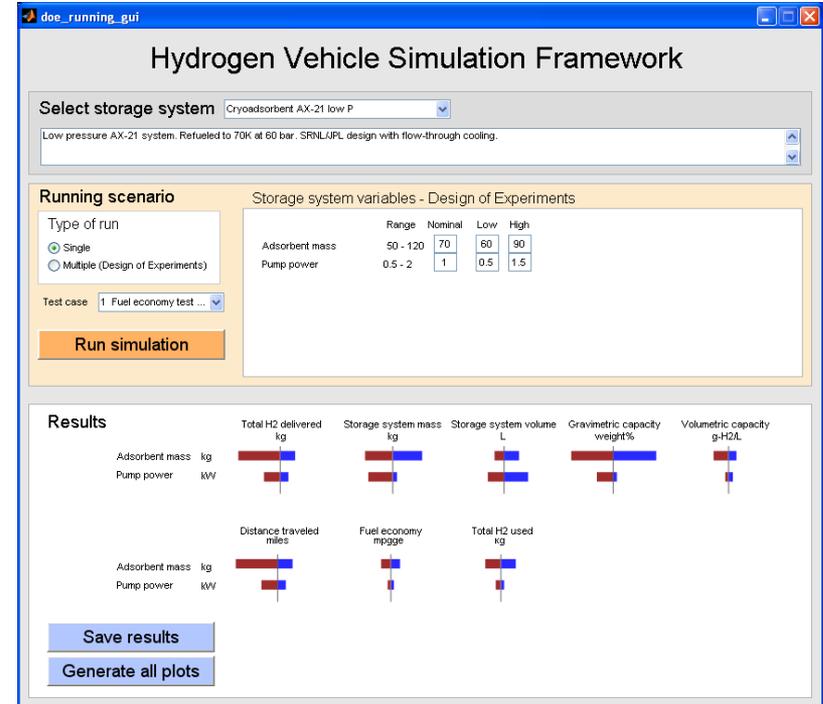
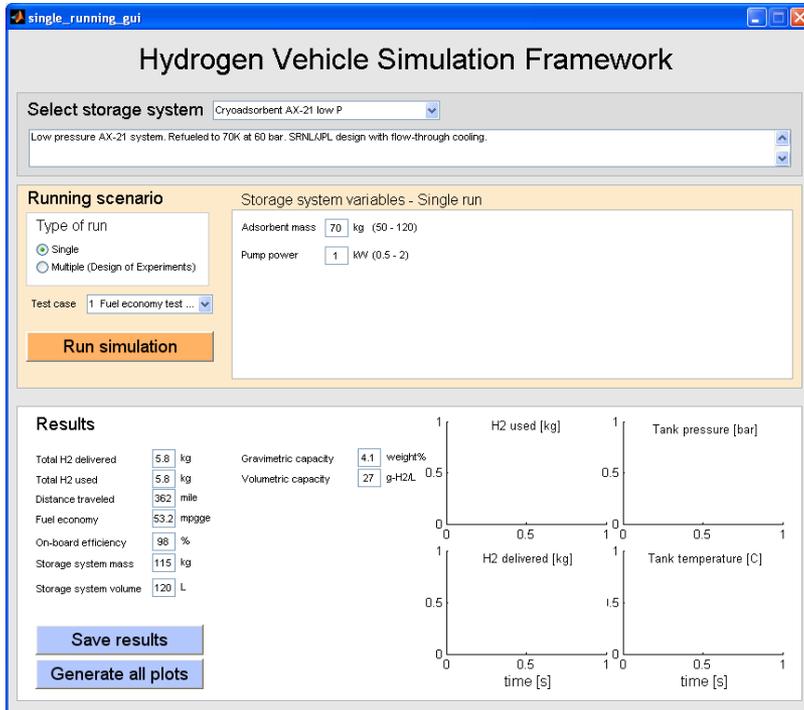
Complete system with combustion

- Satisfies all targets except on-board system efficiency.
- $\Delta H = -40 \text{ kJ/mol-H}_2$, $\Delta S = -114 \text{ J/mol-H}_2/\text{K}$
- 17 wt% pure material capacity
- $T (5 \text{ bar}) = 122.8 \text{ C}$
- On-board efficiency: $\sim 81\%$
- System: 103 kg (5.2 wt%), 126 liters (43 g-H₂/L)
- Operating at 130C delivers 5.4 kg-H₂ (delivered + combusted: 6.6 kg-H₂)



