IV.B.4 Advancement of Systems Designs and Key Engineering Technologies for Materials-Based Hydrogen Storage

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Project End Date: June 30, 2015 (including 1 year no-cost extension)

Overall Objectives

UTRC's overall objectives mirror those of the Hydrogen Storage Engineering Center of Excellence (HSECoE) to advance hydrogen storage system technologies toward the DOE hydrogen program's 2020 storage targets. Outcomes of this project will include:

- A more detailed understanding of storage system requirements.
- Development of higher performance and enabling technologies such as novel approaches to heat exchange, on-board purification and compacted storage material structures.
- Component/system design optimization for prototype demonstration.

Fiscal Year (FY) 2015 Objectives

- Develop vehicle/power plant/storage system integrated system modeling elements to improve specification of storage system requirements and to predict performance for candidate designs
- Assess the viability of on-board purification for various storage material classes and purification approaches
- Collaborate closely with the HSECoE partners to advance materials-based hydrogen storage system technologies

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section (3.3.5) of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan:

(A) System Weight and Volume

(D) Durability/Operability

(H) Balance of Plant (BOP) Components

Technical Targets

The goals of this project mirror those of the HSECoE to advance hydrogen storage system technologies toward the DOE hydrogen program's 2020 storage targets [1]. UTRC minimized the mass and cost of the particulate filtration system, which is part of the BOP of the cryo-adsorption system. The Simulink® framework enabled a comparison of all three materials-based hydrogen storage systems on a common basis by ensuring that each system provided 5.6 kg of usable H_2 to a common proton exchange membrane (PEM) fuel cell and light-duty vehicle model.

The status of UTRC's FY 2015 contributions to the technical targets is documented in Table 1.

TABLE 1. UTRC's Progress toward Meeting Technical Targets for Onboard H_2 Storage Systems

	Characteristic	Units	2020 Target	UTRC
Cryo-adsorbent H_2 storage system	H_2 Quality	% H_2	SAE J2719 and ISO/ PDTS 14687-2 (99.97% dry basis)	Meets

FY 2015 Accomplishments

Accomplishments during the current project period comprise:

- Collaborated with Savannah River National Laboratory on integrating the sorbent hydrogen storage system in the Simulink® framework.
- Implemented access to more model parameters internal to Pacific Northwest National Laboratory's chemical hydrogen storage system model in the Simulink® framework.

- Improved graphical user interface (GUI), operating manual and user-friendliness of the Simulink® framework.
- Developed a method to right-size the particulate filter area by considering the weight and cost of the particulate filter and the effect of pressure drop on hydrogen adsorption.
- Reached out to the hydrogen storage material development community at DOE's Materials-Based Hydrogen Storage Summit, Defining Pathways for Onboard Automotive Applications, Golden, Colorado, January 27–28, 2015, with presentations about the Simulink® framework and about niche application opportunities of hydrogen storage materials.

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INTRODUCTION

Physical storage of hydrogen through compressed gas and cryogenic liquid approaches is well established, but has drawbacks regarding weight, volume, cost, and efficiency, which motivate the development of alternative, low-pressure materials-based methods of hydrogen storage. Recent worldwide research efforts for improved storage materials have produced novel candidates and continue in the pursuit of materials with overall viability. While the characteristics of the storage materials are of primary importance, the additional system components required for the materials to function as desired can have a significant impact on the overall performance and cost. Definition, analysis and improvement of such systems components and architectures, both for specific materials and for generalized material classes, are important technical elements to advance in the development of superior methods of hydrogen storage.

APPROACH

UTRC's approach is to leverage in-house expertise in various engineering disciplines and prior experience with metal hydride system prototyping to advance materials-based H_2 storage for automotive applications. During the sixth year of the HSECoE project, UTRC continued the successful development of the Simulink® modeling framework for comparing H_2 storage systems on a common basis, which can now be downloaded from the National Renewable Energy Laboratory (NREL)-hosted website at www.hsecoe.org. UTRC also used the Darcy flow permeability values of the particulate filters (with and without an adsorbent filter cake), which it had measured in FY 2014, for right-sizing the filter area for a full-size H_2 storage system by considering the effect of pressure drop on the H_2 adsorption by the sorbent in the pressure vessel.

