System Analysis of Physical and Materials-Based Hydrogen Storage

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Project Start Date: October 1, 2004
Project End Date: Project continuation and direction determined annually by DOE

Overall Objectives

- Model various developmental hydrogen storage systems.
- Provide results to DOE for assessment of performance targets and goals.
- Develop models to "reverse-engineer" particular approaches.
- Identify interface issues, opportunities, and data needs for technology development.

Fiscal Year (FY) 2018 Objectives

- Conduct system analysis of cryo-compressed hydrogen (CcH_2) storage for fuel cell buses with the constraint of 7-d dormancy for 95% full tanks.
- Investigate alternate configurations of compressed hydrogen (cH_2) storage tanks for light-duty and heavy-duty vehicles.
- Support Hydrogen Materials Advanced Research Consortium (HyMARC) activities by performing reverse engineering analysis of room-temperature hydrogen storage in sorbents.
- Support H2@Scale initiative by analyzing one-way and two-way liquid hydrogen carrier pathways.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan[1]:

(A) System Weight and Volume

(B) System Cost

(C) Efficiency

(E) Charging/Discharging Rates

(J) Thermal Management

(K) System Life Cycle Assessments.

Technical Targets

This project is conducting system-level analyses to address the DOE 2020 technical targets for onboard hydrogen storage systems:

- System gravimetric capacity: 1.5 kWh/kg
- System volumetric capacity: 1.0 kWh/L
- Minimum hydrogen delivery pressure: 5 bar
- Refueling rate: 1.5 kg/min
- Minimum full flow rate of hydrogen: 0.02 g/s/kW.

FY 2018 Accomplishments

- Showed 500-bar CcH_2 can achieve 215% increase in storage density, 90% improvement in gravimetric capacity, 170% higher volumetric capacity, and 47% savings in carbon fiber (CF) composite as compared to the Type 3 350-bar cH_2 tanks currently in use in fuel cell buses.

[1] https://www.energy.gov/eere/fuelcells/downloads/fuel-cell-technologies-office-multi-year-research-development-and-22

- 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.
- Performed preliminary analysis on the cost of producing/hydrogenating hydrogen carriers, transmitting them to and dehydrogenating them at the city gate, and storing the hydrogen on site ($5.43–$6.02).

INTRODUCTION

Several different approaches are being pursued to develop onboard hydrogen storage systems with the goal of meeting the DOE targets for light-duty vehicle applications. Each approach has unique characteristics, such as pressure and temperature, the thermal energy and temperature of charge and discharge, and kinetics of the physical and chemical process steps involved. The approaches take into account the requirements for the materials and energy interfaces between the storage system, the fuel supply system, and the fuel user. Other storage system design and operating parameters influence the projected system costs as well. Models are being developed to understand the characteristics of storage systems based on the various approaches and to evaluate their potential to meet the DOE targets for onboard applications—including the offboard targets for energy efficiency.

APPROACH

The approach is to develop thermodynamic, kinetic, and engineering models of the various hydrogen storage systems being developed under DOE sponsorship. These models are then used to identify significant component and performance issues and to assist DOE and its contractors in evaluating alternative system configurations and design and operating parameters. Performance criteria are established that may be used, for example, in developing storage system cost models. Data is refined and validated as the models become available from the various developers. An important aspect of this work is to develop overall systems models that include the interfaces between hydrogen production and delivery, hydrogen storage, and the fuel cell.

RESULTS

Cryo-Compressed Hydrogen Storage

We revised our previous analysis of cryo-compressed hydrogen (CcH_2) storage for buses with the additional constraint of 7-d dormancy for 95% full tank [1]. We determined the required thickness of multi-layer vacuum superinsulation (MLVSI) with 0.1 mW/m.K thermal conductivity at 3-mTorr vacuum. Table 1 highlights the following advantages of liquid hydrogen refueled, supercritical CcH_2 storage at 500 bar over the baseline ambient temperature, and 350-bar compressed hydrogen storage (cH_2) in Type 3 vessels:

- >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.

