System Level Analysis of Hydrogen Storage Options

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Overview

Timeline

- Project start date: Oct 2009
- Project end date: N/A
- Project continuation and direction determined annually by DOE

Budget

- FY17 DOE Funding: $840 K
- FY18 DOE Funding: $500 K

Barriers

- H_2 Storage Barriers Addressed:
  - A: System Weight and Volume
  - B: System Cost
  - C: Efficiency
  - E: Charging/Discharging Rates
  - J: Thermal Management
  - K: Life-Cycle Assessments

Partners/Interactions

- PNNL, Hexagon Lincoln (HL)
- BMW, LLNL
- Ford, ORNL, UM
- Delivery Team, Hydrogen Interface Taskforce (H2IT), ANL-H2A, ANL-HDSAM
- Strategic Analysis

Relevance and Impact

Develop and use models to analyze the on-board and off-board performance of physical and material-based automotive hydrogen storage systems

- Conduct independent systems analysis for DOE to gauge the performance of H_2 storage systems
- Provide results to material developers for assessment against system performance targets and goals and help them focus on areas requiring improvements
- Provide inputs for independent analysis of costs of on-board systems.
- Identify interface issues and opportunities, and data needs for technology development
- Perform reverse engineering to define material properties needed to meet the system level targets

Impact of FY2018 work

- Compared to Type 4 700-bar cH_2 tanks currently in use in LDVs, 500-bar CcH_2 can achieve 70% improvement in gravimetric capacity, 90% higher volumetric capacity, and 70% saving in carbon fiber composite (CF)
- Established targets for room temperature sorbents: 106±8 g-H_2/kg excess uptake at 100 bar when compacted to 500±35 kg/m^3 bulk density
- Proposed and demonstrated a concept of reinforcing the dome section with an elongated boss to realize >10% saving in CF composite for Type 4 tanks
- Determined the cost of producing/hydrogenating H_2 carriers, transmitting to and dehydrogenating them at city gate, and storing H_2 ($5.43-$6.02)

Approach

- Develop thermodynamic and kinetic models of processes in physical, complex metal hydride, sorbent, and chemical H_2 storage systems
  - Address all aspects of on-board and off-board storage targets, including capacity, charge/discharge rates, emissions, and efficiencies
  - Perform finite-element analysis of compressed hydrogen storage tanks
  - Assess improvements needed in materials properties and system configurations to achieve storage targets
- Select model fidelity to resolve system-level issues
  - On-board system, off-board spent fuel regeneration, reverse engineering
  - Conduct trade-off analyses, and provide fundamental understanding of system/material behavior
  - Calibrate, validate, and evaluate models
- Work closely with DOE technology developers, national labs and others in obtaining data, and provide feedback
- Participate in meetings and communicate approach and results to foster consistency among DOE-sponsored analysis activities

Accomplishments: FY2018 Tasks and Progress

1. Cryo-compressed H_2 Storage for Light Duty Vehicles (FY2018 Q1)
   - Updated refueling model to include heat transfer in dispenser lines and completed GCtool simulations for LDVs
   - Prepared and submitted a paper on CcH_2 storage for fuel cell electric buses
2. H_2 storage in room-temperature (RT) sorbents (FY2018 Q2)
   - Modeled adsorption isotherms for sorbents with metal ions capable of binding multiple H_2 molecules (ST133)
   - System analysis and reverse engineering of RT H_2 storage in sorbents
3. Compressed H_2 storage for medium and heavy duty fuel cell vehicles (FY2018 Q3)
   - Completed scoping analysis of Type 3 700-bar tanks and Type 4 tanks with metal end caps. Published a paper on Type 4 tanks in IJHE.
4. Hydrogen carriers for delivery (FY2018 Q4)
   - Support H2@Scale hydrogen distribution network activities

			Date Completed	% Complete
1	Complete system analysis of cryo-compressed hydrogen storage for light duty fuel cell vehicles relative to the 2020 system targets for gravimetric capacity (4.5 wt%), volumetric capacity (30 g/L), and WTE efficiency (60%)	12/17	12/17	100
2	Develop models for sorbents with metal cations capable of absorbing multiple H_2 molecules on single metal site. Conduct system analysis of ambient temperature sorbents relative to the 2020 system targets for gravimetric capacity (4.5 wt%), volumetric capacity (30 g/L), and WTE efficiency (60%)	03/18	03/18	100
3	Conduct ABAQUS analysis of compressed hydrogen storage for medium and heavy duty fuel cell vehicles with emphasis on storage pressure, tank capacity, weight and volume, and packaging configuration	06/18		50
4	Analyze material requirements and energy consumption for storing hydrogen in carriers in support of H2@Scale hydrogen distribution network	09/18		30

Accomplishments: Cryo-Compressed (CcH_2) Hydrogen Storage for FC Buses

Renewed interest in liquid H_2 (LH_2) delivery pathway during transformation to widespread H_2 fuel use

- Gaseous H_2 (GH_2) delivery in tube trailers viable only at small market penetration (<5%)
- Gaseous pipeline delivery and distribution economic at large market penetration (>30%)
- Combination of GH_2 and LH_2 delivery at intermediate market penetration: e.g., 25% GH_2 and 75% LH_2 changing to 85% LH_2 delivery and 15% on-site SMR as market delivery (http://www.arb.ca.gov/regact/2012/cfo2012/cfoisor.pdf)

LH_2-refueled CcH_2 particularly suitable for fleet buses and heavy-duty vehicles

- Limited infrastructure required if the vehicles return to a central depot for overnight parking
- Predictable duty cycles, few extended parking events
- LH_2 pump commercially available, 100 kg/h pumping rate, discharge pressure up to 875 bar

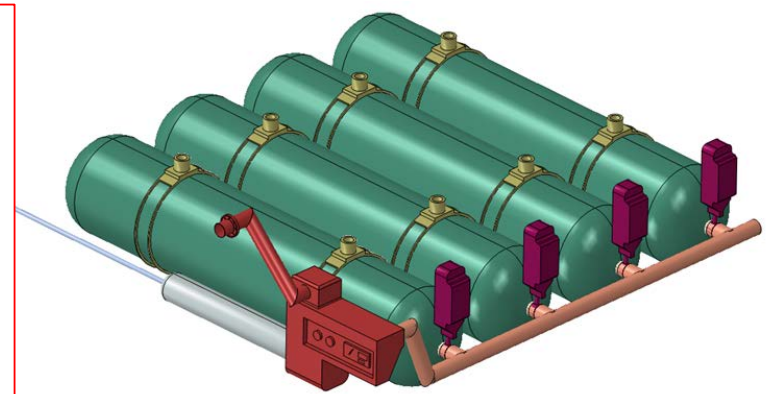
Current practice for FC buses

- H_2 storage as compressed gas at 350 bar, ambient temperature
- Type 3 pressure vessels with aluminum liner and T700 CF composite
- 40 kg H_2 stored in 8 tanks (5 kg per tank), L/D = 5, 5 kg/min refueling rate

Accomplishments: Supercritical CcH_2 Storage for FC Buses

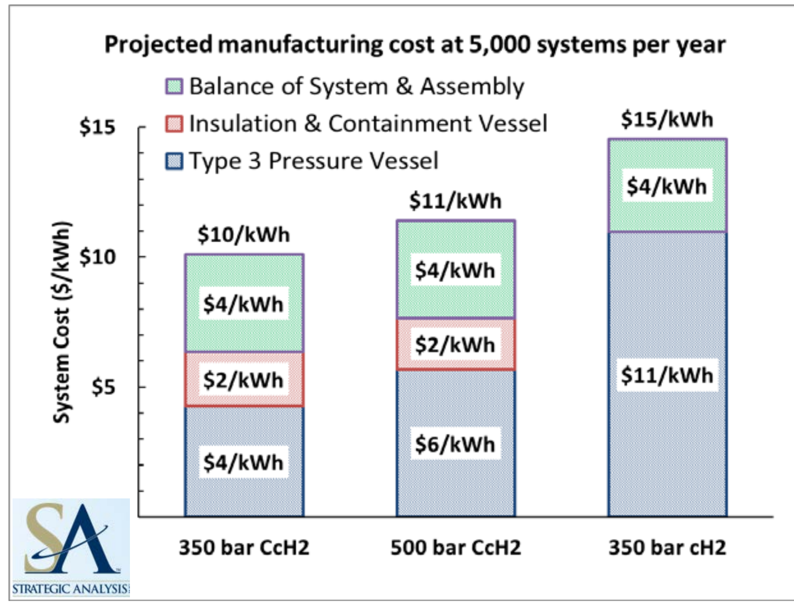
Advantages of 500-bar CcH_2 system over Type-3, 350-bar, RT cH_2 storage systems in current FC buses

- >215% increase in storage density
- >90% higher gravimetric capacity
- 170% higher volumetric capacity
- 47% saving in carbon fiber (CF) composite
- >25% lower cost at 5,000 systems/year annual production



Liquid H_2 refueled, supercritical CcH_2 storage system with MLVSI, 0.1 mW/m.K effective conductivity, 3 mTorr vacuum, 7-d dormancy at 95% full

Storage Method	CcH_2	CcH_2	cH2
Storage Pressure	350 bar	500 bar	350 bar
Usable H_2	4 x 10 kg	4 x 10 kg	8 x 5 kg
Liner	2-mm SS	2-mm SS	7.1 mm Al
Storage Temperature	64 K	70 K	288 K
Storage Density	70.3 g/L	75.5 g/L	24 g/L
Gravimetric Capacity	9.6%	8.4%	4.4%
Volumetric Capacity	46.1 g/L	50.1 g/L	18.5 g/L
CF Composite	4 x 36 kg	4 x 53.1 kg	8 x 50 kg
Insulation Thickness	18.2 mm	10.3 mm	NA
Heat Gain	3.8 W	5.7 W	NA
Dormancy: 95% Full	7.0 d	7.0 d	NA
Cost	$10/kWh	$11/kWh	$15/kWh



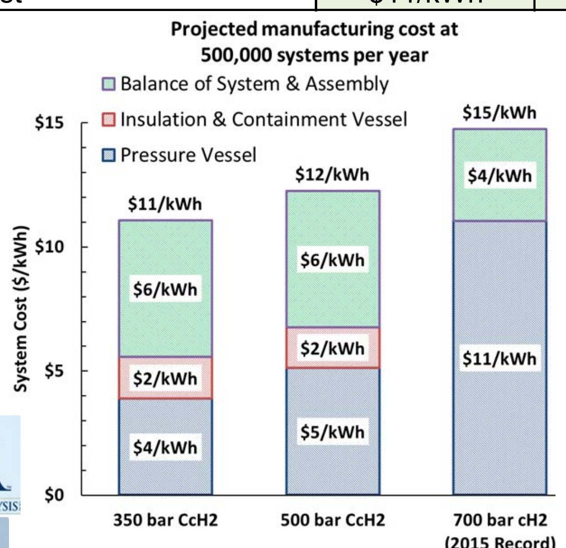
- Even greater savings in CF composite and cost at 350-bar storage pressure