RESULTS

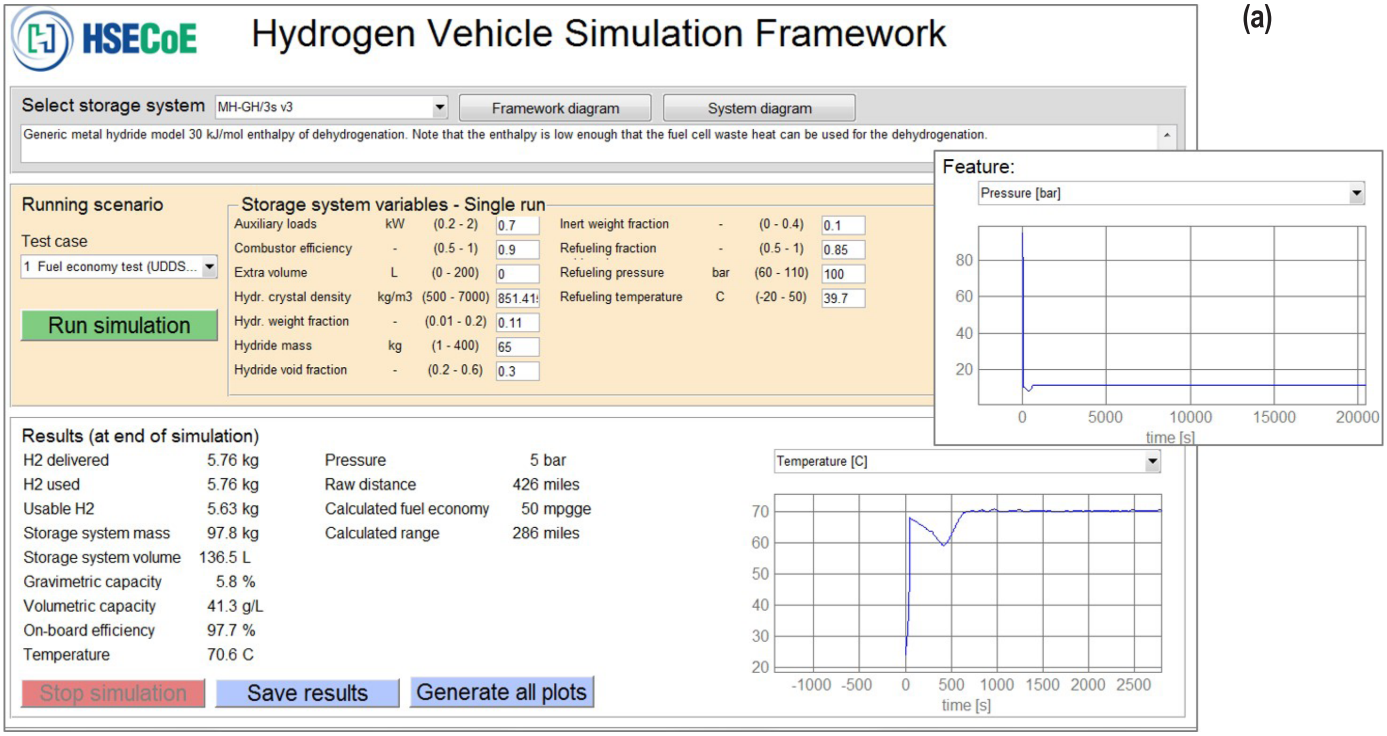
The Simulink® framework with a GUI was updated and disseminated on the web through NREL's website at www.hsecoe.org. It now contains models of the 350 bar and 700 bar compressed gas storage systems and the three models of the materials-based H_2 storage systems: ideal metal hydride, chemical hydrogen storage, and cryo-adsorption. Beta testing will continue in order to make the use of the storage system models more user-friendly to H_2 storage material developers and hydrogen storage program managers that are interested in determining how well a newly proposed material will meet the system level targets. A simplified view of the GUI of each of the materials-based H_2 storage systems is shown in Figure 1.

Figure 1a illustrates how the pressure in the ideal metal hydride system quickly drops to the equilibrium pressure of the metal hydride at the operating temperature of the tank. Figure 1b1 illustrates the high initial auxiliary power request of a chemical hydrogen storage system with a slurry of ammonia borane (AB). This initial auxiliary power is used to bring the reactor to the operating temperature that is required for the exothermic AB thermolysis. Figure 1b2 illustrates the auxiliary power request by the chemical hydrogen storage system with a slurry of aluminum hydride (alane). The endothermic release of H_2 requires constant power in order to maintain the reactor temperature. Figure 1c1 illustrates the thermal swing in a cryo-adsorption system with flow-through cooling. Heating the sorbent is used to reduce the heel of adsorbed H_2 in the tank and consumes auxiliary power. Figure 1c2 shows the drop in tank pressure in a cryo-adsorption system with the modular adsorption tank insert despite heating the adsorbent in a similar fashion as for the system in Figure 1c1. The simulation stops when the delivery pressure to the fuel cell drops below 5 bar. Each of the figures shows the material and system variables that are currently available to the user of the Simulink® framework. It has been proposed to greatly enhance the number of variables that can be varied in order to make the system simulation more useful to material developers.

The Simulink® framework is used to test whether the vehicle can follow pre-defined drive cycles by exercising the combined vehicle model, fuel cell model and H_2 storage systems. The model will control the power generation in order to reach the required speed within 2 mph and within 1 s of what is specified by the drive cycle, as shown in Figure 2. The user will be informed about any speed trace misses, which provides an opportunity to improve the characteristics of the specific H_2 storage system.

Figure 3 highlights the performance of the various H_2 storage systems in combination with the selected fuel cell system and light-duty vehicle characteristics. The shaded blue area illustrates a typical range of battery systems. DOE's 2020 target is clearly indicated with the red circle on the dark

(a)



Hydrogen Vehicle Simulation Framework

Select storage system: MH-GH/3s v3

Generic metal hydride model 30 kJ/mol enthalpy of dehydrogenation. Note that the enthalpy is low enough that the fuel cell waste heat can be used for the dehydrogenation.

Running scenario

Test case: 1 Fuel economy test (UDDS...