Table 1. Supercritical CcH_2 Storage for Fuel Cell Buses

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

Compressed Hydrogen Storage

As part of a larger study on alternate Type 4 tank configurations for 700-bar cH_2 storage, we conducted ABAQUS/WCM simulations to investigate the possible reduction in the number of helical layers by reinforcing the entire dome section with an aluminum boss in a 147-L tank with 391-mm inner diameter and 5-mm high-density polyethylene (HDPE) liner. A previous Mirai study on extended boss showed 5% reduction in helical winding with smaller diameter and longer flange [2], but our simulations showed no significant reduction. Figure 1a compares our boss-reinforced dome concept with the baseline boss and the elongated boss in the Mirai study. Figure 1b shows the modeled stress distribution in the boss-reinforced dome indicating small regions undergoing plastic deformation at refueling pressure. A future study will investigate the fatigue performance of the boss covering the whole dome section and the possible advantages of autofrettage in meeting any fatigue criteria that may apply. Our finite element simulations indicate that boss reinforcement reduces the thickness of CF composite helical layers by ~5.0 mm, or 13% of 37.1 mm in baseline boss configuration. This 15% reduction in total weight of CF composite is offset by a 23.2 kg increase in the weight of boss. Figure 1c compares the strains along fiber direction and indicates 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. The reduction in CF composite may be greater in tanks with an aspect ratio higher than 5, as in these simulations, and will be investigated in future work.