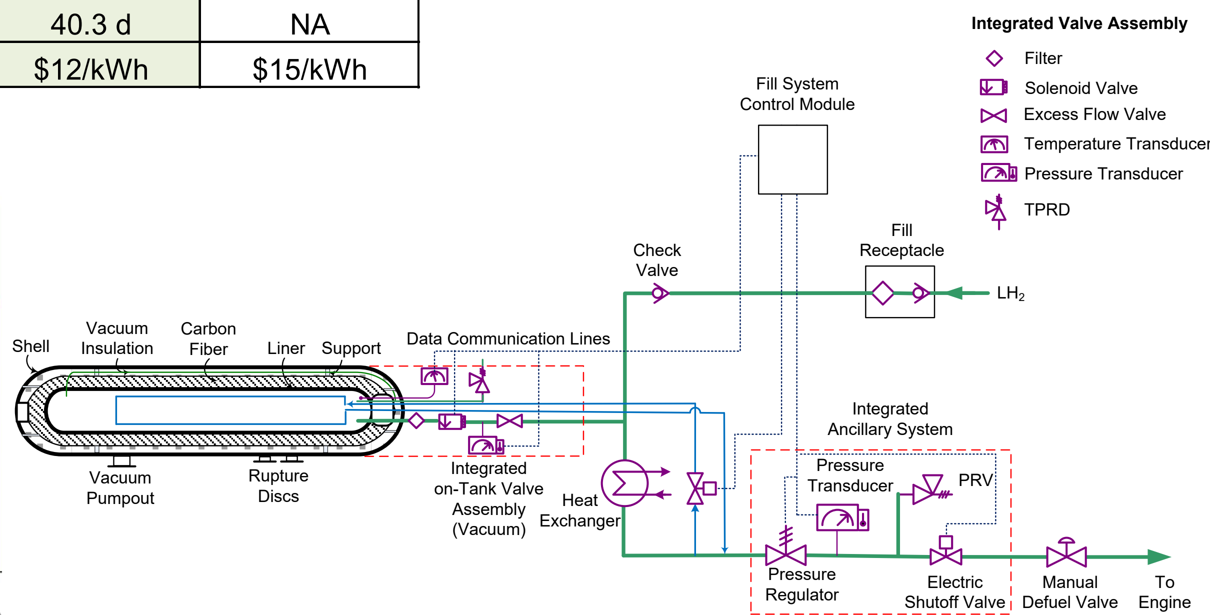
Accomplishments: Supercritical CcH_2 Storage for Light Duty Vehicles

Storage Method	CcH_2	CcH_2	cH2
Storage Pressure	350 bar	500 bar	700 bar
Usable H_2	1 x 5.6 kg	1 x 5.6 kg	1 x 5.6 kg
Liner	2-mm SS	2-mm SS	5-mm HDPE
Storage Temperature	62 K	67 K	288 K
Storage Density	71.2 g/L	76.7 g/L	40.2 g/L
Gravimetric Capacity	7.5%	7.0%	4.2%
Volumetric Capacity	35.5 g/L	44.2 g/L	24.6 g/L
CF Composite	1 x 20.0 kg	1 x 29.4 kg	1 x 96 kg
Dormancy			
Insulation Thickness	33.7 mm	14.6 mm	NA
Heat Gain	2.1 W	3.3 W	NA
95% Full	7.0 d	7.0 d	NA
75% Full	33.2 d	26.3 d	NA
60% Full	44.3 d	40.3 d	NA
Cost	\$11/kWh	\$12/kWh	\$15/kWh

Advantages of 500-bar CcH_2 system over Type 4, 700-bar, RT cH_2 storage systems

- ~90% increase in storage density
- ~70% higher gravimetric capacity
- ~80% higher volumetric capacity
- ~70% saving in carbon fiber (CF) composite
- 20% saving in system cost at high volume manufacturing



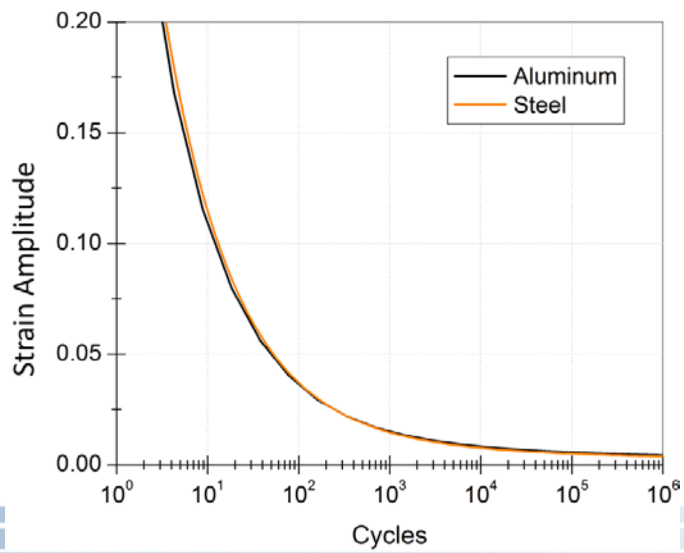


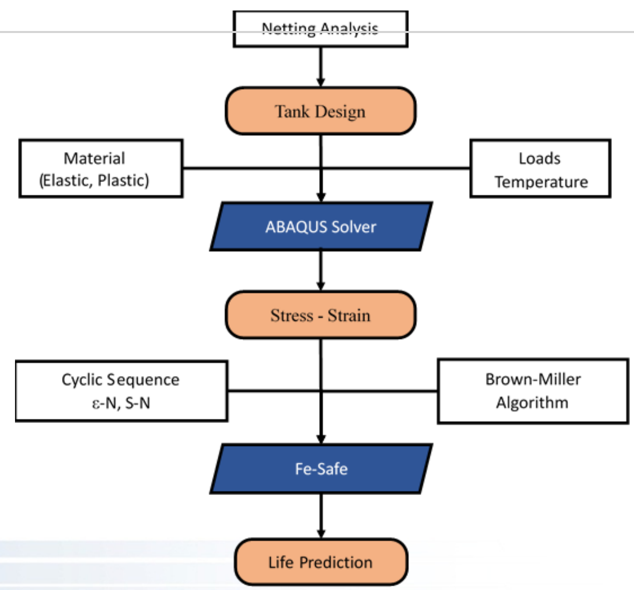
Accomplishments: CcH_2 Storage: Tools, Models and Data

Failure Modes	Material Properties[1]	Analysis Tools
Static Analysis		
Von Mises stress after autofrettage limited to 95% of yield stress (DOT-NGV2)	Stress-strain curves: liner, CF	ABAQUS/WCM
Burst pressure (2.25 safety factor)	Translation efficiency	
Leak-before-break (LBB)	Fracture toughness	
Liner separation	Adhesive peel test	
Fatigue Analysis		
5500 pressure cycles for LDVs	Strain-life curve	FE-SAFE
15,000 pressure cycles for MDVs and HDVs		
Combined pressure-temperature cycling	CTE: liner, CF	Thermo-mech. fatigue
Buckling Analysis		
Liner subjected to compression load by outer composite during autofrettage process		ABAQUS

[1]All material properties needed over the complete range of operating temperatures

CTE: coefficient of thermal expansion

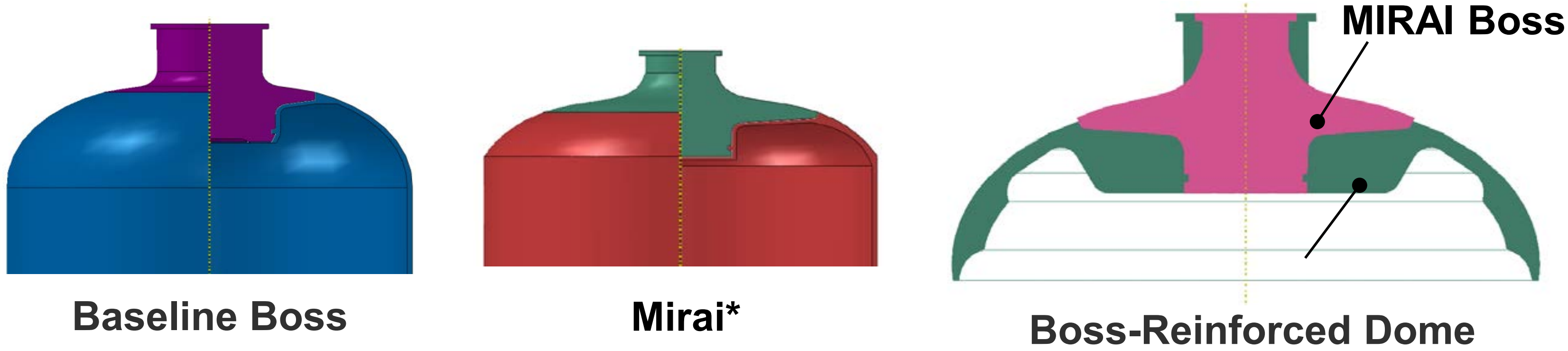




Accomplishments: Boss-Reinforced Dome Section for 700 Bar Type IV Tank

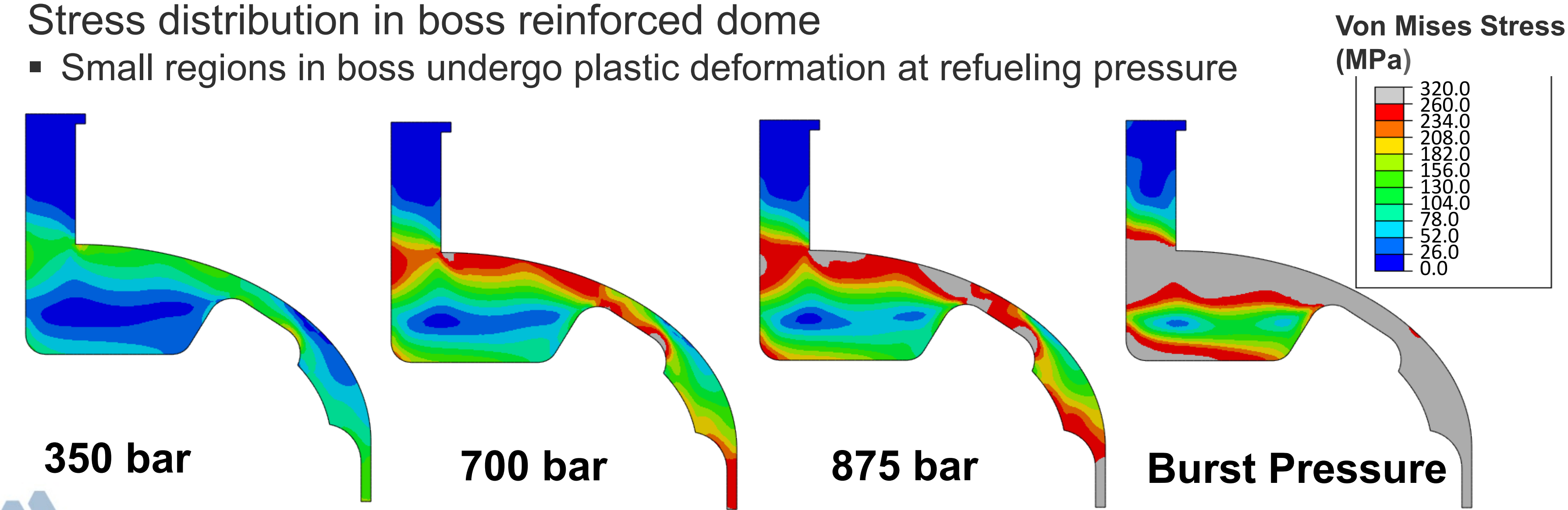
ABAQUS study to investigate the possible reduction in helical windings by reinforcing the entire dome section with extended boss