Storage system variables - Single run

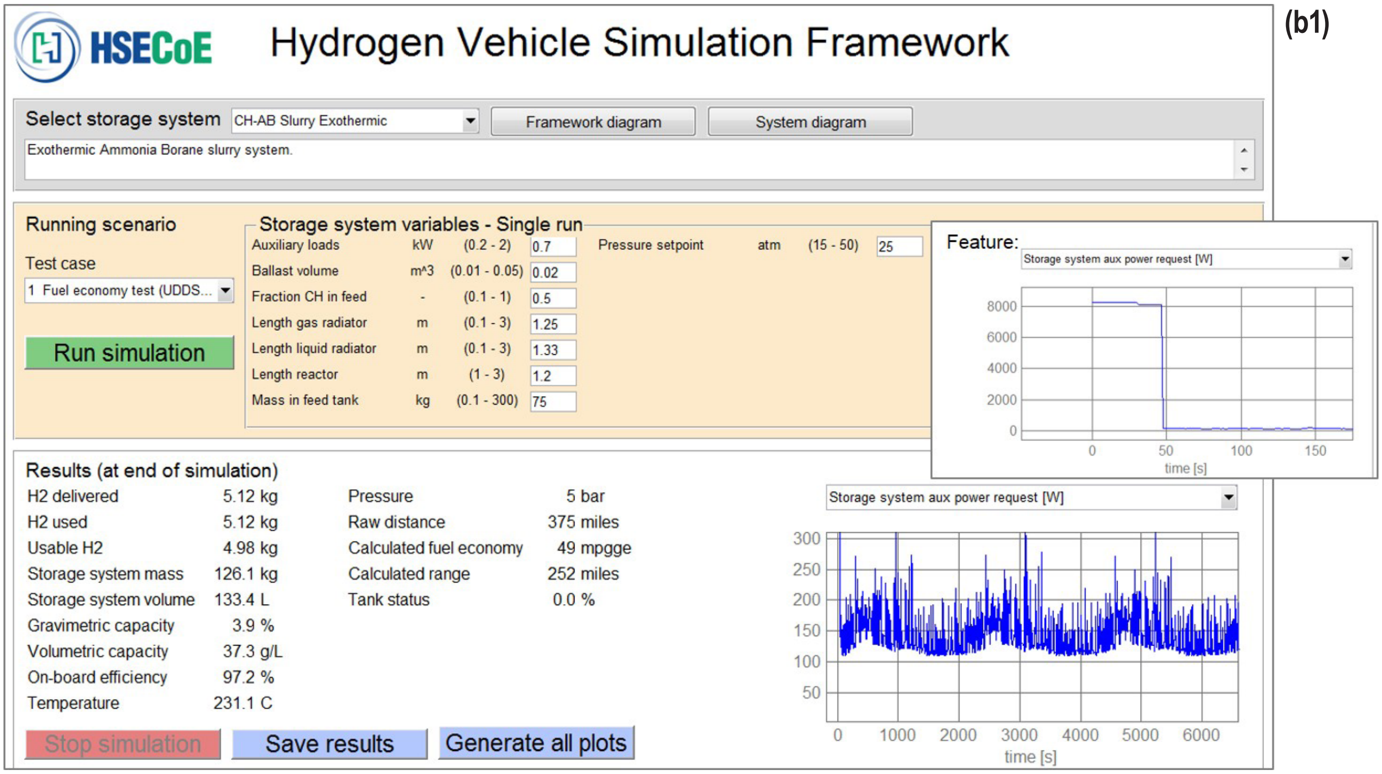
Auxiliary loads	kW	(0.2 - 2)	0.7
Combustor efficiency	-	(0.5 - 1)	0.9
Extra volume	L	(0 - 200)	0
Hydr. crystal density	kg/m3	(500 - 7000)	851.41
Hydr. weight fraction	-	(0.01 - 0.2)	0.11
Hydride mass	kg	(1 - 400)	65
Hydride void fraction	-	(0.2 - 0.6)	0.3
Inert weight fraction	-	(0 - 0.4)	0.1
Refueling fraction	-	(0.5 - 1)	0.85
Refueling pressure	bar	(60 - 110)	100
Refueling temperature	C	(-20 - 50)	39.7

Results (at end of simulation)

H2 delivered	5.76 kg	Pressure	5 bar
H2 used	5.76 kg	Raw distance	426 miles
Usable H2	5.63 kg	Calculated fuel economy	50 mpgge
Storage system mass	97.8 kg	Calculated range	286 miles
Storage system volume	136.5 L		
Gravimetric capacity	5.8 %		
Volumetric capacity	41.3 g/L		
On-board efficiency	97.7 %		
Temperature	70.6 C		

FIGURE 1a. GUI development for materials-based H_2 storage systems: ideal metal hydride system

(b1)



Hydrogen Vehicle Simulation Framework

Select storage system: CH-AB Slurry Exothermic

Exothermic Ammonia Borane slurry system.

Running scenario

Test case: 1 Fuel economy test (UDDS...