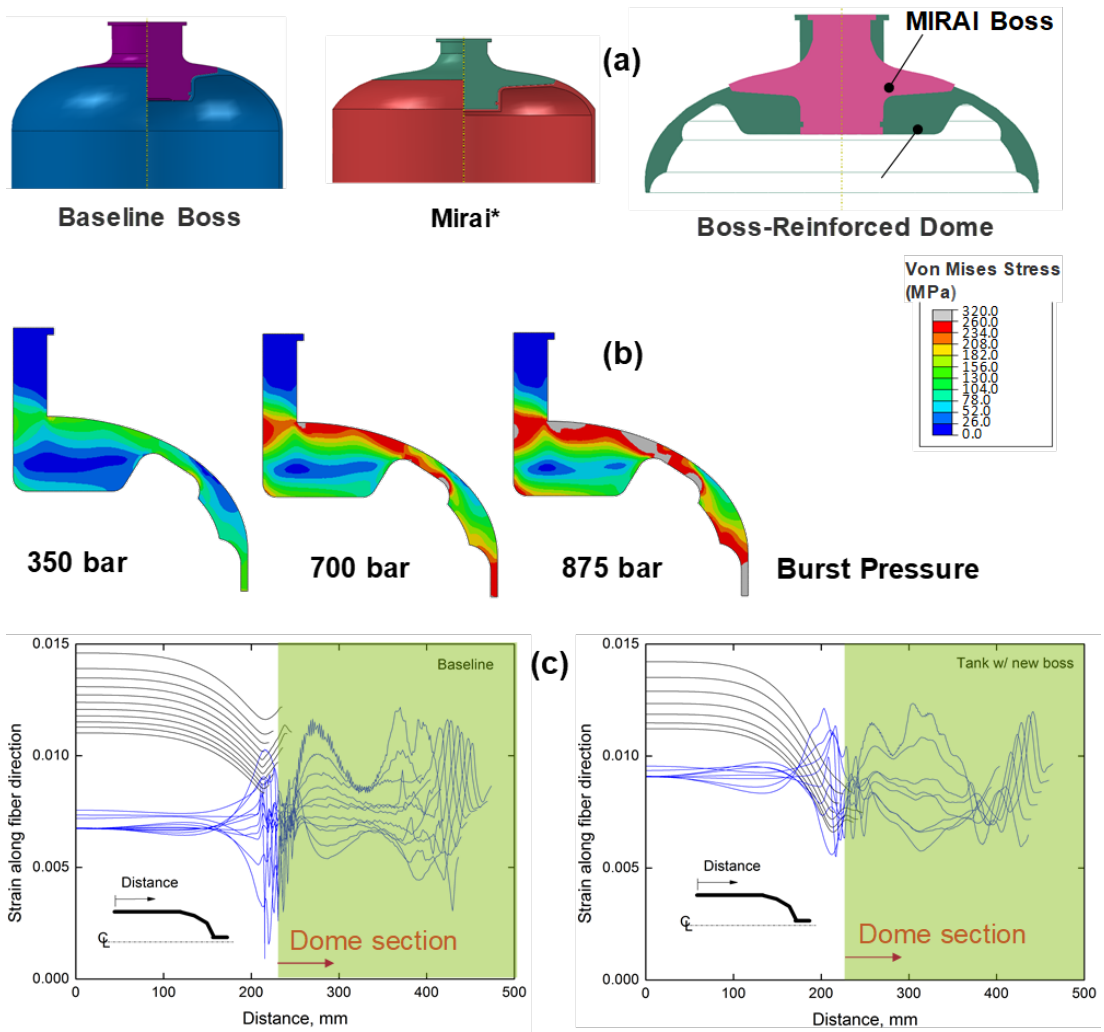

Figure 1 Boss-reinforced dome section for 700-bar Type IV tank: a) dome section; b) stress distribution in boss-reinforced dome; c) strain along fiber direction

Room-Temperature Hydrogen Storage in Sorbents

We conducted a reverse engineering analysis to determine the attributes required to meet the system targets with room-temperature sorbents in the onboard hydrogen system (Figure 2a). Table 2 lists the material attributes of interest and the system operating conditions. As in our earlier work [3], the key system requirements are 5.6 kg recoverable hydrogen and 5-bar minimum delivery pressure for the storage medium; 2.25 safety factor for the Type 4 containment vessel with 5-mm HDPE liner and 2,550-MPa strength Toray carbon fiber; and heat transfer system for 1.5 kg/min hydrogen refueling rate and 1.6 g/s hydrogen mininum full flow rate. We used a single Langmuir isotherm to represent hydrogen uptake in a sorbent.

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

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

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

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

Table 2. List of Material Properties and Operating Conditions in Reverse Engineering Analysis

		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	Off-board Coolant Temperature	K	298			T_c
Temperatures	Storage Temperature	K	308			T_c + 10°C
	Discharge Temperature	K	333			60°C on-board coolant T
Operating	Storage Pressure	bar	100	50 - 250	Study variable	
Pressures	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	

The main conclusion from the analysis is that 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. The required uptake is also a function of ΔH° and ΔS°. Figure 2b shows hydrogen uptake in a hypothetical material that has the required sorption capacity with –ΔH° = 13.2 kJ/mol and –ΔS° = 66.5 J/mol.K. For such a material, Figure 2c shows that the uptake requirement is slightly less stringent (smaller N_{ex}^{max}) at 150–175 bar storage pressure. Here, N_{ex}^{max} refers to peak excess uptake that occurs at a pressure (P_{max}), which is a function of ΔH° and temperature. For a given –ΔH°, N_{ex}^{max} is a measure of the required adsorption site density. Along with ΔH°, N_{ex}^{max} may be regarded as a material property. A material with higher N_{ex}^{max} is likely more difficult to discover meaning that it is preferable to select a storage pressure that requires the smallest N_{ex}^{max}.

Figure 2d indicates that 13.2 kJ/mol enthalpy of adsorption (–ΔH°) is about the optimum value for –ΔS° = 66.5 J/mol.K, 100–5 bar pressure swing, and 35°–60°C temperature swing. Figure 2e shows the general relationship between optimum –ΔH° and –ΔS° for specified operating pressures and temperatures.