- Previous Mirai study* for boss showed 5% reduction in helical winding with smaller diameter and longer flange, but ABAQUS/WCM simulations at ANL showed no reduction



Stress distribution in boss reinforced dome

- Small regions in boss undergo plastic deformation at refueling pressure



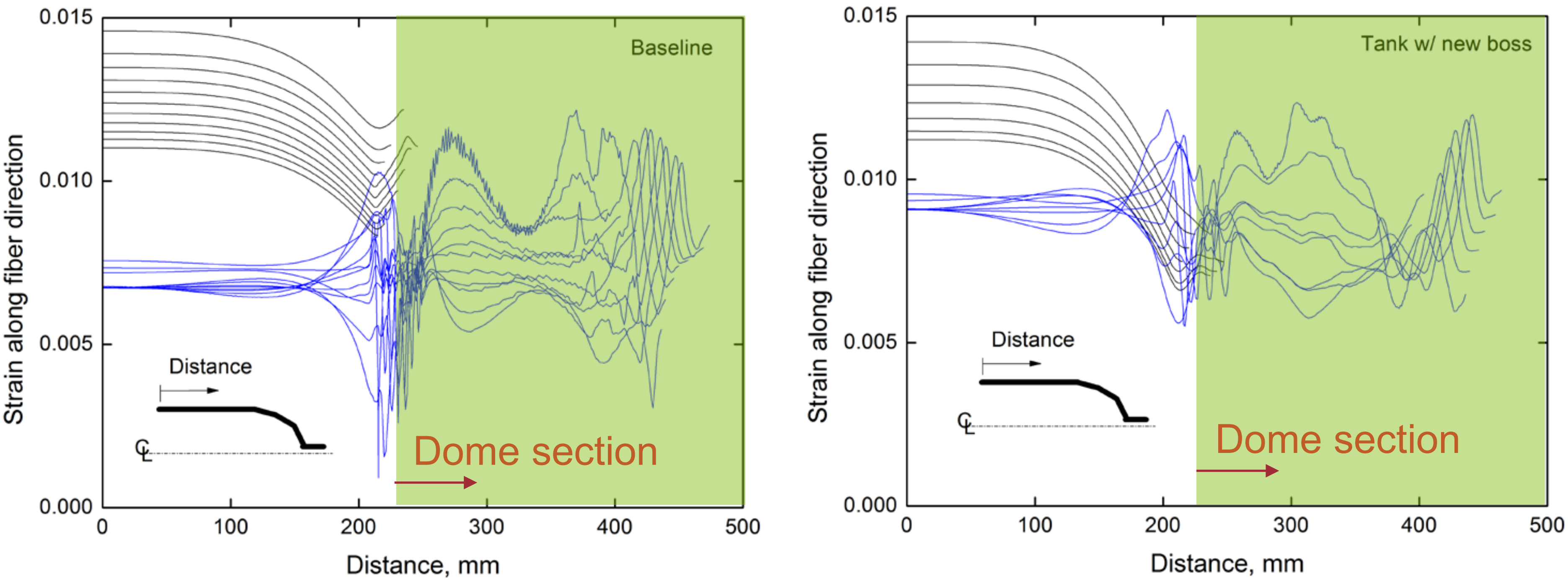
*A. Yamashita, M. Kondo, S. Goto, and N. Ogami, Development of High-Pressure Hydrogen Storage System for the Toyota "Mirai", *SAE International,* 2015

Accomplishments: Comparison of Strains along Fiber Direction

FE simulations for 147-L tank, 391-mm ID (empty), 5-mm HPDE liner

Boss reinforcement reduces the thickness of CF composite helical layers by ~5.0 mm (or 13% of 37.1 mm in baseline boss configuration)

- 15% reduction in total weight of carbon fiber composite offset by 23.2 kg increase in weight of boss
- Slight reduction in the level of strain in the composite material in the dome section, but higher strain in the helical layers in the cylinder section



Baseline **New Boss Configuration**

Accomplishments: Status of 700-bar cH_2 System

Updated system physical parameters, winding pattern, dome reinforcement

- Tank empty pressure: 1 (20 bar) or 2-stage (10-15 bar) pressure regulator and supply pressure effect, 1.1-2.1% saving in CF
- Ambient temperature: consistent with SAE regulations (15°C vs. 20°C), 1.1% saving in CF
- Tank design: conventional (Conv.) vs. alternate (Alt.) design similar to Mirai tank, 4.9% saving in CF
- Boss design: Boss-reinforced dome, 15% saving in CF, offset by heavier boss

	A	B	C	D	E	F	G
Empty pressure, bar	20(1)	20	15(2)	10(3)	15	10	10
Ambient temperature, °C	20	15	15	15	15	15	15
Tank design	Conv.	Conv.	Conv.	Conv.	Alt.(4)	Alt.	Alt.
Boss design	Conv.	Conv.	Conv.	Conv.	Conv.	Conv.	Reinf.5
CF composite, kg	97	95.9	94.9	93.9	90.3	89.3	75.8
Gravimetric capacity, wt%	4.19	4.23	4.26	4.29	4.41	4.45	4.24
Volumetric capacity, g-H_2/L	24.38	24.64	24.88	25.13	25.23	25.48	25.17

(1) Quantum 1 or 2-stage pressure regulator

(2) Aerodyne Controls 2-stage pressure regulator

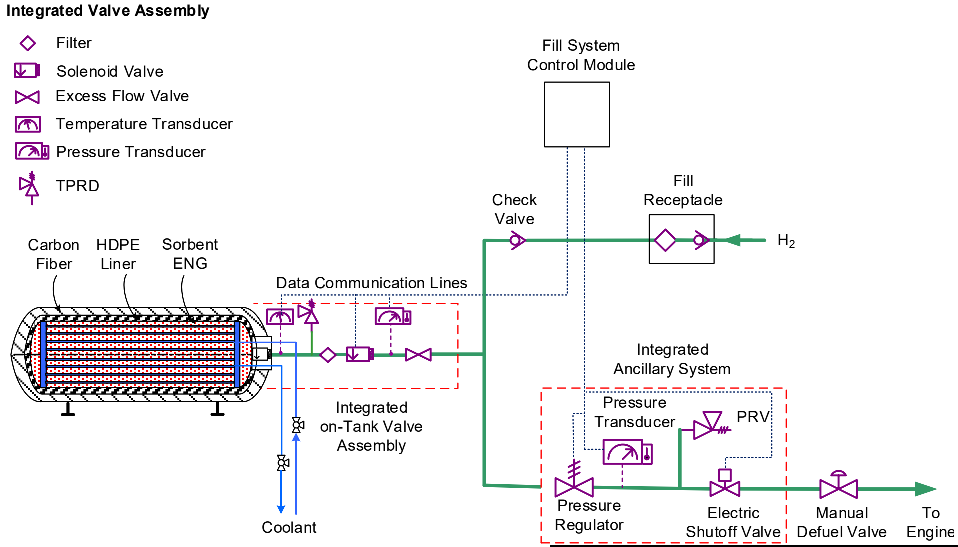
(3) JTEKT 2-stage pressure regulator in Toyota Mirai, empty pressure unknown

(4) Similar in design to the storage tank used in Toyota Mirai

(5) Boss-reinforced dome concept

A: 2015 DOE Hydrogen and Fuel Cells Program Record #15013 "Onboard Type IV Compressed Hydrogen Storage System – Cost and Performance Status 2015"

Accomplishments: On-Board RT Sorbent Hydrogen Storage System



Key System Requirements

Storage Medium
- 5.6 kg recoverable H_2
- 5-bar minimum delivery P

Type-4 Containment Vessel
- HDPE liner (5 mm)
- Toray 2550 MPa CF, SF=2.25

Heat Transfer System
- 1.5 kg/min H_2 refueling rate
- 1.6 g/s H_2 min full flow rate

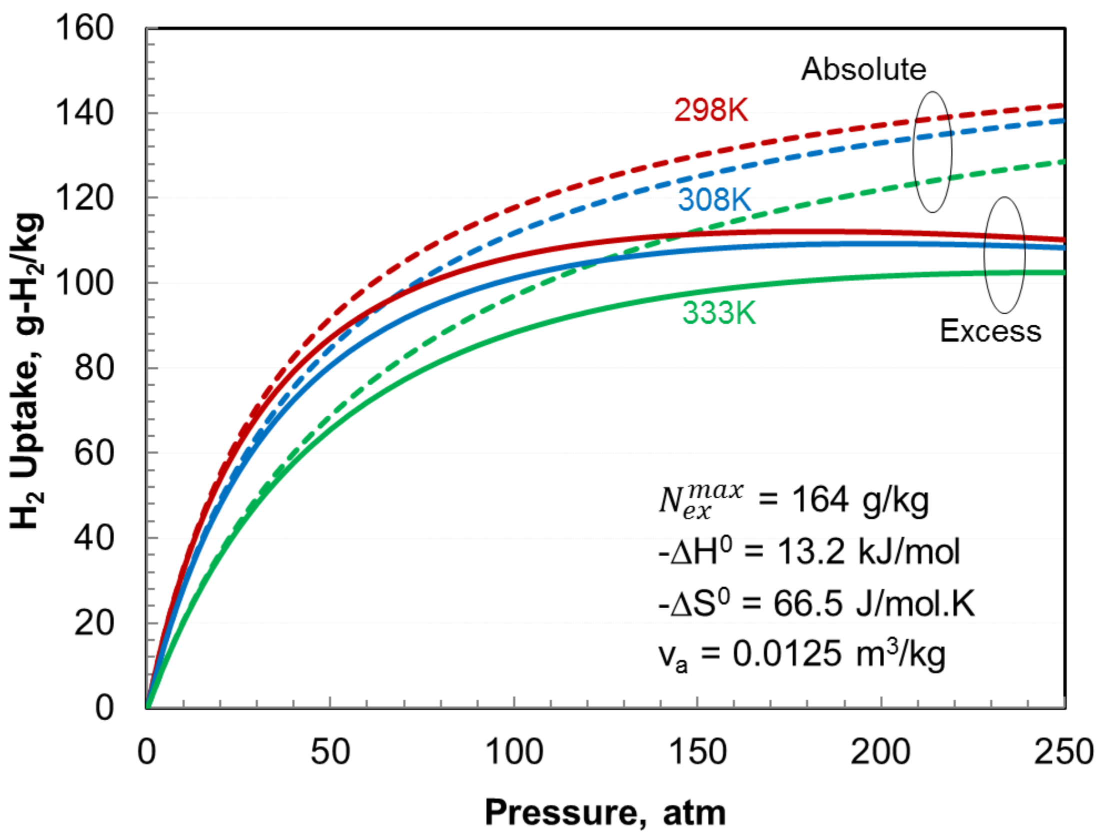
		Units	Target Value	Reference Value	Constraint / Variable	Comments
Sorbent	Excess Uptake at 308 K	g-H_2/kg	101.2	30-72	5.5 wt% gravimetric capacity	ST133
	Enthalpy of Adsorption (-ΔH^0)	kJ/mol	13.2	5-20	Study variable	17-18.5 Catecholate-Ca^{2+}
	Adsorption Volume	m^3/kg	0.012	TBD		MOF-5
	Entropy of Adsorption (-ΔS^0)	J/mol/K	66.5	30-100		MOF-5, SLI
	Bulk Density of Compact	kg/m^3	513	310 - 610	40 g/L volumetric capacity	IJHE 37 (2012) 2723-2727
	Permeability	m^2	TBD	TBD		IJHE 38 (2013) 3268-3274
Operating Temperatures	Off-board Coolant Temperature	K	298			T_c
	Storage Temperature	K	308			T_c + 10^{o}C
	Discharge Temperature	K	333			60^{o}C on-board coolant T
Operating Pressures	Storage Pressure	bar	100	50 - 250	Study variable	
	Minimum Delivery Pressure	bar	5			DOE target
H_2 Flow Rates	Refueling Rate	kg/min	1.5			DOE target
	Minimum Full Flow Rate	g/s	1.6			DOE target
Heat Transfer	ENG/Sorbent Mass Ratio		0.05	0.05		Layered ENG & sorbent
	Bed Thermal Conductivity	W/m/K	6.3		Model value for layered ENG	IJHE 41 (2016) 4690-4702
	Number of HX Tubes		79		1.5 kg/min H_2 refueling rate	