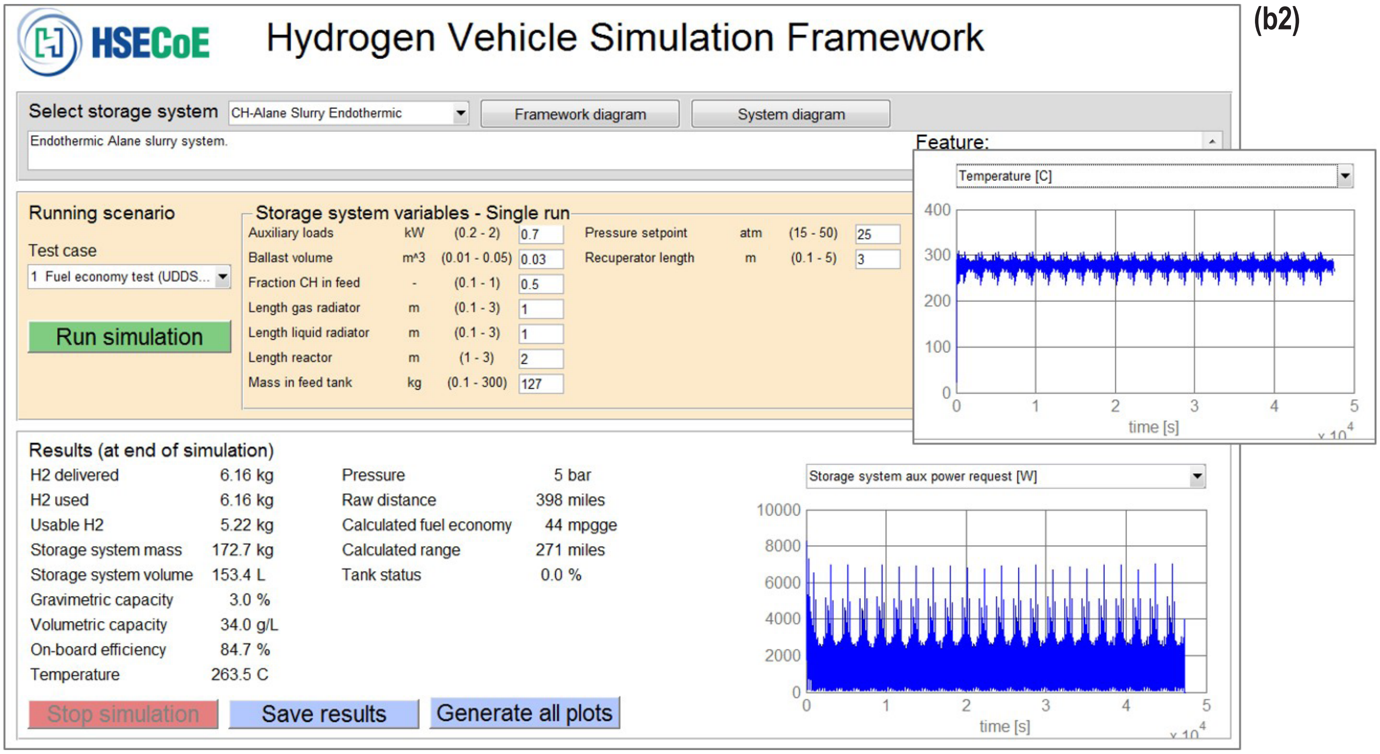
Storage system variables - Single run

Auxiliary loads	kW	(0.2 - 2)	0.7
Ballast volume	m^3	(0.01 - 0.05)	0.02
Fraction CH in feed	-	(0.1 - 1)	0.5
Length gas radiator	m	(0.1 - 3)	1.25
Length liquid radiator	m	(0.1 - 3)	1.33
Length reactor	m	(1 - 3)	1.2
Mass in feed tank	kg	(0.1 - 300)	75
Pressure setpoint	atm	(15 - 50)	25

Results (at end of simulation)

H2 delivered	5.12 kg	Pressure	5 bar
H2 used	5.12 kg	Raw distance	375 miles
Usable H2	4.98 kg	Calculated fuel economy	49 mpgge
Storage system mass	126.1 kg	Calculated range	252 miles
Storage system volume	133.4 L	Tank status	0.0 %
Gravimetric capacity	3.9 %		
Volumetric capacity	37.3 g/L		
On-board efficiency	97.2 %		
Temperature	231.1 C		

FIGURE 1b1. GUI development for materials-based H_2 storage systems: chemical H_2 storage: AB-slurry



Hydrogen Vehicle Simulation Framework

Select storage system: CH-Alane Slurry Endothermic

Endothermic Alane slurry system.

Running scenario

Test case: 1 Fuel economy test (UDDS...

Storage system variables - Single run

Auxiliary loads	kW	(0.2 - 2)	0.7
Ballast volume	m^3	(0.01 - 0.05)	0.03
Fraction CH in feed	-	(0.1 - 1)	0.5
Length gas radiator	m	(0.1 - 3)	1
Length liquid radiator	m	(0.1 - 3)	1
Length reactor	m	(1 - 3)	2
Mass in feed tank	kg	(0.1 - 300)	127
Pressure setpoint	atm	(15 - 50)	25
Recuperator length	m	(0.1 - 5)	3

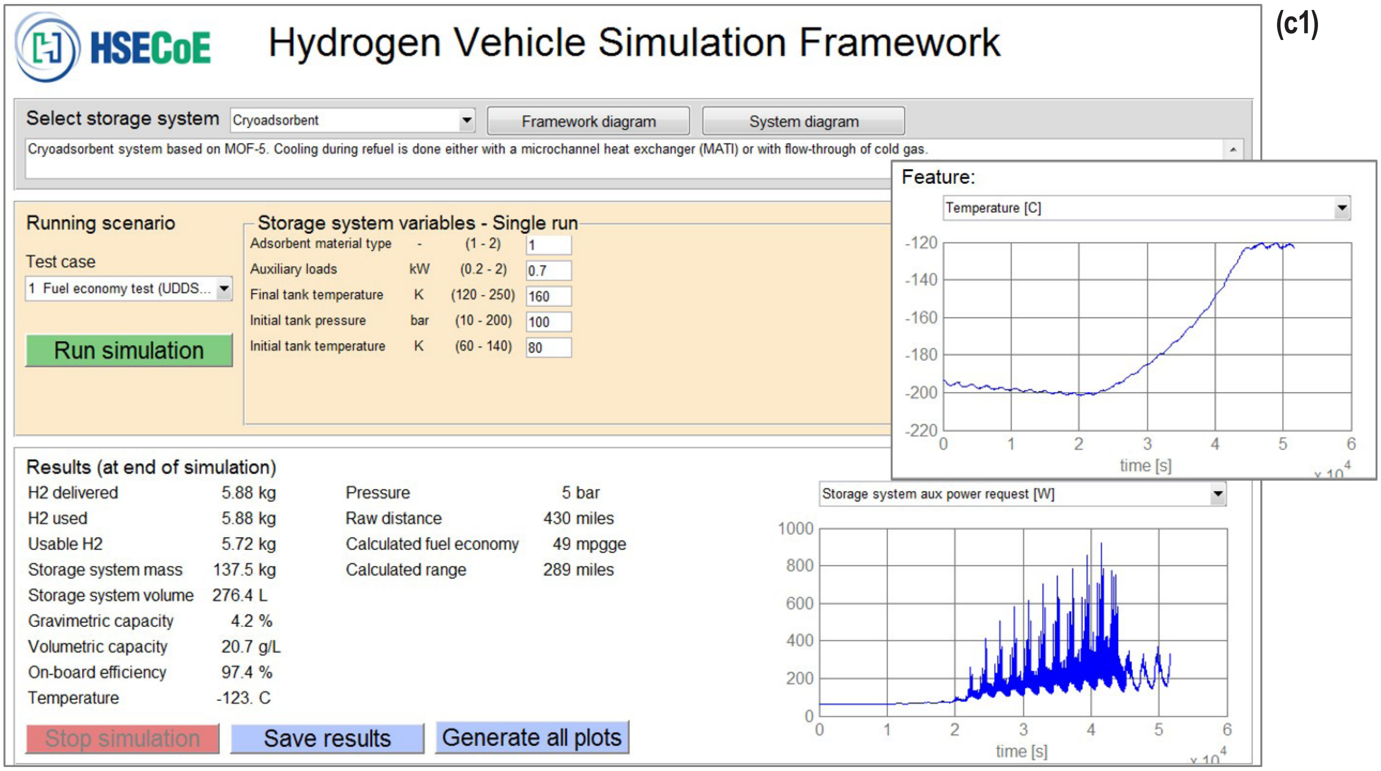
Results (at end of simulation)