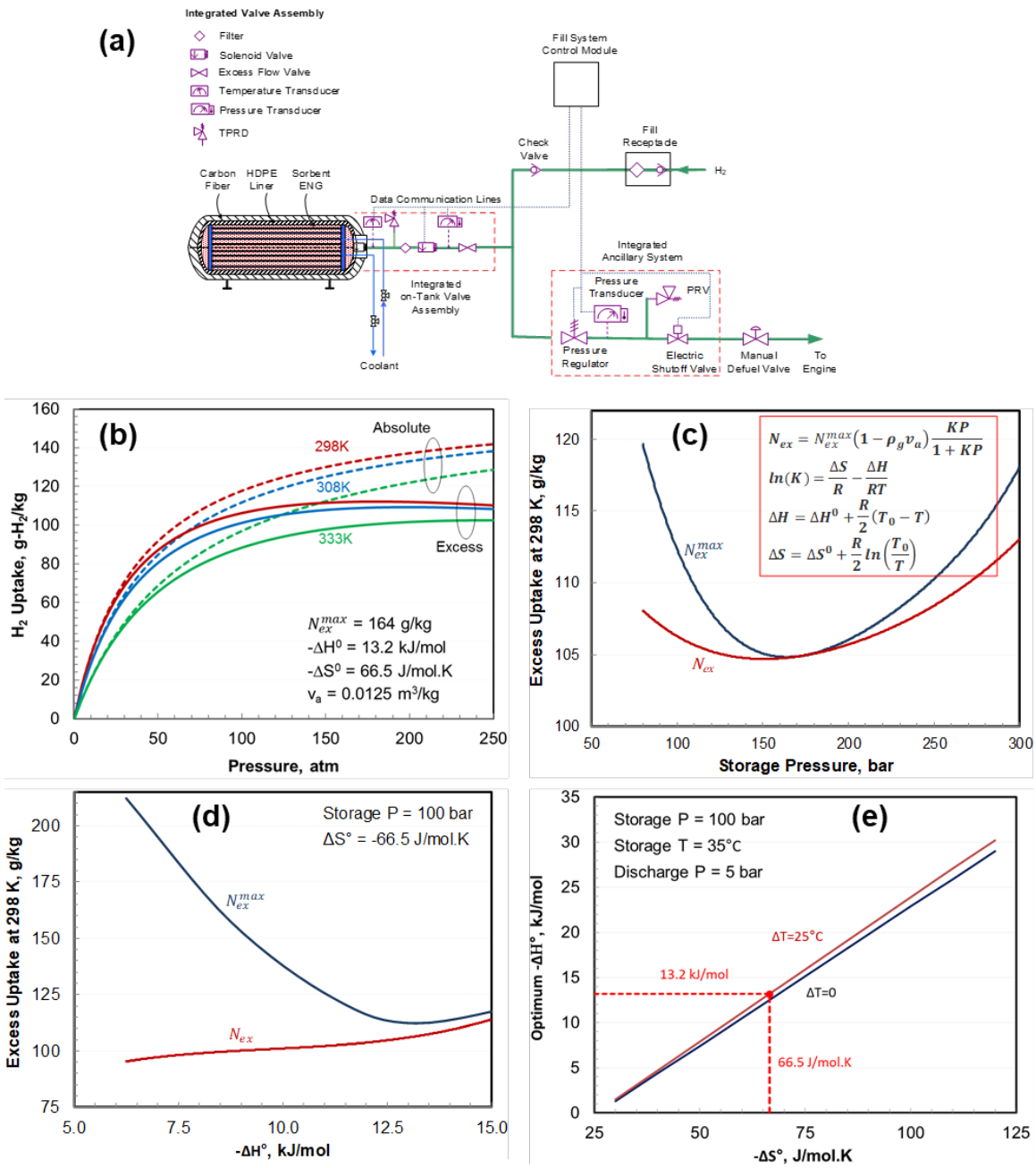

Figure 2. Hydrogen storage in room-temperature sorbents: a) schematic of the onboard storage system; b) hydrogen uptake in a hypothetical room-temperature sorbent with attributes necessary to meet the system targets; c) optimum storage pressure; d) optimum ΔH^0 for $-\Delta S^0$ = 66.5 J/mol.K; e) relationship between optimum ΔH^0 and ΔS^0

Table 3 summarizes the results for three materials with low, medium, and high ΔS°. It includes the optimum ΔH°, required uptake, refueling heat load, and CF composite for 100-bar storage pressure. The required uptakes are nearly double the maximum theoretical uptakes in metalated catachols calculated assuming four H_2 molecules absorbed per Ca^{2+} cation [4].