RK Ahluwalia, J-K Peng, TQ Hua, Sorbent Material Property Requirements for On-board Hydrogen Storage for Automotive Fuel Cell Systems, IJHE 40 (2015) 6373-6390

Accomplishments: Reference Sorbent Targets

Reaching system targets of 5.5 wt% gravimetric capacity and 40 g/L volumetric capacity requires a sorbent with 101 g-H_2/kg excess (112 g-H_2/kg absolute) uptake at 100 bar and 35°C, when layered with 5-wt% ENG and compacted to 513 kg/m^3 bulk density

- ~90% H_2 desorbed with 95 bar pressure swing and 25°C temperature swing



Theoretical Absolute Uptake* at 25°C, 100 bar, g-H_2/kg	
MOF-5	6.0
Ni_2(m-dobdc)	9.1
UiO-66*	1.5
UiO-66-Ca	24.2
UiO-67*	3.0
UiO-67-Ca	21.4
UiO-67-Ca_2	34.6
UiO-68*	4.0
UiO-68-Ca	19.5
UiO-68-Ca_2	31.1
UiO-68-Ca_4	47.5

***Based on formula units, 4 H_2 adsorbed per Ca^{2+} cation, and listed uptake in UiO MOFs**

***K. V. Kumar et al, Computational and Theoretical Chemistry, 1061 (2015) 36-45**

Accomplishments: Optimum Storage Pressure

For $-\Delta H^0$ = 13.2 kJ/mol ($-\Delta S^0$ = 66.5 J/mol.K), sorbent uptake requirement slightly less stringent (smaller N_{ex}^{max}) at 150-175 bar storage pressure

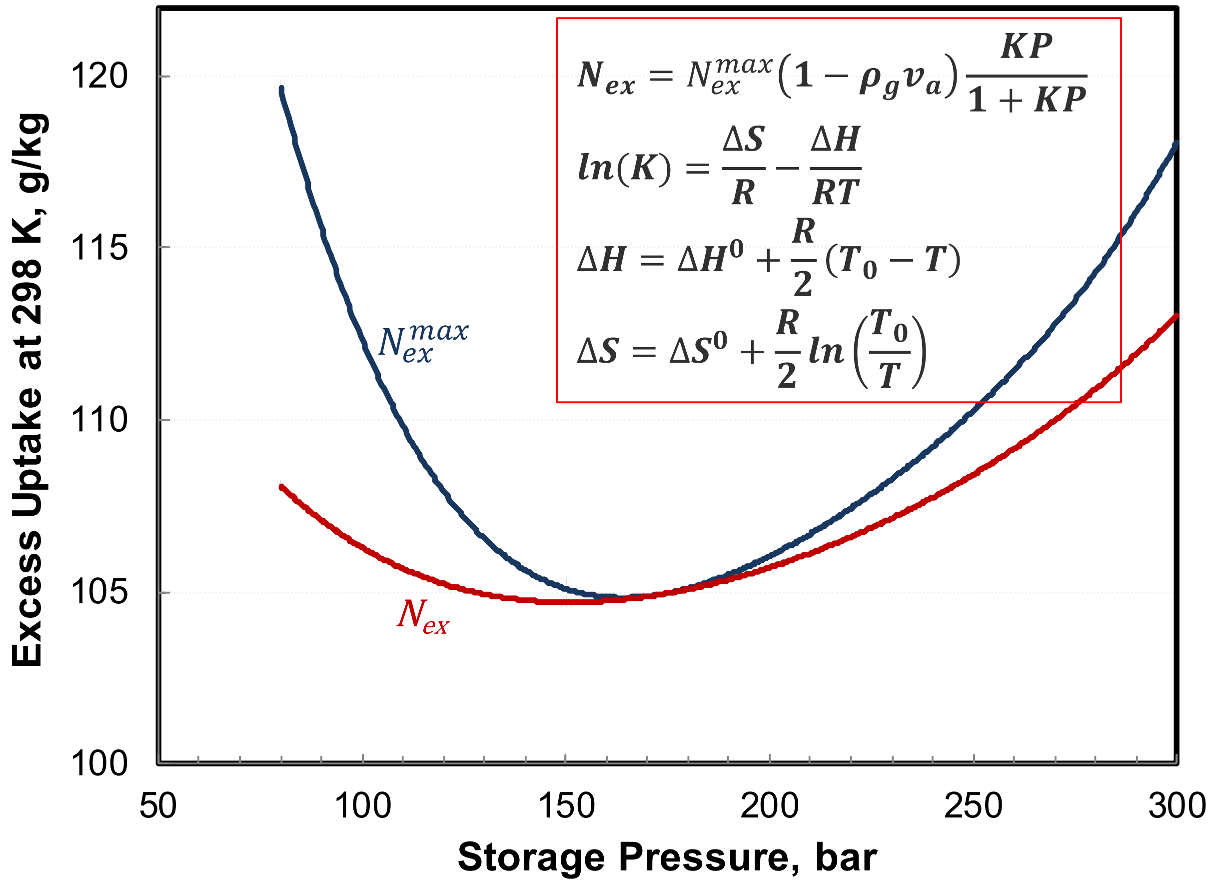
- N_{ex}^{max}: Peak excess uptake occurs at a pressure (P_{max}) which is a function of ΔH^0 and temperature
- For given ΔH^0, N_{ex}^{max} is a measure of the required adsorption site density

N_{ex}: Required uptake at 298 K to meet system gravimetric capacity target

- N_{ex} varies in a narrow range over 75-250 bar storage pressures.

Along with ΔH^0, N_{ex}^{max} may be regarded as a material property

- Material with higher N_{ex}^{max} likely more difficult to discover
- Preferable to select storage pressure that requires smallest N_{ex}^{max}



$$N_{ex} = N_{ex}^{max}(1-\rho_g v_a)\frac{KP}{1+KP}$$

$$ln(K) = \frac{\Delta S}{R} - \frac{\Delta H}{RT}$$

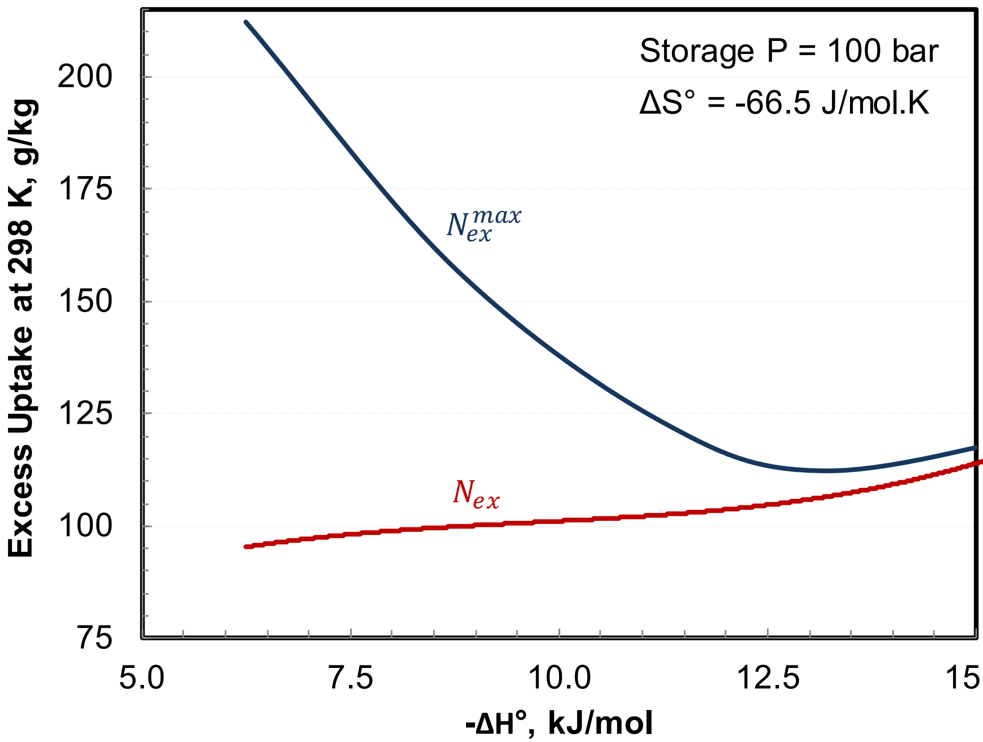
$$\Delta H = \Delta H^0 + \frac{R}{2}(T_0 - T)$$

$$\Delta S = \Delta S^0 + \frac{R}{2} ln\left(\frac{T_0}{T}\right)$$

Accomplishments: Optimum Enthalpy of Adsorption

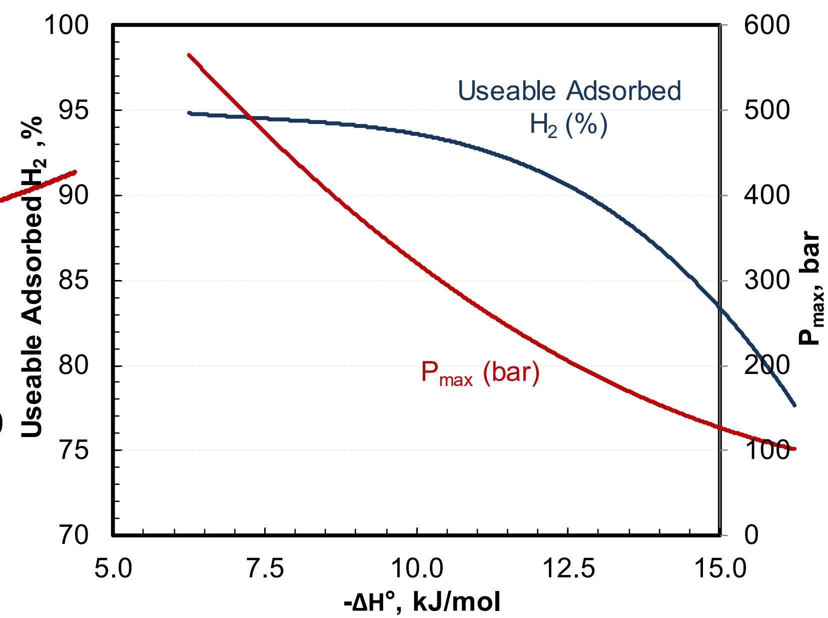
13.2 kJ/mol enthalpy of adsorption ($-\Delta H^0$) is about the optimum value for $-\Delta S^0$ = 66.5 J/mol.K, 100-5 bar pressure swing, 35-60°C temperature swing