H2 delivered	6.16 kg	Pressure	5 bar
H2 used	6.16 kg	Raw distance	398 miles
Usable H2	5.22 kg	Calculated fuel economy	44 mpgge
Storage system mass	172.7 kg	Calculated range	271 miles
Storage system volume	153.4 L	Tank status	0.0 %
Gravimetric capacity	3.0 %		
Volumetric capacity	34.0 g/L		
On-board efficiency	84.7 %		
Temperature	263.5 C		

Temperature [C]

Storage system aux power request [W]

FIGURE 1b2. GUI development for materials-based H_2 storage systems: chemical H_2 storage: alane-slurry



Hydrogen Vehicle Simulation Framework

Select storage system: Cryoadsorbent

Cryoadsorbent system based on MOF-5. Cooling during refuel is done either with a microchannel heat exchanger (MATI) or with flow-through of cold gas.

Running scenario

Test case: 1 Fuel economy test (UDDS...

Storage system variables - Single run

Adsorbent material type	-	(1 - 2)	1
Auxiliary loads	kW	(0.2 - 2)	0.7
Final tank temperature	K	(120 - 250)	160
Initial tank pressure	bar	(10 - 200)	100
Initial tank temperature	K	(60 - 140)	80

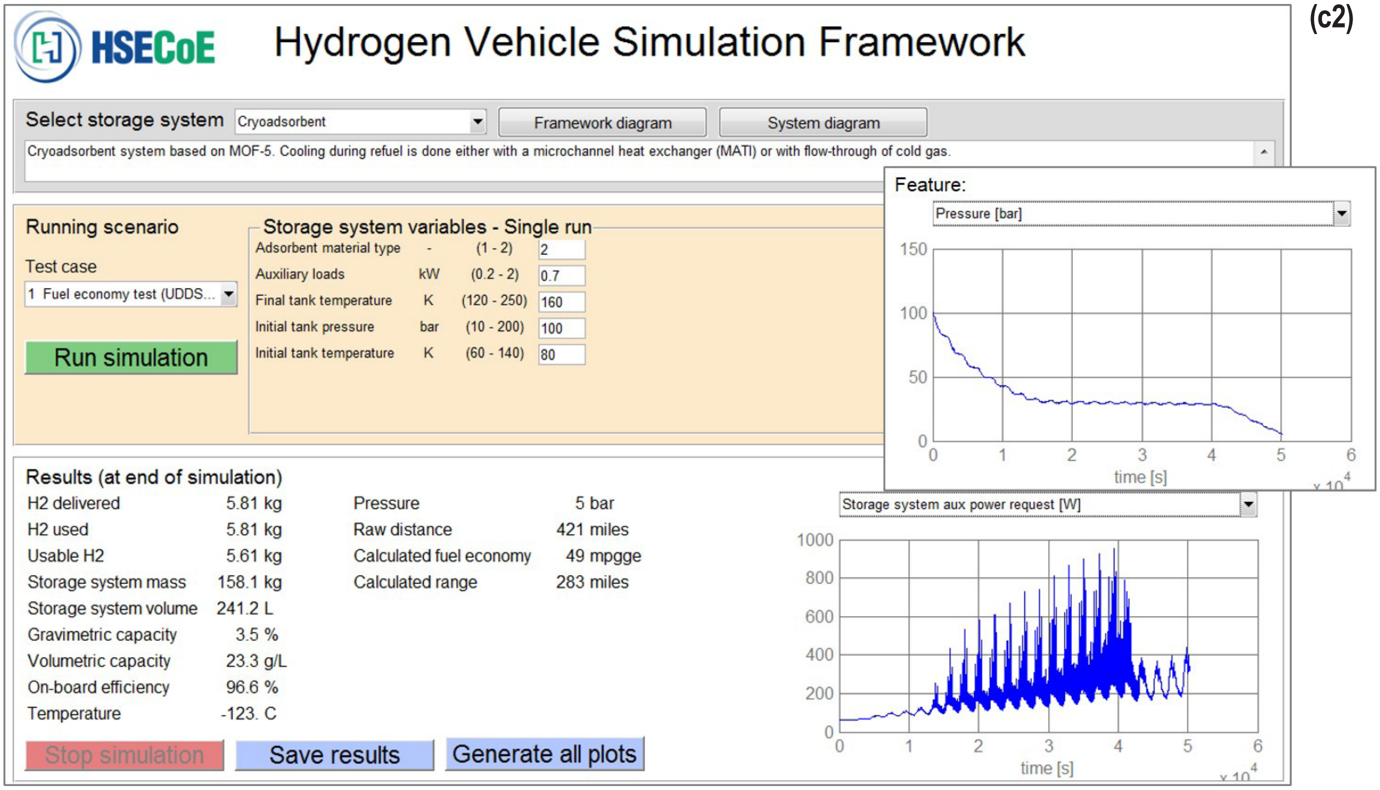
Results (at end of simulation)