Table 3. Summary of Results for Low, Medium, and High ΔS^0 Sorbents

	Unit	Low ΔS^o	Medium ΔS^o	Medium ΔS^o	High ΔS^o
Entropy of Adsorption ($-\Delta S^o$)	J/mol.K	30	50	66.5	100
Enthapy of Adsorption ($-\Delta H^o$)	kJ/mol	1.5	7.9	13.2	23.9
Excess Uptake at 100 bar, 308 K	g-H_2/kg	93.6	97.2	101.2	114.1
H_2 Stored in Sorbent	%	91.2	91.1	91.0	90.7
H_2 Stored in Pores and Voids	%	8.8	8.9	9.0	9.3
Bulk Density of Sorbent-ENG Compact	kg/m^3	551	532	513	465
Refueling Heat Load	MJ/kg-H_2	1.2	4.3	7.0	12.2
Carbon Fiber Composite	kg	7.6	7.6	7.6	7.6
Storage Temperature	K	308	308	308	308
Discharge Temperature	K	333	333	333	333
Storage Pressure	bar	100	100	100	100
Minimum Delivery Pressure	bar	5	5	5	5

Liquid Hydrogen Carriers

In support of H2@Scale activities, we initiated a new task to analyze liquid hydrogen carrier (LHC) pathways. As shown in Figure 3, the initial study includes three pathways that were selected to cover different classes of carriers. Liquid ammonia and liquid methyl cyclohexane (MCH)/toluene represent a class of carriers that require a steam methane reforming (SMR) plant for hydrogen production. Liquid methanol represents a class of carriers that do not require a hydrogen production step. Liquid methanol and ammonia are one-way carriers, while MCH/toluene is a two-way carrier. Liquid ammonia and MCH are easier to produce using renewable hydrogen than methanol that would also require a source for CO_2.