- P_{max} too high for lower $-\Delta H^0$: e.g., 300 bar for $-\Delta H^0$ = 10.3 kJ/mol
- Usable adsorbed H_2 decreases for larger $-\Delta H^0$: 80% for $-\Delta H^0$ = 15.6 kJ/mol



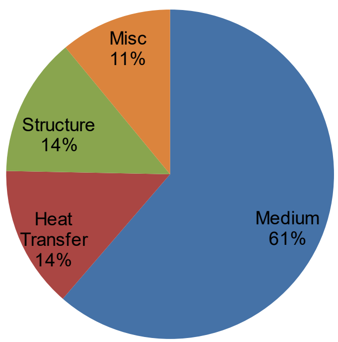
Usable adsorbed H_2 (N_{ex}^r): Difference in N_{ex} after charge (s) and N_{ex} after discharge (d)

$$N_{ex}^r = N_{ex}(P_s, T_s) - N_{ex}(P_d, T_d)$$

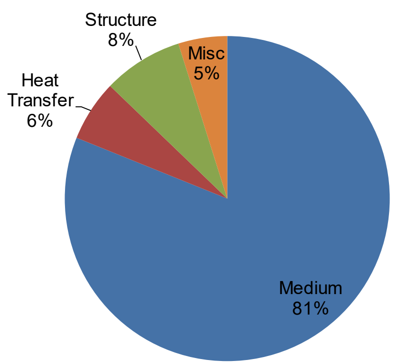


Accomplishments: Summary and Next Steps

- Verify projected maximum room temperature capacities with LBNL ST133 leads
- Determine sorbent requirements to match performance of 700-bar system
- Investigate lower storage temperatures
- Translate sorbent requirements to required H_2 uptake in specific linkers and metal organic frameworks
- Model dual sites to represent H_2 uptake in linker and MOF



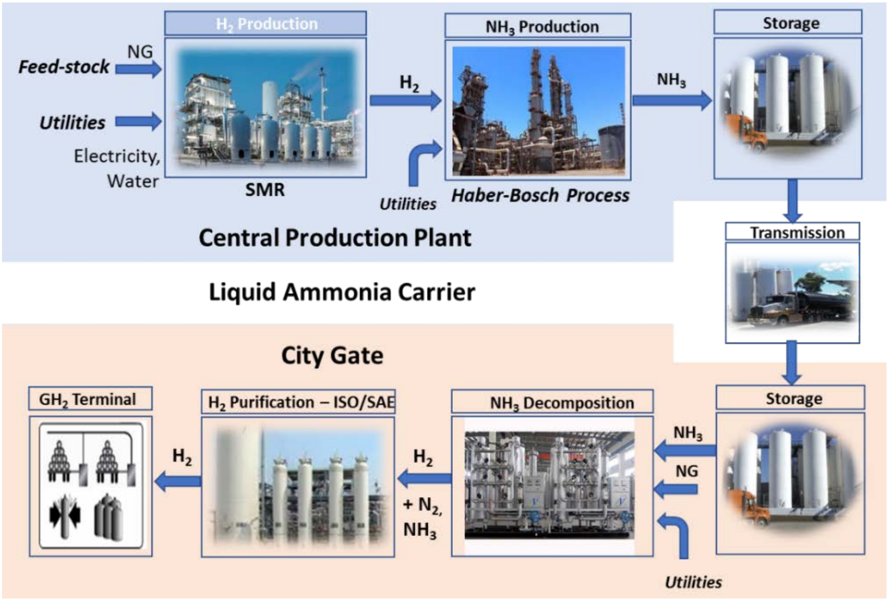
Weight Distribution

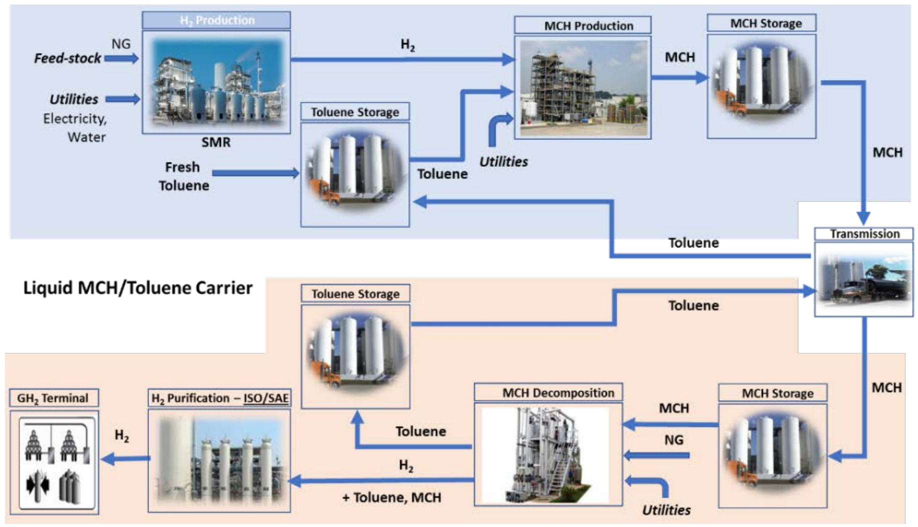


Volume Distribution

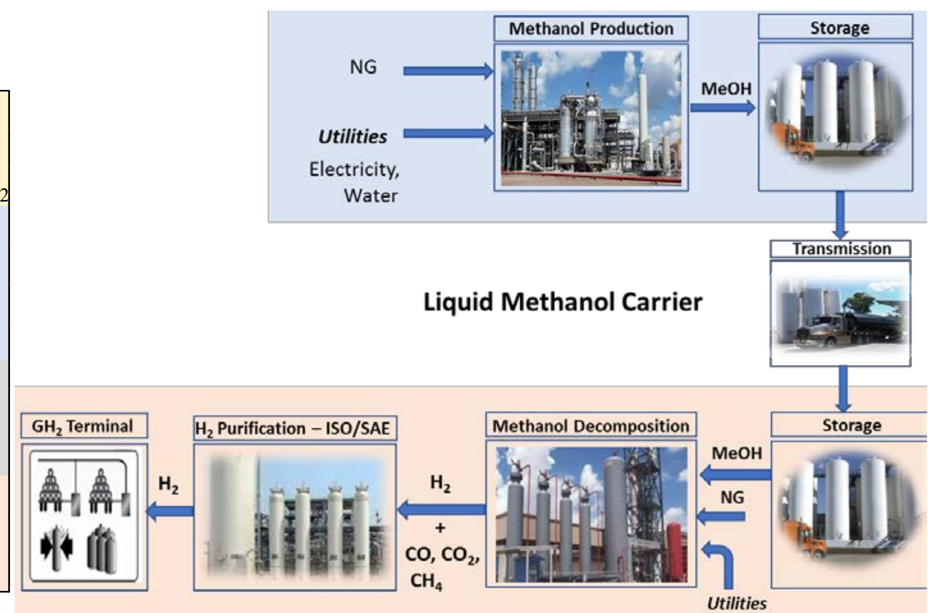
Summary Results				
	Unit	Low ΔS^o	Medium ΔS^o	High ΔS^o
Entropy of Adsorption ($-\Delta S^o$)	J/mol.K	50	66.5	100
Enthapy of Adsorption ($-\Delta H^o$)	kJ/mol	7.9	13.2	23.9
Excess Uptake at 100 bar, 308 K	g-H_2/kg	97.2	101.2	114.1
H_2 Stored in Sorbent	%	91.1	91.0	90.7
H_2 Stored in Pores and Voids	%	8.9	9.0	9.3
Bulk Density of Sorbent-ENG Compact	kg/m^3	532	513	465
Refueling Heat Load	MJ/kg-H_2	4.3	7.0	12.2
Carbon Fiber Composite	kg	7.6	7.6	7.6
Storage Temperature	K	308	308	308
Discharge Temperature	K	333	333	333
Storage Pressure	bar	100	100	100
Minimum Delivery Pressure	bar	5	5	5

Accomplishments: Hydrogen Carrier Pathways





MP	BP	H_2 Capacity		Production		Decomposition		
°C	°C	wt%	g/L	P, bar	T, °C	P, bar	T, °C	ΔH kJ/mol-H_2
Ammonia								
-78	-33.4	17.6	121	150	375	20	800	30.6
				Haber-Bosch Process		High-Temperature Cracking		
				Fe Based Catalyst		Ni Catalyst		
Methanol								
-98	64.7	18.75	149	51	250	3	290	16.6
				$Cu/ZnO/Al_2O_3$ Catalyst		Steam Reforming		
MCH								
-127	101	6.1	47	24	220	3.5	400	68.3
				Non-PGM Catalyst		Pt/Al_2O_3 Catalyst		