H2 delivered	5.88 kg	Pressure	5 bar
H2 used	5.88 kg	Raw distance	430 miles
Usable H2	5.72 kg	Calculated fuel economy	49 mpgge
Storage system mass	137.5 kg	Calculated range	289 miles
Storage system volume	276.4 L		
Gravimetric capacity	4.2 %		
Volumetric capacity	20.7 g/L		
On-board efficiency	97.4 %		
Temperature	-123. C		

Temperature [C]

Storage system aux power request [W]

FIGURE 1c1. GUI development for materials-based H_2 storage systems: cryo-adsorption: flow-through-cooling



Select storage system: Cryoadsorbent

Cryoadsorbent system based on MOF-5. Cooling during refuel is done either with a microchannel heat exchanger (MATI) or with flow-through of cold gas.

Running scenario

Test case: 1 Fuel economy test (UDDS...

Storage system variables - Single run

Adsorbent material type	-	(1 - 2)	2
Auxiliary loads	kW	(0.2 - 2)	0.7
Final tank temperature	K	(120 - 250)	160
Initial tank pressure	bar	(10 - 200)	100
Initial tank temperature	K	(60 - 140)	80

Feature: Pressure [bar]

Results (at end of simulation)

H2 delivered	5.81 kg	Pressure	5 bar
H2 used	5.81 kg	Raw distance	421 miles
Usable H2	5.61 kg	Calculated fuel economy	49 mpgge
Storage system mass	158.1 kg	Calculated range	283 miles
Storage system volume	241.2 L		
Gravimetric capacity	3.5 %		
Volumetric capacity	23.3 g/L		
On-board efficiency	96.6 %		
Temperature	-123. C		

Storage system aux power request [W]

FIGURE 1c2. GUI development for materials-based H_2 storage systems: cryo-adsorption: modular adsorption tank insert

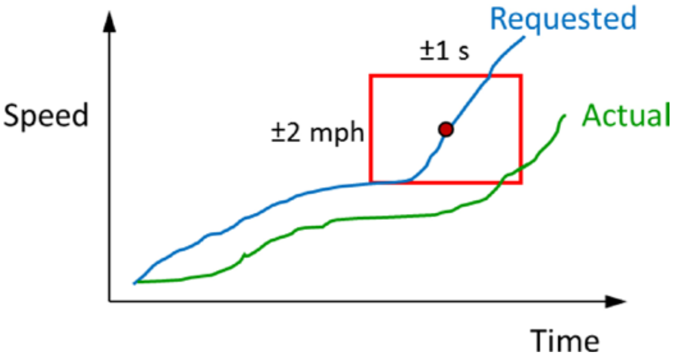


FIGURE 2. EPA trace (requested) and the actual speed trace as a function of time with the target box that will trigger alerts in the Simulink® framework in order to provide the designers an opportunity to improve their H_2 storage system (e.g., increase buffer size or install more H_2 storage material)

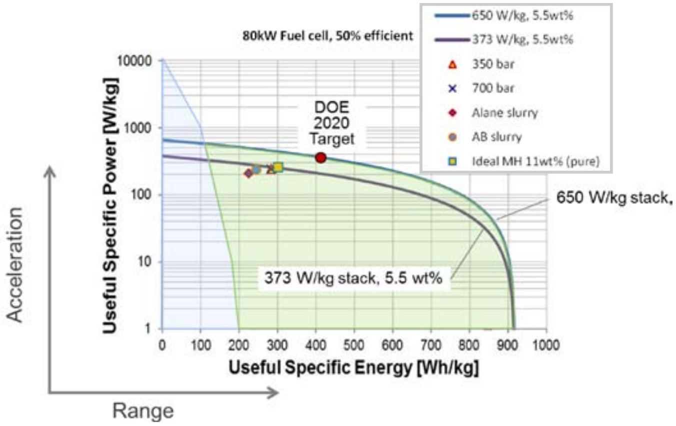


FIGURE 3. Location of the combined PEM fuel cell and H_2 storage systems within the HSECoE on a map of power density and energy density and in comparison to DOE's 2020 targets

blue line that bounds the achievable values of the specific power and specific energy of the combined fuel cell and H_2 storage system. The specific power of the current fuel cell system (373 W/kg) in the Simulink® framework model is considerably lower than the DOE target for such a fuel cell system (650 W/kg), and this lowers the achievable specific power towards the purple line. The ideal metal hydride model (yellow square) shows the achievable specific energy of the combined fuel cell plus H_2 storage system for an H_2 storage system with the targeted 5.5 wt% gravimetric capacity. The other H_2 storage systems are heavier than this ideal metal hydride model and this is reflected in the lower specific energy. A similar diagram could be drawn for the volumetric energy density, which would show the low volumetric energy density for the current adsorption-based H_2 storage systems.