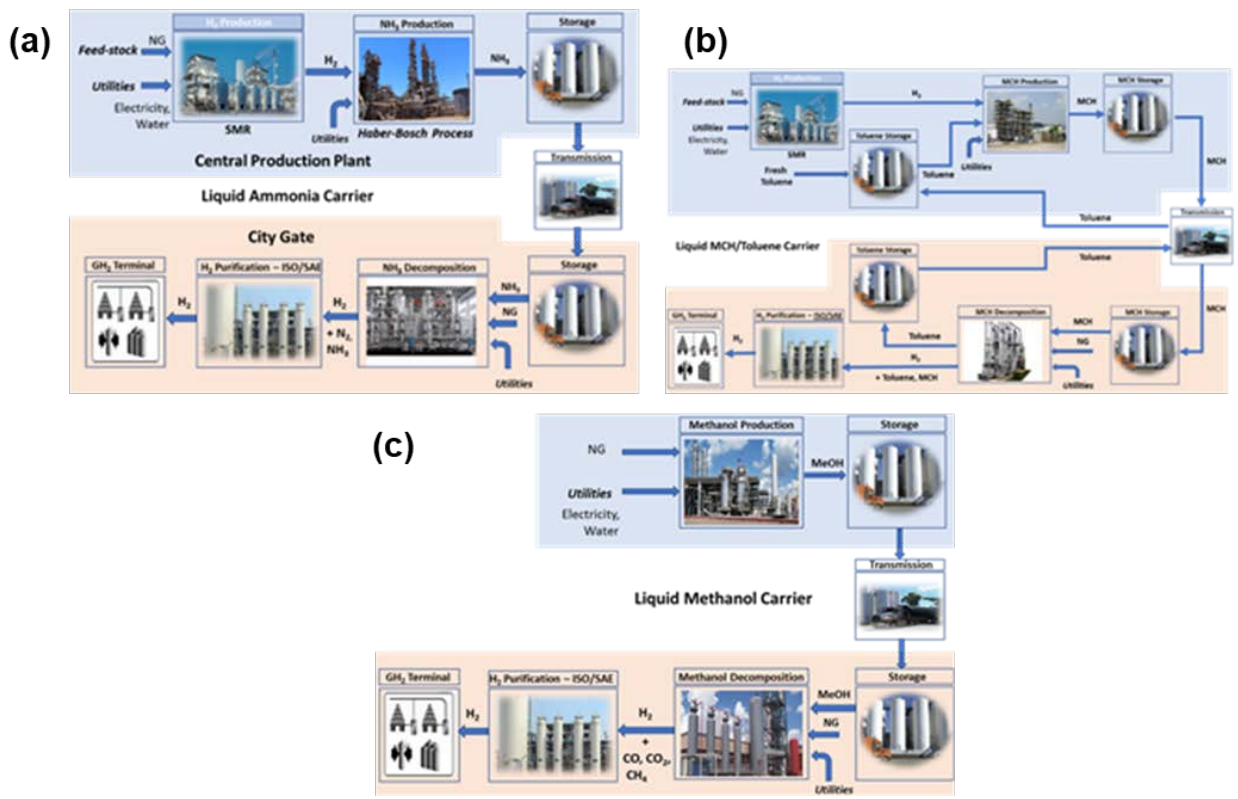

Figure 3. Hydrogen carrier pathways: a) liquid ammonia; b) liquid MCH/toluene; c) liquid methanol

Table 4 summarizes the physical properties of the carriers along with their hydrogen capacity and methods of production and decomposition. It also includes information on various modeling tools, financial assumptions, and performance parameters used to analyze the production, transmission, decomposition, and storage steps for the carrier pathways shown in Figure 3.

Table 4. Hydrogen 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			

We obtained initial results for a scenario in which the LHC production plant is located 150 km from the city gate and the annual average daily use for the city is 50,000 kg H_2/day. The scenario may be applicable to a mid-size city like Sacramento, California, with limited market in an early transition stage. As a reference, we also analyzed a baseline gaseous hydrogen (GH_2) pathway with central SMR and truck transmission to gas terminal.

Figure 4a presents the levelized hydrogen cost at city gate broken down in terms of the costs for the various steps in the LHC pathway: hydrogen production, LHC production, LHC transmission, LHC decomposition, and hydrogen terminal. The hydrogen carrier options analyzed in this initial study incur incremental costs of 0.84–1.43 $/kg H_2. To be competitive with the baseline GH_2 scenario, the combined cost of LHC production, decomposition and make-up, and hydrogen purification must be <0.77–1.10 $/kg H_2. The LHC-related costs as analyzed are 2.52 $/kg H_2 for ammonia, 1.95 $/kg H_2 for methanol, and 2.15 $/kg H_2 for MCH.

Figure 4b presents the breakdown of levelized hydrogen cost at city gate in terms of the costs for initial capital investment, operating and maintenance (O&M), fuel, and utilities. The following is a brief summary of the sources of the increases in levelized costs compared to the 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

Figure 4c compares the energy efficiency of the different pathways. The endothermic dehydrogenation step including hydrogen purification by pressure swing adsorption (PSA) at city gate is the largest contributor to the 38%–50% increase in energy consumption for hydrogen carriers. The total energy consumption in Figure 4c includes fuel plus electrical energy, assuming 33% efficiency in generating electrical power.