Accomplishments: H_2 Carrier Study - Tools and Parameters

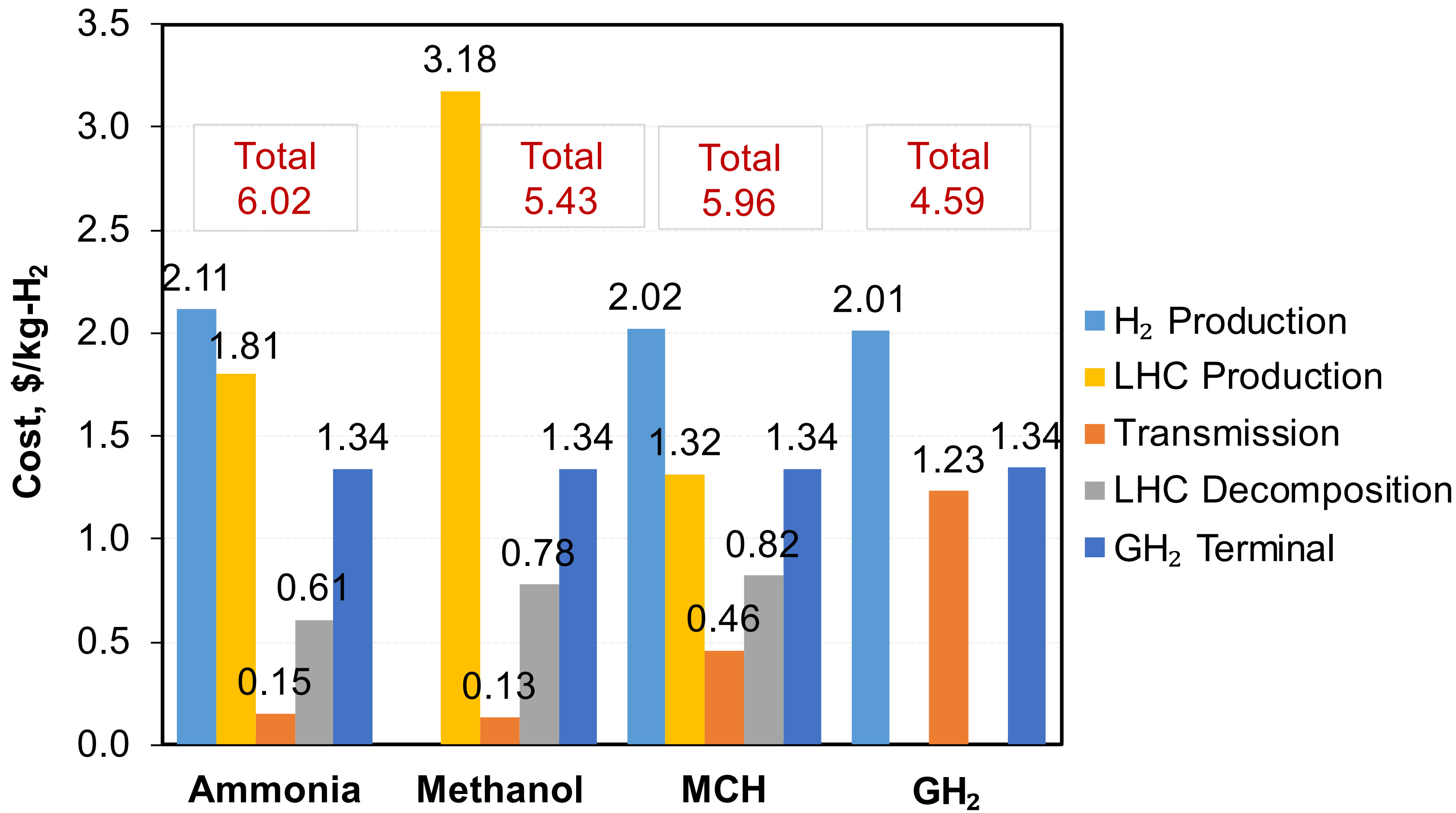
Financial Assumptions	City H_2 annual average daily use = 50,000 kg-H_2/day; Operating capacity factor = 90%; Internal rate of return (IRR) = 10%; Depreciation (MACRS)=15 yrs; Plant life=30 yrs; Construction period=3 yrs			
	NG	**Electricity**	**Water**	**Toluene**
Feedstock and Utilities	6.00 \$/MBtu	5.74 ¢/kWh	0.54 ¢/gal	0.768 \$/kg
H_2 Production by SMR, /kg-H_2	0.156 MBtu	0.569 kWh	3.35 gal	
Hydrogenation				
Ammonia	Haber-Bosch process and cryogenic air separation unit; 350 tpd;			
Methanol	Steam reforming of CH_4/CO_2 to synthesis gas $(H_2\text{-}CO)/(CO+CO_2)$=2.05; Conversion to methanol; methanol purification; 320 tpd;			
Toluene	99% conversion of toluene to MCH over non-PGM catalyst			
Dehydrogenation				
Ammonia	Catalytic decomposition of ammonia at high temperatures; H_2 purification by PSA at 20 atm (85% recovery)			
Methanol	Catalytic steam reforming, H_2 purification by PSA at 20 atm (85% recovery)			
MCH	90% conversion of MCH to toulene; 4.1% make-up toluene H_2 purification by PSA at 20 atm (90% recovery)			
Transmission	HDSAM v 3.1, Truck Liquid Delivery			
	Ammonia	**Methanol**	**MCH**	**GH_2**
Payload (kg)	22,500	22,500	22,500	1,042
Volume (m^3)	37	28	29	36
H_2 (kg)	3398	3465	1112	1042
GH_2 Terminal	HDSAM v 3.1, Compressed Gas H_2 Terminal			

Rath, L. (2011). Cost and performance baseline for fossil energy plants: Coal to synthetic natural gas and ammonia. DOE/NETL-2010/1402.
Tan, E. et al. (2015). Process design and economics for the conversion of lignocellulosic biomass to hydrocarbons via indirect liquefaction. NREL/TP-5100-62402.
Campbell, C. (2014). Hydrogen storage and fuel processing strategies. PhD Thesis, Newcastle University

Accomplishments: Levelized H_2 Cost at City Gate (50,000 kg-H_2/d)

Hydrogen carrier options incur incremental costs of 0.84-1.43 \$/kg-H_2

- To be competitive with the baseline GH_2 scenario, cost of LHC production, decomposition and make-up and H_2 purification must be < 0.77-1.10 \$/kg-H_2
- LHC related costs as analyzed: 2.52 (ammonia), 1.95 (methanol), 2.15 (MCH) \$/kg-H_2

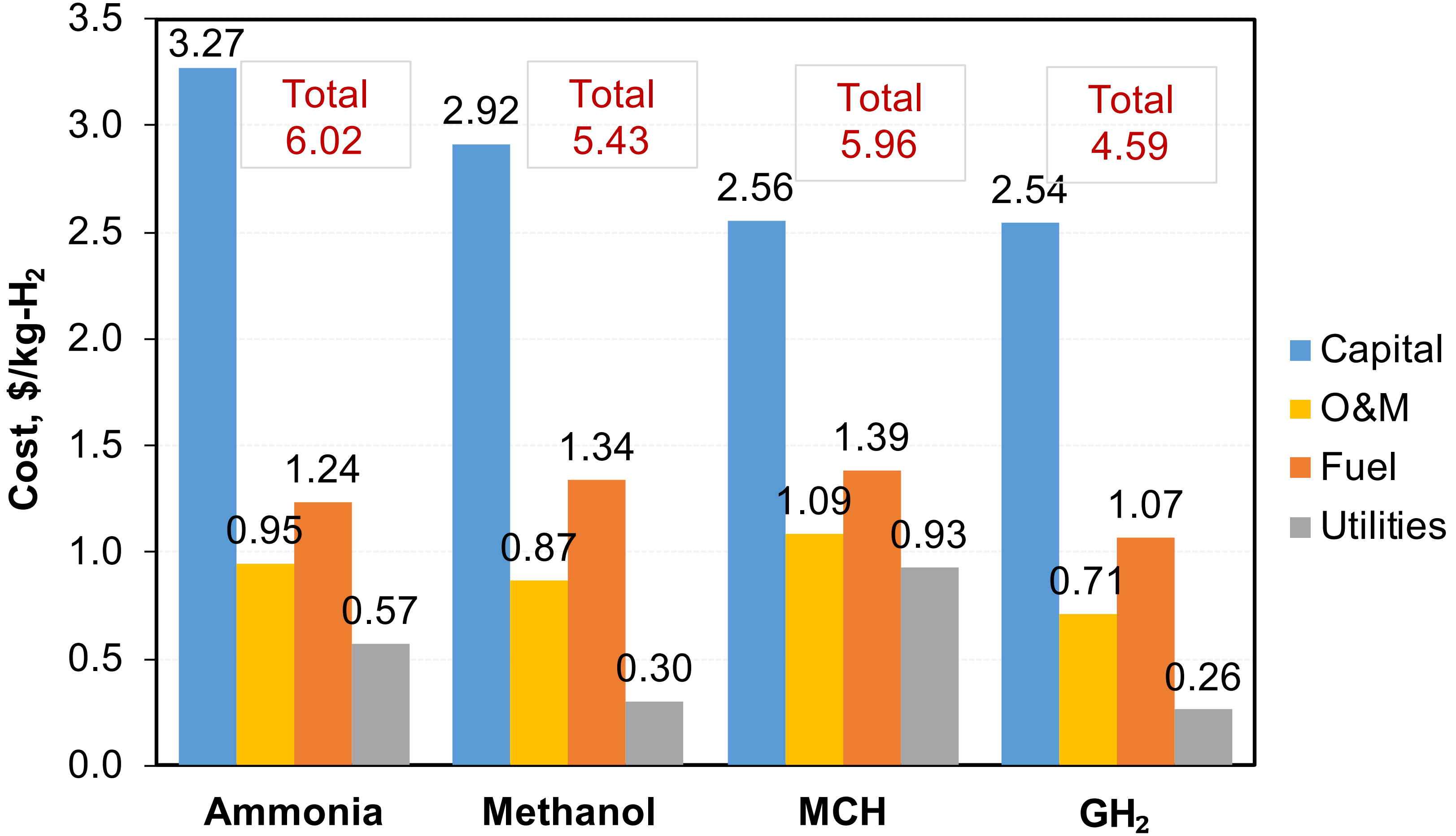


Baseline GH_2 scenario: Central SMR, H_2 compression & storage; truck transmission; GH_2 terminal

Accomplishments: Breakdown of Levelized H_2 Cost at City Gate

Sources of increases in levelized costs compared to GH_2 scenario

- Ammonia: 54% capital; comparable O&M and fuel; ~10% utilities
- Methanol: 54% capital; 41% O&M and fuel; small for utilities
- MCH: 43% capital; comparable O&M, fuel and utilities