IPPSSM framework development: GUI interface

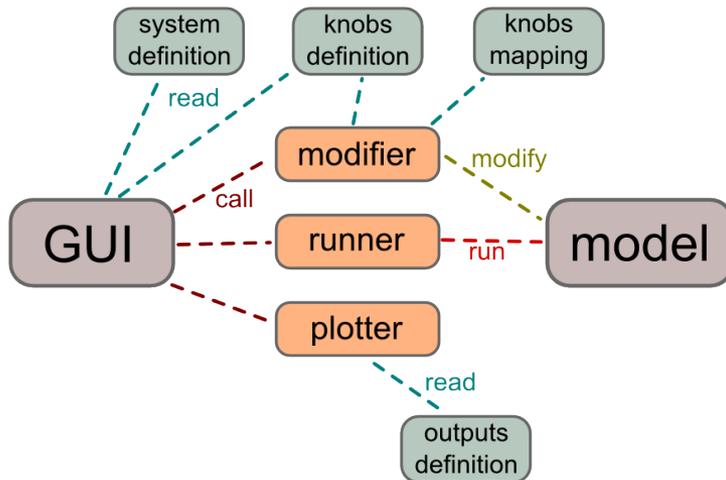
- Goal: make the framework more user-friendly and expand its capabilities



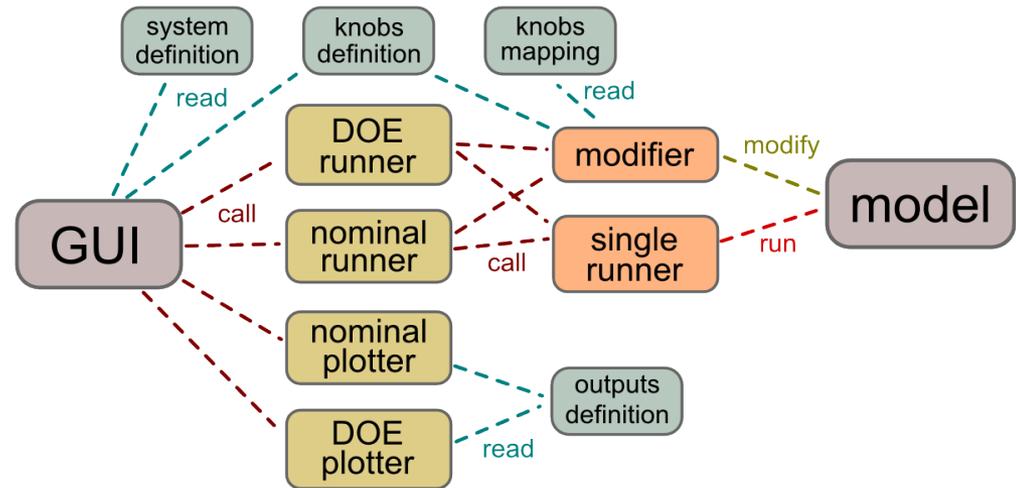
- Conditions:
 - Single system, single run
 - Single system, parameter sweeps
 - System-to-system comparisons

Framework GUI structure: designed for change

Single run mode



Multiple runs mode



- GUI designed for change: modules with small responsibilities
 - Currently: Matlab[®]-based
 - Potentially: web-based

Gas/Liquid Separator Parameters

Parameter	Range
GLS Target Volume	≤ 19 liters
GLS Target Weight	≤ 5.4 kg
GLS Operating Temperature	~ 200 - 250°C
GLS Operating Pressure	~ 35 bar (508 psi)
Gas Type	Nitrogen
Gas Flow Rate	1,067 slpm (0°C , 1atm))
Liquid Type	Silicone Oil AP 100
Flow Rate	~ 61 ml/s (1.4 L/min)
Density	0.8-1.4 (g/mL) at 20°C
Viscosity	~ 20 -100 (cP) at 25°C
Surface Tension	~ 0.0375 (N/m)

Flammability Test Apparatus (for Gases or Liquids)