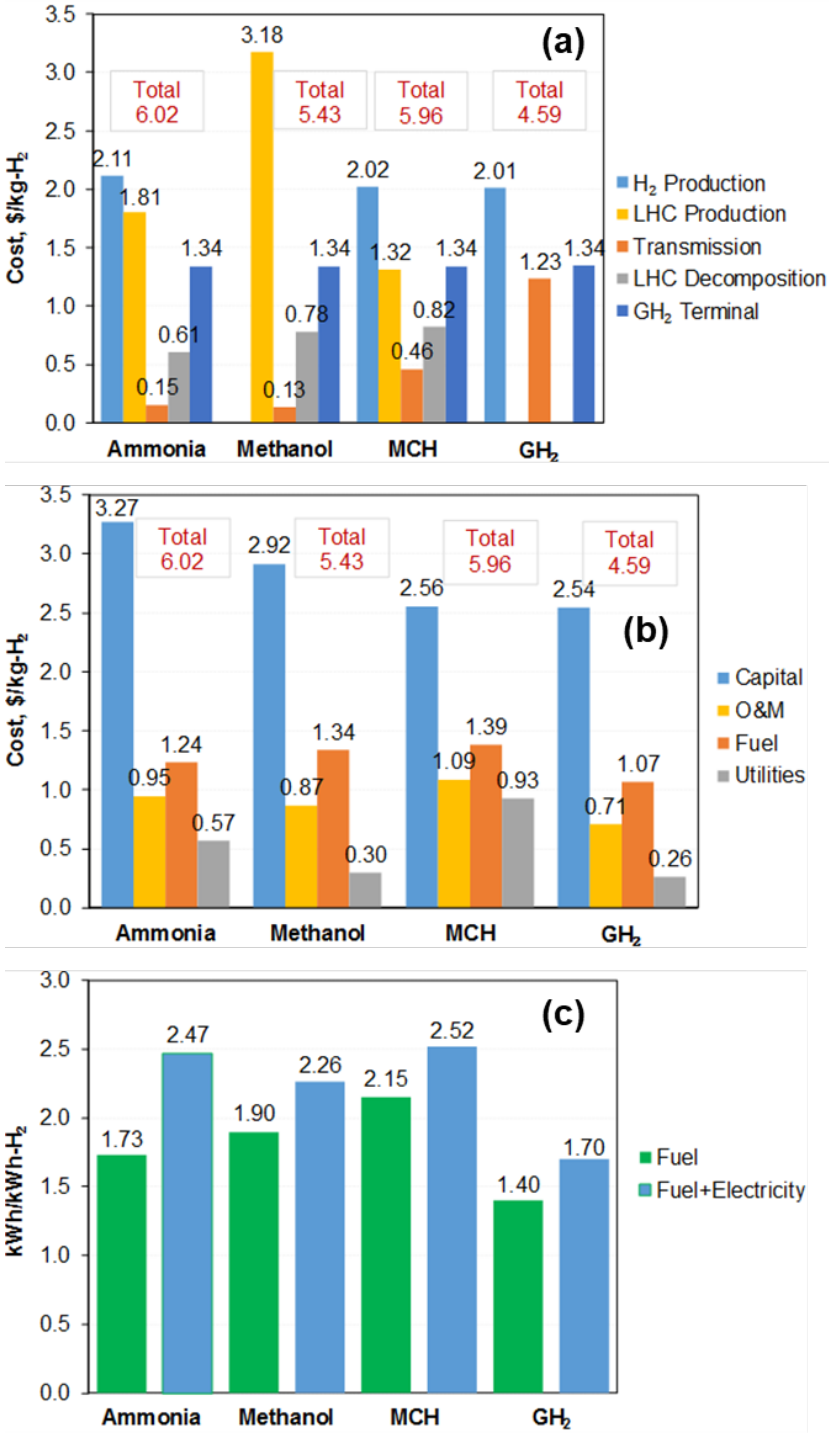

Figure 4. Analysis of hydrogen carrier pathways: a) levelized hydrogen cost at city gate (50,000 kg H_2/day); b) breakdown of levelized hydrogen cost at city gate; (c) energy efficiency