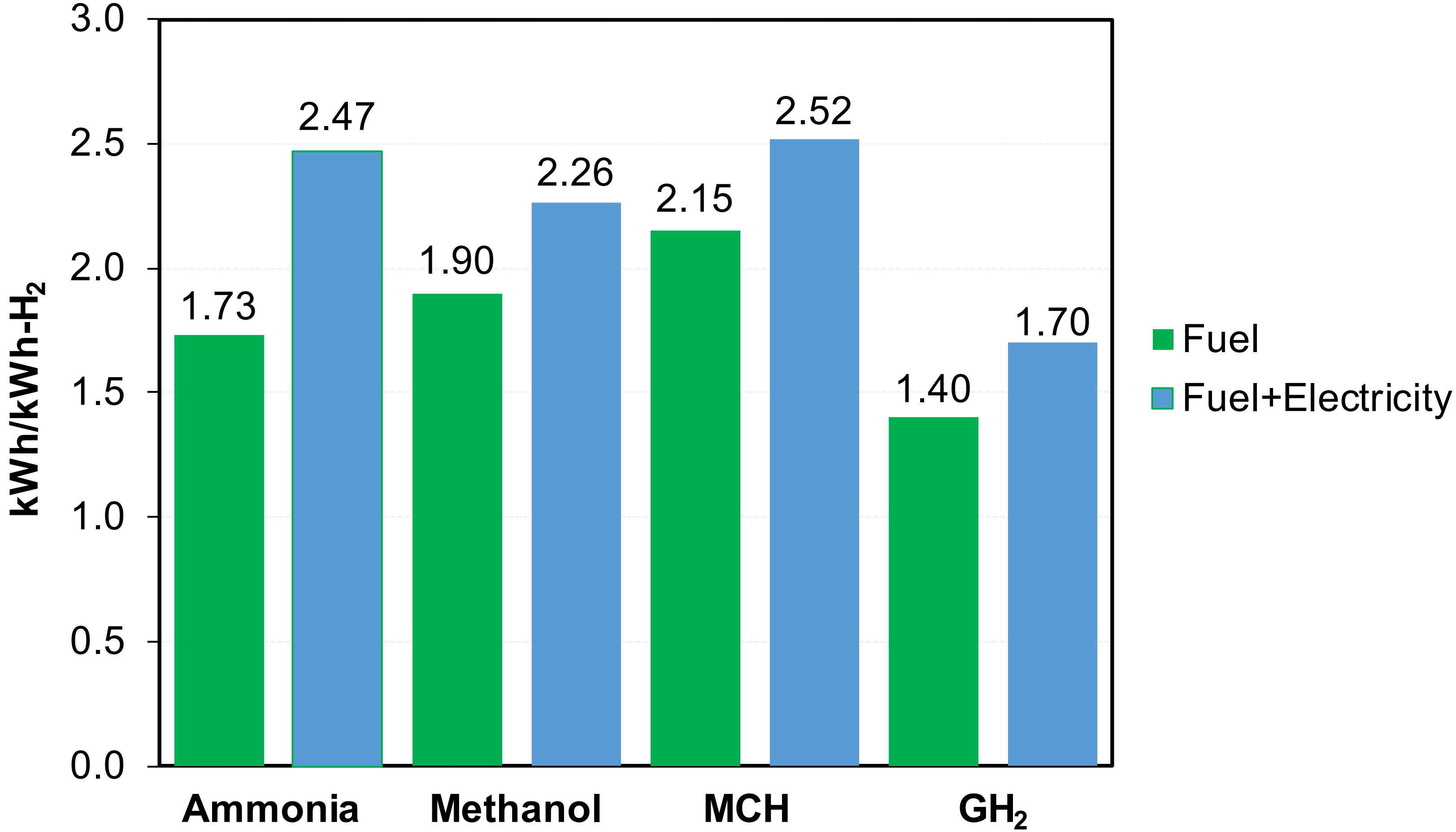


For cost breakdown, fuel refers to natural gas (NG); utilities include electricity, water & make-up toluene

Accomplishments: Energy Efficiency

Endothermic dehydrogenation step including PSA at city gate is the largest contributor to the increase in energy consumption

- Total energy includes fuel plus electrical energy, assuming 33% efficiency in generating electrical power
- 38-50% higher energy consumption for the hydrogen carriers



For calculating energy efficiency, make-up toluene is included with fuel

Accomplishments: Summary and Next Steps

1. Analyze scenarios that favor hydrogen carriers
   - Large production plants that yield economy of scale and deployment of more efficient, less expensive technologies
   - Long transmission distances unsuitable for pipeline transmission or truck delivery of gaseous or liquid hydrogen
   - Market entry and other scenarios in which the carriers are supplied by the existing plants or have mix use

2. Develop process models for toluene/MCH pathway
   - Higher pressure dehydrogenation to remove the H_2 compression step
   - Reduction of MCH losses by refrigeration or higher pressure operation
   - Calibrate model and results against data from SPERA Hydrogen System

3. Analyze alternate two-way liquid organic carriers including perhydro dibenzyltoluene (MSH/H18-MSH) proposed by Hydrogenious

4. Investigate carriers that are particularly suitable for renewable hydrogen production and energy storage

5. Conduct reverse engineering to determine desirable properties of hydrogen carriers

FY2018 Collaborations

Cryo-Compressed Hydrogen	LLNL, BMW: LH_2 pumps, fatigue behavior of metal liners, supercritical hydrogen storage, vacuum insulation, model validation
Compressed Hydrogen Storage	PNNL Team: 700-bar tank performance (ST101) Ford: Alternate tank design concepts
Sorbents	LBNL: Binding multiple H2 molecules per metal cation (ST133)
Metal Hydrides	ORNL: reverse engineering of high-pressure metal hydrides, acceptability envelope
Off-Board Fuel Cycle Efficiency	ANL (H2A Group), ANL (HDSAM), H2IT Taskforce
Off-Board Cost	ANL (H2A Group), ANL (HDSAM), H2IT Taskforce
On-Board Cost	Strategic Analysis Inc (SA)

- Argonne develops the storage system configuration, determines performance, identifies and sizes components, and provides this information to SA for manufacturing cost studies

Propose Future Work

1. Cryo-compressed H_2 Storage
   - Publish a paper on CcH_2 storage for fuel cell electric buses
   - Work with DOE, LLNL, and PNNL to develop material property database and tools for certification
2. H_2 storage in room-temperature sorbents
   - Verify the projected maximum room temperature capacities with LBNL ST133 leads
   - Determine sorbent requirements to match performance of 700-bar system
   - Investigate lower storage temperatures
   - Translate the sorbent requirements to required H_2 uptake in specific linkers and metal organic frameworks
   - Model dual sites to represent H_2 uptake in linker and MOF
3. Compressed H_2 storage for medium and heavy duty fuel cell vehicles
   - Manufacturability of elongated boss
   - Validation of Type 3, 700-bar cH_2 storage analysis results
   - Document Type 3 vs Type 4 tanks at different storage pressures
4. Hydrogen carriers for delivery
   - Analyze scenarios that favor hydrogen carriers
   - Independent review and consultation with Hydrogen Interface Taskforce and delivery experts

Any proposed future work is subject to change based on funding levels.

Project Summary

Relevance:	Independent analysis to evaluate on-board and off-board performance of materials and systems
Approach:	Develop and validate physical, thermodynamic and kinetic models of processes in physical and material-based systems Address all aspects of on-board and off-board targets including capacities, rates and efficiencies
Progress:	Showed that compared to Type 4 700-bar cH_2 tanks, 500-bar CcH_2 can achieve 70% higher gravimetric capacity, 80% higher volumetric capacity, and 70% saving in CF composite Established targets for room temperature sorbents: 106±8 g-H_2/kg excess uptake at 100 bar when compacted to 500±35 kg/m^3 bulk density Demonstrated a concept of reinforcing the dome section with a metal boss for >10% saving in CF composite for Type 4 tanks Determined the cost of producing/hydrogenating H_2 carriers, transmitting to and dehydrogenating them at city gate, and storing H_2 ($5.43-$6.02)
Collaborations:	Ford, HL, LANL, LLNL, Materia, ORNL, PNNL, SA
Proposed Future Work:	Material properties and tools for CcH_2 material certification Compare and validate H_2 uptake in room temperature sorbents Seek independent review of metal boss reinforced dome concept Analyze scenarios that favor hydrogen carriers

Reviewer Comments

Generally favorable reviews with the following comments/recommendations

- Explain the reason for conducting some analyses, e.g., the application of CcH_2 storage to fuel cell buses.
- Savings of 1.1 % carbon fiber is too small. Explore more revolutionary approaches to reducing the thickness of CF composite.
- Complete the analysis of high-pressure metal hydride storage tanks.
- Focus on forward-thinking ideas and critical issues with potential for major breakthrough

FY18 work scope consistent with above recommendations

√ We prepared a paper on CcH_2 storage for fuel cell buses that explains its unique potential in an emerging infrastructure that relies on liquid H_2 delivery

√ We proposed and analyzed the concept of metal-boss reinforced dome section for reducing the number of helical windings by more than 25%

√ We completed the analysis of high-pressure, low-enthalpy metal hydrides for on-board H_2 storage. The paper is being prepared for submission

√ We completed a reverse engineering analysis of room-temperature sorbents to complement material discovery efforts on binding multiple H_2 molecules per metal cation inserted in MOFs

√ We initiated a new analysis of one-way and two-way carriers for hydrogen delivery to city gate

Technical Back-Up Slides

Ambient-Temperature Type 3 Tanks: Fatigue Analysis

ABAQUS WCM and FE-SAFE Models

- Autofrettage process to induce residual compressive stress in liner and increase the fatigue life of the composite tank

Process and Material Options

- Autofrettage at ambient temperature
- Autofrettage (proof) pressure
- Aluminum liners
- Brown-Miller strain life curve

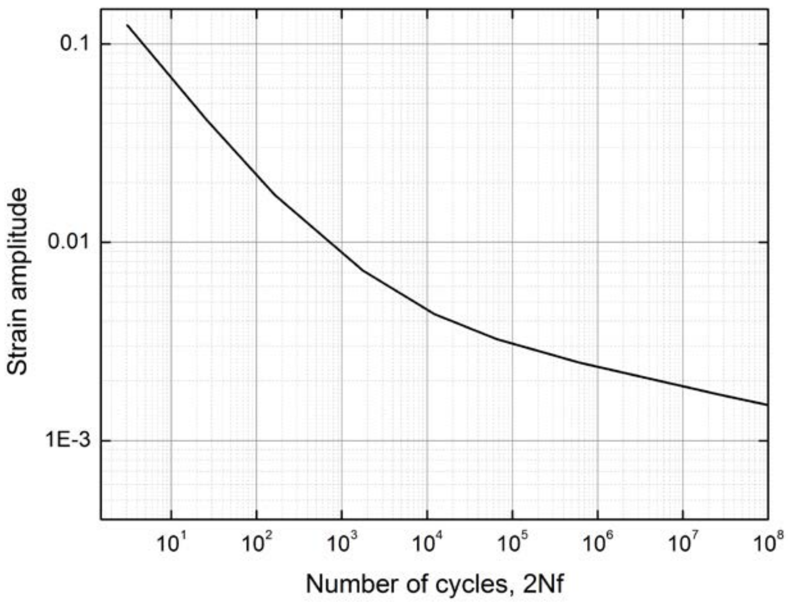
  for aluminum

$$\frac{\Delta\gamma}{2} + \frac{\Delta\varepsilon_N}{2} = 1.65\frac{\sigma_f'}{E}\left(2N_f\right)^b + 1.75\varepsilon_f'\left(2N_f\right)^c$$

σ_f' fatigue strength coefficient

ε_f' fatigue ductility coefficient

b, c fatigue exponents



Strain life curve

Applicable Codes and Standards

- SAE durability test cycles: 5500 for light duty vehicles

Evaluation of Boss-Reinforced Dome Concept

Carbon Fiber Composite Windings*

- Baseline boss: 67.5 kg helical, 39.8 kg hoop, 107.3 kg total
- New boss: 49.5 kg helical, 41.6 kg hoop, 91.1 kg total

Aluminum Boss

- Baseline boss: 3.4 kg
- New boss: 26.6 kg

System Gravimetric and Volumetric Capacities

- Baseline boss: 1.31 kWh/kg gravimetric, 0.81 kWh/L volumetric
- New boss: 1.25 kWh/kg gravimetric, 0.81 kWh/L volumetric

Savings in material cost with the new boss configuration:

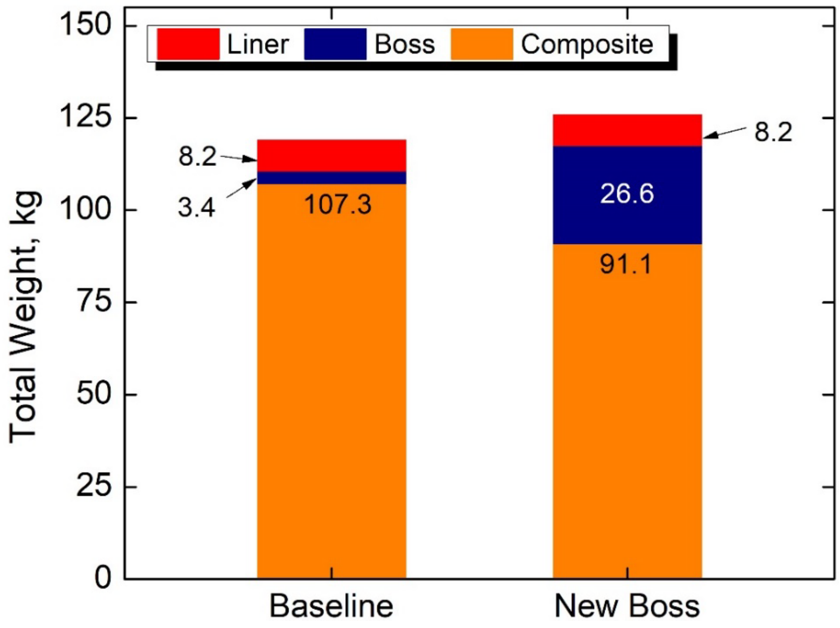
$\Delta(CF) = - \$282.5$

$\Delta(Boss) = \$94.9$

$\Delta(Liner) = \$0.07$

$\Delta(Total\ cost) = -\$187.6$

(-1.00 \$/kWh)



*Results to be updated for low cost resin and alternate sizing discussed in 2015 DOE Hydrogen and Fuel Cells Program Record #: 15013

Langmuir Isotherm Model

$$N_e = N_{max}(1-\rho_g v_a)\frac{KP}{1+KP}$$

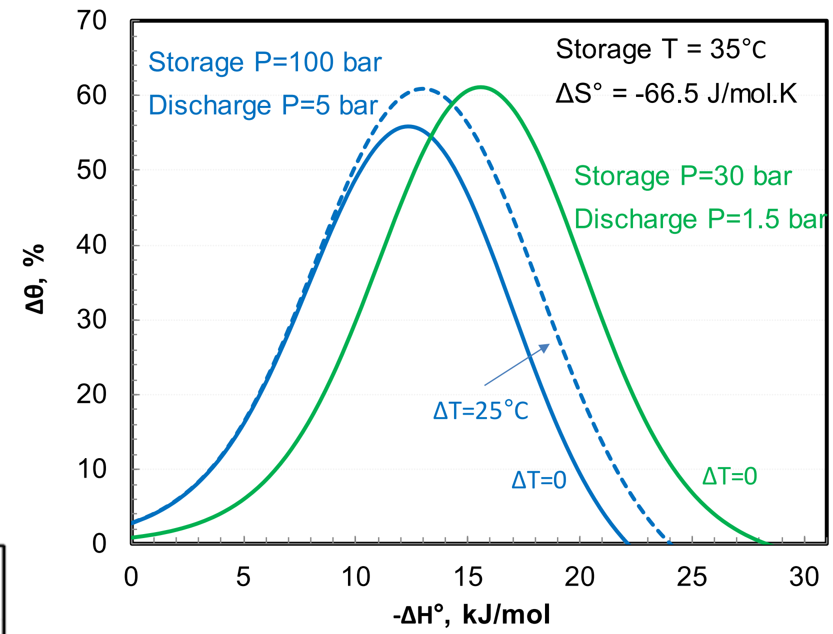
$$\theta = \frac{KP}{1+KP}$$

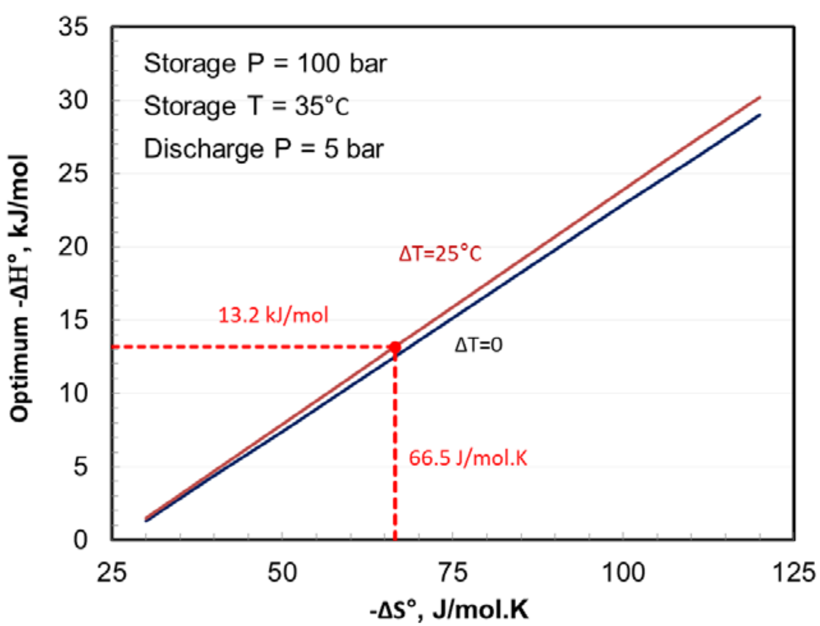
$$ln(K) = \frac{\Delta S}{R} - \frac{\Delta H}{RT}$$

$$\Delta H = \Delta H^0 + \frac{R}{2}(T_0 - T)$$

$$\Delta S = \Delta S^0 + \frac{R}{2} ln\left(\frac{T_0}{T}\right)$$

Optimum ΔH^0 for maximum usable H_2 depends on operating pressures

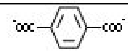
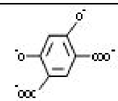
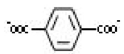
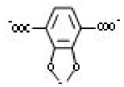
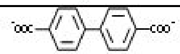
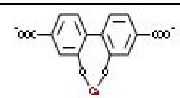
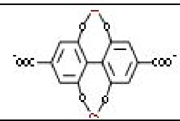
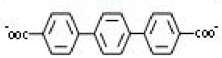
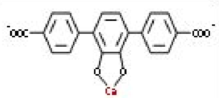
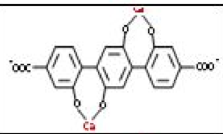
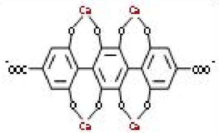




Optimum ΔH^0 is a function of ΔS^0

Theoretical Uptake in Metalated UiO MOFs

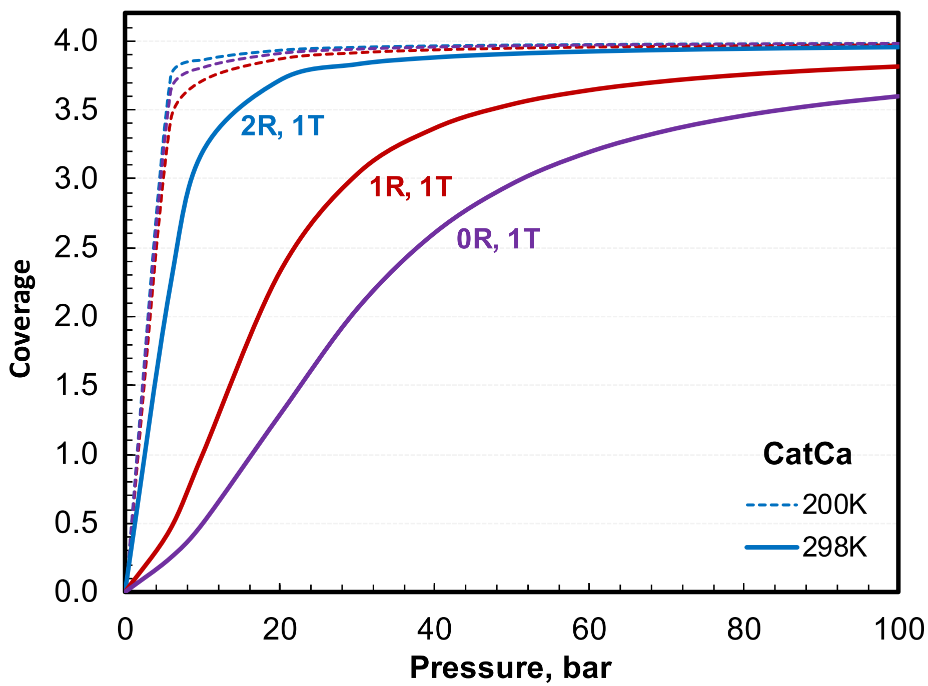
Based on formula units, 4 H_2 adsorbed per Ca^{2+} cation, and listed uptake in UiO MOFs

	Linker Structure	Unit Formula	Absolute Uptake g-H_2/kg
MOF-5		$Zn_4O(CO_2C_6H_4CO_2)_3$	6.0
Ni_2(m-dobdc)		$Ni_2(CO_2C_6H_2O_2CO_2)$	9.1
UiO-66		$Zr_6O_4(OH)_4(CO_2C_6H_4CO_2)_6$	1.5
UiO-66-Ca		$Zr_6O_4(OH)_4(CO_2C_6H_2CaO_2CO_2)_6$	24.2
UiO-67		$Zr_6O_4(OH)_4(CO_2(C_6H_4)_2CO_2)_6$	3.0
UiO-67-Ca		$Zr_6O_4(OH)_4(CO_2\text{-}(C_6H_3)_2CaO_2\text{-}CO_2)_6$	21.4
UiO-67-Ca_2		$Zr_6O_4(OH)_4(CO_2\text{-}(C_6H_2)_2(CaO_2)_2\text{-}CO_2)_6$	34.6
UiO-68		$Zr_6O_4(OH)_4(CO_2(C_6H_4)_3CO_2)_6$	4.0
UiO-68-Ca		$Zr_6O_4(OH)_4(CO_2\text{-}C_6H_4\text{-}C_6H_2CaO_2\text{-}C_6H_4\text{-}CO_2)_6$	19.5
UiO-68-Ca_2		$Zr_6O_4(OH)_4(CO_2\text{-}C_6H_3\text{-}CaO_2\text{-}C_6H_2\text{-}CaO_2\text{-}C_6H_3\text{-}CO_2)_6$	31.1
UiO-68-Ca_4		$Zr_6O_4(OH)_4(CO_2\text{-}C_6H_2\text{-}(CaO_2)_2\text{-}C_6\text{-}(CaO_2)_2\text{-}C_6H_2\text{-}CO_2)_6$	47.5

Room Temperature Sorbents

M. Head-Gordon and J. R. Long (ST133): Binding Multiple H_2 Molecules per Metal Cation

- E. Tsivion, S. P. Veccham and M. Head-Gordon, High Temperature Hydrogen Storage of Multiple Molecules: Theoretical Insights from Metalated Catechols, ChemPhysChem 2017, 18, 184-188.
- Ca-catecholate, Mg-catecholate and thio-catecholate in UiO-66 MOF



Sequential Adsorption Model

- Thermodynamic quantities for 2R, 1T DFT calculations for CatCa by Tsivion, Veccham and Gordon

H_2	1	2	3	4
ΔE, kJ/mol	-16.0	-15.7	-15.3	-15.0
ΔH, kJ/mol	-7.5	-7.2	-6.8	-6.4
ΔS, J/mol/K	-41.3	-38.8	-35.9	-33.0

- Approaching 100% coverage of metalated linkers in UiO-66 at 100 bar, room temperature
- 22.7 g-H_2/kg (2.25 wt%) projected increase in H_2 uptake if all the original linkers in the MOF are replaced by metalated linkers