A cryo-adsorption-based H_2 storage system requires a particulate filter in order to contain the adsorbent in the thermally insulated area of the pressure vessel and in order to filter out any particulates from the H_2 gas that is sent to the PEM fuel cell to a particulate concentration <1,000 µg/m^3 while ensuring that any particulates will be smaller than 10 µm, per SAE J2719 guidelines. Particulate filters with such a performance were demonstrated in FY 2014. The Darcy permeability values with and without filter cake were also measured at that time. In FY 2015, UTRC used this data for developing a method to right-size the particulate filter area for DOE's light-duty automotive application. The flow of H_2 gas during fill and discharge causes a pressure drop across the particulate filter. This affects H_2 adsorption as the H_2 pressure downstream of the particulate filter will be less than the pressure that is available from the forecourt. It also affects H_2 desorption as the H_2 pressure upstream of the particulate filter will need to be higher than the minimum delivery pressure (i.e., 5 bar) to the fuel cell system. Both effects reduce the amount of usable H_2 gas from the H_2 storage system. This can be compensated for by installing more adsorbent in the cryo-adsorption vessel, as illustrated in Figure 4. Installing additional adsorbent increases the size of the pressure vessel and its weight. The weight penalty from installing more adsorbent and increasing the pressure vessel can be reduced by installing a larger particulate filter. The weight and cost of the particulate filter can be quite significant though. The combined effect is illustrated in Figure 5 for both the H_2 fill scenario (flow-through cooling) and for a H_2 discharge scenario near the tank empty condition. Table 2 shows the required particulate filtration areas for either minimizing system weight or system cost. An area of about 49 cm^2 of a filter media with a Darcy flow permeance of 1.72×10^{-13} m^2 (with filter cake) to 8.54×10^{-13} m^2 (without filter cake) appears to be a good compromise for the cryo-adsorption system when considering both the pressure drop during fill conditions and near the tank-empty condition.

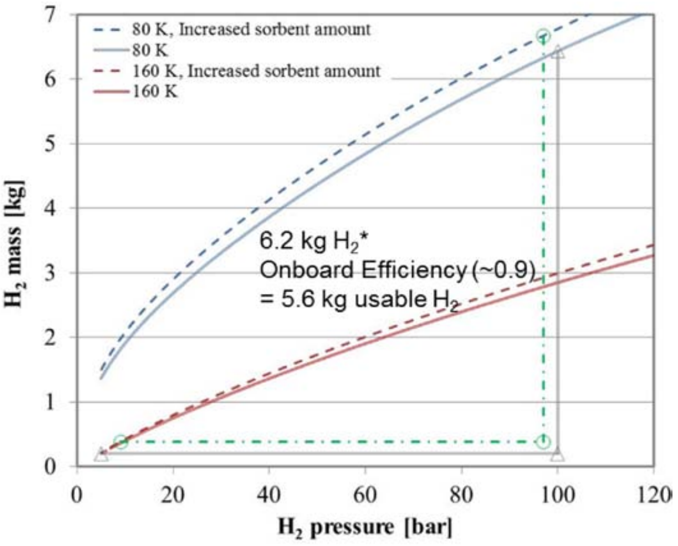


FIGURE 4. Particulate filter right-sizing method by taking into account the impact of pressure drop through the particulate filter during fill-conditions and near the empty-tank condition

CONCLUSIONS AND FUTURE DIRECTIONS

Conclusions derived from the work in FY 2015 are as follows:

- Users of the Simulink® modeling framework will benefit from having access to more H_2 storage material and H_2 storage system model parameters in the graphical user interface. This goes beyond the original objective of comparing each of the three materials-based H_2 storage systems on a common basis.
- There is an optimum particulate filter size for cryo-adsorption systems due to the effect of pressure drop across the filter on H_2 adsorption. The current high cost of particulate filters favors installing less filter area than what would be optimal for the overall weight of the H_2 storage system.

Phase 3 was completed on June 30, 2015.

FY 2015 PUBLICATIONS/PRESENTATIONS

1. Kriston P. Brooks, Troy A. Semelsberger, Kevin L. Simmons, and B.A. van Hassel, "Slurry-based chemical hydrogen storage systems for automotive fuel cell applications," Journal of Power Sources, 2014, 268, pp. 950 – 959.

2. Bart A. van Hassel, Randolph C. McGee, Allen Murray, and Shiling Zhang, "Engineering Technologies for Fluid Chemical Hydrogen Storage Systems," Invited Talk, 14th International Symposium on Metal-Hydrogen Systems: Fundamentals and Applications, Salford, Manchester, UK, July 20–25, 2014.

3. Bart A. van Hassel, Randolph C. McGee, Allen Murray, and Shiling Zhang, "Engineering Technologies for Fluid Chemical Hydrogen Storage Systems," 14th International Symposium on Metal-Hydrogen Systems: Fundamentals and Applications, Salford, Manchester, UK, July 20–25, 2014, Accepted by Journal of Alloys and Compounds.

4. B.A. van Hassel, Hydrogen Storage Systems for Mobile Applications, *IEA Task 32, Salford, Manchester, UK, July 25–26, 2014.*

5. Igor I. Fedchenia, Bart A. van Hassel, and Ron Brown, "Solution of Inverse Thermal Problem for Assessment of Thermal Parameters of Engineered H_2 Storage Materials," Inverse Problems in Science & Engineering, 2015, 23 (3), pp. 425-442.

6. Bart A. van Hassel, Jagadeswara R. Karra, Jose Santana, Salvatore Saita, Allen Murray, and Daniel Goberman, Richard Chahine, and Daniel Cossement, "Ammonia Sorbent Development for On-Board H_2 Purification," Separation and Purification Technology, 2015, 142, 215-226.

7. Bart A. van Hassel, Jagadeswara. R. Karra, David Gerlach, and Igor I. Fedchenia, "Dynamics of fixed-bed adsorption of ammonia on impregnated activated carbon for hydrogen purification," To be submitted to Separation and Purification Technology, In Preparation.