CONCLUSIONS AND UPCOMING ACTIVITIES

- Compared to Type 3 350-bar cH_2 tanks currently in use in fuel cell buses, 500-bar CcH_2 can achieve 215% increase in storage density, 90% improvement in gravimetric capacity, 170% higher volumetric capacity, and 47% saving in CF composite while satisfying the constraint of 7-d dormancy for 95% full tanks.
- A reverse-engineering analysis shows that meeting the system targets of 5.5 wt% gravimetric capacity and 40 g/L volumetric capacity requires room temperature sorbents with 106 ± 8 g H_2/kg excess uptake at 100 bar when compacted to 500 ± 35 kg/m^3 bulk density.
- Reinforcing the dome section with an elongated metal boss has the potential to realize >10% savings in CF composite for Type 4 tanks. Greater savings may be possible in tanks with a higher aspect ratio.
- We have determined the baseline cost of producing/hydrogenating one-way and two-way liquid hydrogen carriers (ammonia, methanol, and MCH/toluene), transmitting them to and dehydrogenating them at the city gate, and storing hydrogen. For the baseline scenario in which the LHC production plant is located 150 km from the city gate, 50,000 kg H_2/day average daily use, and other assumptions listed in Table 4, the levelized cost at the city gate is 4.59–6.02 $/kWh H_2.
- In FY 2019, we will work with DOE, Lawrence Livermore National Laboratory, and Pacific Northwest National Laboratory to develop a material property database and tools for certification.
- In FY 2019, we will identify and analyze scenarios that favor hydrogen carriers.
- In FY 2019, we will analyze physical hydrogen storage systems for medium- and heavy-duty vehicles.

FY 2018 PUBLICATIONS/PRESENTATIONS

1. T.Q. Hua, H.S. Roh, and R.K. Ahluwalia, "Performance Assessment of 700-bar Compressed Hydrogen Storage for Light Duty Vehicles," *International Journal of Hydrogen Energy* 42 (2017): 25121-25129.
2. R.K. Ahluwalia, J.K. Peng, H.S. Roh, T.Q. Hua, C. Houchins, and B.D. James, "Supercritical Cryo-compressed Hydrogen Storage for Fuel Cell Electric Buses," *International Journal of Hydrogen Energy* 43 (2018): 10215-10231.
3. R.K. Ahluwalia, J.K. Peng, and T.Q. Hua, "Chemical Hydrogen Storage Material Requirements for Automotive Fuel Cell Systems," In preparation for submission to *International Journal of Hydrogen Energy*, 2018.
4. R.K. Ahluwalia, J.K. Peng, and N. T. Stetson, "Characteristics of Low-Enthalpy Metal Hydrides for On-Board High-Pressure Hydrogen Storage Applications," In preparation for submission to *International Journal of Hydrogen Energy*, 2018.
5. R.K. Ahluwalia, T.Q. Hua, J.K. Peng, and H.S. Roh, "System Level Analysis of Hydrogen Storage Options," Hydrogen Storage Tech Team Meeting, Southfield, MI, January 18, 2018.

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1. R.K. Ahluwalia, J.K. Peng, H.S. Roh, T.Q. Hua, C. Houchins, and B.D. James, "Supercritical Cryo-compressed Hydrogen Storage for Fuel Cell Electric Buses," *International Journal of Hydrogen Energy* 43 (2018): 10215-10231.
2. A. Yamashita, M. Kondo, S. Goto, and N. Ogami, "Development of High-Pressure Hydrogen Storage System for the Toyota Mirai," SAE Technical Paper 2015-01-1169 (2015), doi:10.4271/2015-01-1169.
3. R.K. Ahluwalia, J-K Peng, and T. Q. Hua, "Sorbent Material Property Requirements for On-board Hydrogen Storage for Automotive Fuel Cell Systems," *International Journal of Hydrogen Energy* 40 (2015): 6373-6390.

4. E. Tsivion, S.P. Veccham, and M. Head-Gordon, "High Temperature Hydrogen Storage of Multiple Molecules: Theoretical Insights from Metalated Catechols," *ChemPhysChem* 18 (2017): 184-188.