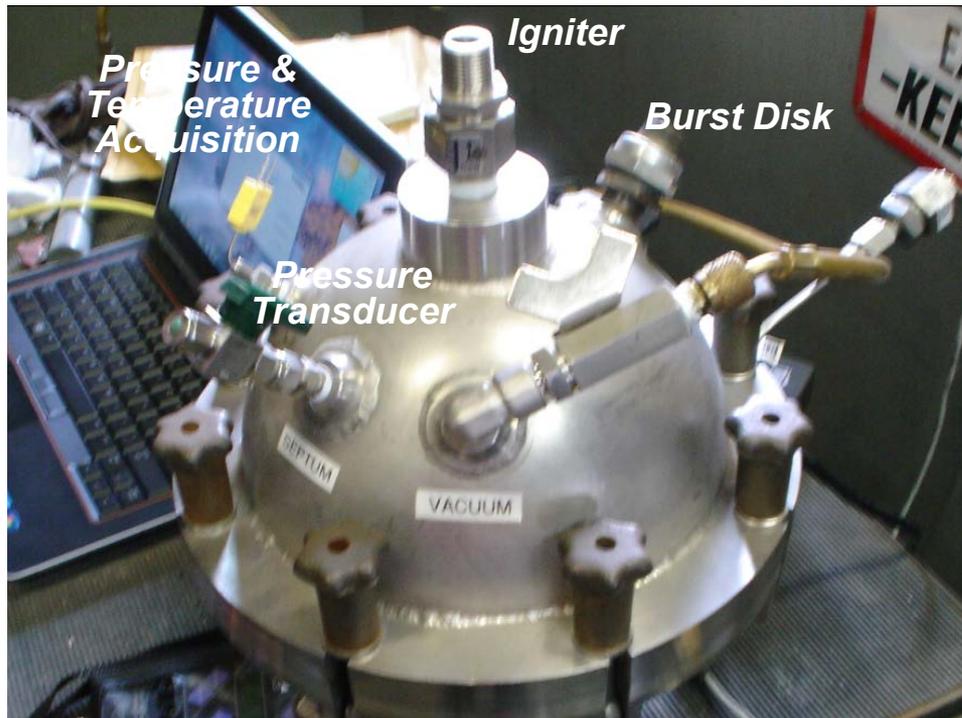


Figure 1: KG Apparatus showing the igniter, burst disk, ports for vacuum, gases, and liquids.

The burst desk is designed for 350 psi.

The data acquisition is set for 1000 samples per second for T & P.

The KG apparatus will be used for measuring the flammability of the slurry (solid AB in silicon oil).

Flammability tests follows *ASTM E-2079*



Figure 2: Two parts of the stainless steel sphere (8.8 liters free volume).

UTRC Contributed to Cryo-adsorption Tank Test Plan

Failure Mechanism	Effects	Validation Test
1) Liner's microcracks initiation and propagation as a result of exposure to LH2 temperature.	Should this failure mechanism occur, H ₂ permeation / leakage through the liner could increase over time.	<u>Cryogenic cycling test</u> (for both Type-III and Type-IV liners). Use electron microscopy to compare the liner microstructure before and after the cryogenic cycling test.
2) Delamination and/or blistering of the carbon composite overwrap.	Loss of structural integrity of the tank.	Cryogenic cycling test. Use electron microscopy to compare the composite microstructure before and after the cryogenic cycling test.
3) Debonding of the carbon fiber / epoxy resin bonding matrix material.	Loss of structural integrity of the tank.	Cryogenic cycling test. Use electron microscopy to compare the composite microstructure before and after the cryogenic cycling test.
4) Air leaks into tank due to thermal shock caused by exposure to the cryogenic liquid.	Leaked air condenses at ~ 79°K and, hence, oxygen enrichment is a concern.	Tank leak testing / cryogenic pressure burst test. Pressurize the tank with LN2 (77 °K or below if possible).

UTRC Contributed to Cryo-adsorption Tank Test Plan (Cont.)

Failure Mechanism	Effects	Validation Test
<p>5) Degradation of mechanical properties (fracture toughness and tensile strength) of the liner and the composite fiber as a results of exposure to LH2.</p>	<p>Loss of structural integrity of the tank.</p> <p>Increased H2 permeation through the liner material.</p>	<p>Mechanical testing of the composite fiber and the liner material.</p> <p>Samples have to be mechanically tested while the submerged in LN2.</p>
<p>6) Type IV liner failure due to thermal fatigue stress concentration.</p>	<p>Liner failure and hydrogen leakage.</p>	<p>Cyclical thermal fatigue test.</p> <p>Cycle the test sample between being submerged in LN2 for several hours and being exposed to ambient air for several hours.</p>

Phase 2: UTRC - Pressure Vessel Safety Tests

Proposed Test	Test Procedure
1. Cryogenic cycling.	<ul style="list-style-type: none"> • Subject the tank to cryogenic cycles using liquid nitrogen at temperature in the range: $50^{\circ}\text{K} \leq T \leq 77^{\circ}\text{K}$ and at pressure equal to 1 bar. Using temperatures $< 77^{\circ}\text{K}$ is dependent of the existing lab capabilities. • Each cryogenic cycle involves cooling down the tank from room temperature to cryogenic temperature and then warming up to room temperature.
2. Mechanical testing of tank's carbon fiber composite and liner material (Types III and IV).	<ul style="list-style-type: none"> • Immerse test samples (carbon composite overwrap or the liner) in LN2 at 50 or 77°K for extended period of time. • Test the samples for fracture toughness and tensile strength while the sample is submerged in the LN2.
3. Cryogenic pressure cycling using LN2 (@ $T \leq 77^{\circ}\text{K}$).	Subject the tank to pressure cycles between 20 bar (10% of NWP) and 200 bar (100% of NWP) . OR, cycle between 10% NWP and 125% NWP (250 bar). (FMVSS 304)
4. Thermal cycling. (Ambient temperature outside tank).	Subject the tank to temperature cycles between 20°K and 77°K and at 1 bar pressure.
5. Sequential pressure and temperature cycling. (Ambient temperature outside tank).	Subject the pressure cycles between 20 bar and 250 bar followed by one temperature cycle between 20°K and 77°K at 1 bar. Repeat this sequence for a TBD number of cycles.
6. Burst pressure test. (Ambient temperature outside tank).	Subject the new tank (as well as a pressure cycled tank) to a burst test using liquid nitrogen at 77°K.
7. Hydrogen permeation test (Type-IV liner).	Test either the entire tank or a specimen of the liner for H2 permeation. Use LH2 at 20°K and 125% NWP.