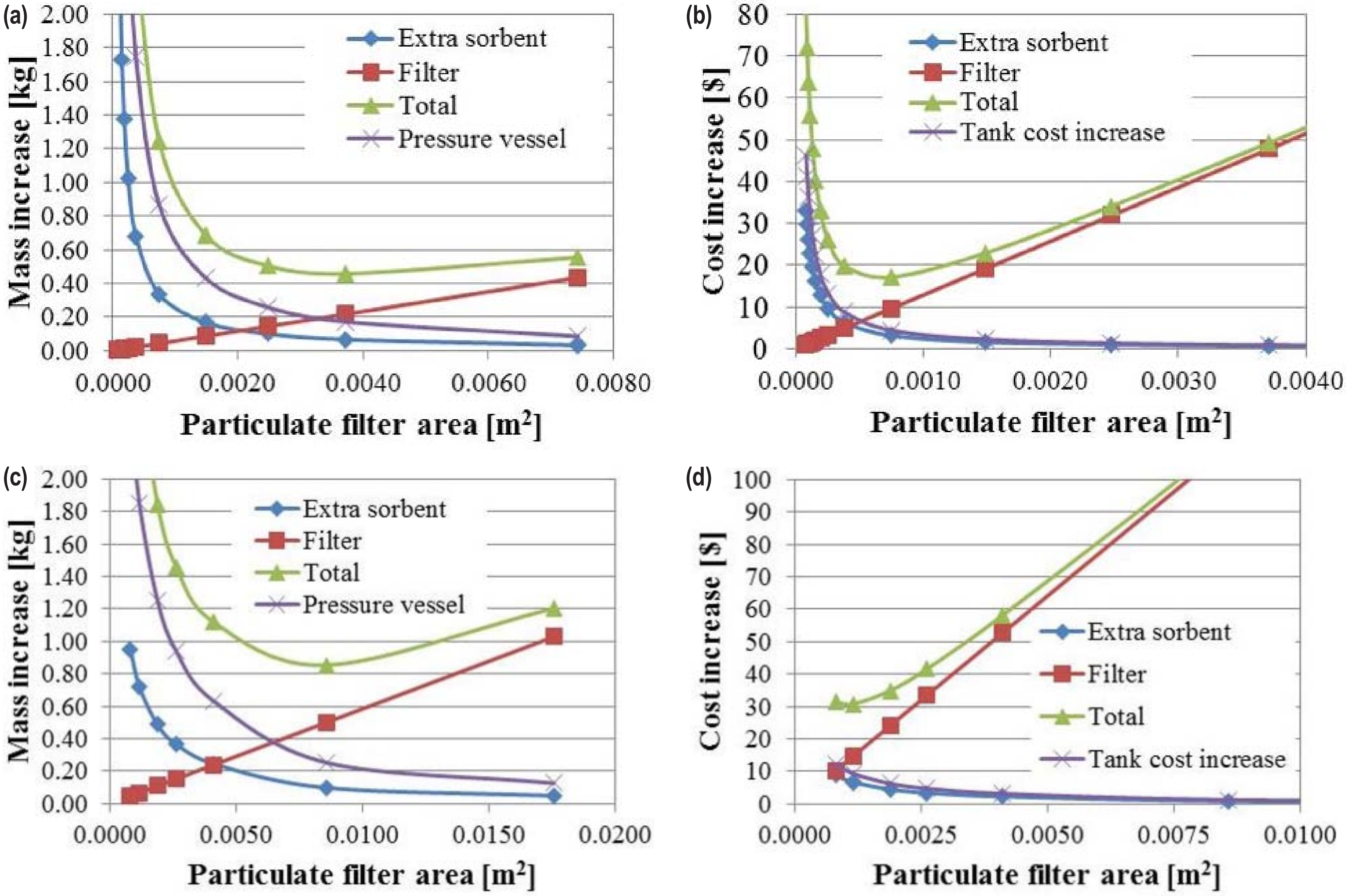


FIGURE 5. Impact of the particulate filter area and cost on the overall system while keeping the usable H_2 amount fixed at 5.6 kg

TABLE 2. Right-Sizing of Particulate Filter Area for Cryo-Adsorption System

Condition	Criterion	Area [cm^2]	Pressure Drop [bar]	Total Weight Increase [kg]	Cost Increase [$]
Filling: 80 K, 100 bar, 0.060 kg-H_2/s, Filter permeability: 8.54 x 10^{-13} m^2	Weight minimum	37	0.2	0.46	$49
	Cost minimum	7	1	1.25	$17
Near empty tank: 160 K, 5 bar, 0.016 kg-H_2/s, Filter permeability: 1.72 x 10^{-13} m^2	Weight minimum	86	0.5	0.85	$122
	Cost minimum	12	3	2.64	$31

8. B.A. van Hassel, Hydrogen Storage Systems for Mobile Applications, *IEA Task 32, Chamonix, France, January 18–23, 2015.*

9. B.A. van Hassel, "Niche Application Opportunities," Invited Talk, DOE Materials-Based Hydrogen Storage Summit, Defining pathways for onboard automotive applications, Golden, CO, USA, *January 27-28, 2015.*

10. José Miguel Pasini, Jon Cosgrove, Matthew Thornton, Jeff Gonder, Kriston Brooks, David Tamburello, Michael Veenstra, "H_2 Models on the Web," Invited Talk, DOE Materials-Based Hydrogen Storage Summit, Defining pathways for onboard automotive applications, Golden, CO, USA, *January 27–28, 2015.*

11. Bart A. van Hassel and Jagadeswara R. Karra, Particulate Filtration for Sorbent-based H_2 Storage, Special Issue of Applied Physics A about H_2 Storage, Editor: Michael Hirscher.

12. B.A. van Hassel, "Niche Application Opportunities," Invited Talk, Gordon Research Conference, Hydrogen-Metal Systems, Fundamental Aspects of Hydrogen Interaction with Materials and Novel Energy Applications, July 12–17, 2015, Stonehill College, Easton, MA, USA.

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2. Information Report on the Development of a Hydrogen Quality Guideline for Fuel Cell Vehicles, SAE International Surface Vehicle Information Report, J2719 APR2008, Revised 2008-04.