IV.D.1 Hydrogen Storage Engineering Center of Excellence (HSECoE)

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- United Technologies Research Center (UTRC)
- General Motors Corp (GM)
- Ford Motor Corp. (FMC)
- National Renewable Energy Laboratory (NREL)
- Los Alamos National Laboratory (LANL)
- Jet Propulsion Laboratory (JPL)
- University of Michigan (UM)
- California Institute of Technology (Cal Tech)
- Oregon State University (OSU)
- Lincoln Composites LLC
- University of Québec, Trios Rivieres (UQTR)

Project Start Date: February 1, 2009
Project End Date: July 31, 2014

Fiscal Year (FY) 2012 Objectives

- Develop system models that will lend insight into overall fuel cycle efficiency.
- Compile all relevant materials data for candidate storage media and define future data requirements.
- Develop engineering and design models to further the understanding of onboard storage energy management requirements.
- Develop innovative onboard system concepts for metal hydride, chemical hydride, and adsorption hydride materials-based storage technologies.
- Design components and experimental test fixtures to evaluate the innovative storage devices and subsystem design concepts, validate model predictions, and improve both component design and predictive capability.
- Design, fabricate, test, and decommission the subscale prototype components and systems of each materials-based technology (adsorbents, metal hydrides, and chemical hydrogen storage materials).

Technical Barriers

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

(A) System Weight and Volume
(B) System Cost
(C) Efficiency
(D) Durability/Operability
(E) Charging/Discharging Rates
(G) Materials of Construction
(H) Balance of Plant Components
(J) Thermal Management
(K) System Life Cycle Assessments
(L) High Pressure Conformality
(P) Lack of Understanding of Hydrogen Physisorption and Chemisorption
(S) By-Product/Spent Material Removal

Technical Targets

This project directs the modeling, design, build and demonstration of prototype hydrogen storage systems for each metal hydride, chemical hydride and hydrogen sorption material meeting as many of the DOE Technical Targets for light-duty vehicular hydrogen storage. The current status of these systems vs. the Onboard Hydrogen Storage System Technical Targets are given in Table I.

FY 2012 Accomplishments

Center Wide Accomplishments

- Completed assessment of metal hydrides for further evaluation in phase 2. Terminated work on metal hydride system due to low probability of these materials meeting the required properties in the 2017 timeframe.

TABLE I. System Status vs. Technical Targets

	Technical Target	Units	2010	2015	Ultimate	Metal Hydride	Chemical Hydride	Adsorbent
Non-Quant-ified	Permeation & Leakage	scc/hr	#	#	#	s	s	s
	Toxicity		#	#	#	s	s	s
	Safety		#	#	#	s	s	s
	Gravimetric Density	$kgH_2/kgSystem$	0.045	0.055	0.075	**0.012**	**0.038**	**0.039**
Manditory	Min. Delivery Temp.	°C	-40	-40	-40	-40	-40	-40
	Max. Delivery Temp.	°C	85	85	85	85	85	85
	Min. Delivery Pressure (PEM)	bar	5	5	3	5	5	5
	Max. Delivery Pressure	bar	12	12	12	12	12	12
	Min. Operating Temperature	°C	-30	-40	-40	-30	-	-30
	Max. Operating Temperature	°C	50	60	60	50	50	50
Desirable	Min. Full Flow Rate	$[gH_2/s]/kW$	0.02	0.02	0.02	0.02	0.02	0.02
	System Cost*	$/kWh net	4	2	TBD	**49.0**	**25.6**	**18.5**
	On-Board Efficency	%	90	90	90	**78**	97	95
	Volumetric Density	$kgH_2/liter$	0.028	0.040	0.070	**0.012**	0.034	0.024
	Cycle Life	N	1000	1500	1500	1000	1000	1000
	Fuel Cost*	$/gge	3-7	2-6	2-3	7.3	-	4.89
	Loss of Useable Hydrogen	$[gH_2/hr]/kgH_2$	0.1	0.05	0.05	0.1	0.1	**0.44**
	WPP Efficency	%	60	60	60	**44.1**	**37.0**	**40.1**
	Fuel Purity	%	99.97	99.97	99.97	99.97	99.97	99.99
	Transient Response	sec.	0.75	0.75	0.75	0.75	0.49	0.75
	Start Time to Full Flow (-20°C)	sec.	15	15	15	15	1	15
	Fill Time	min.	4.2	3.3	2.5	**10.5**	**5.4**	**4.2**
	Start Time to Full Flow (20°C)	sec.	5	5	5	5	1	5

** Previous Values* # non-quantified s - satisfactory
PEM = polymer electrolyte membrane

- Competed down-select of adsorbent materials with selection of metal-organic framework (MOF)-5.
- Completed down-select of chemical hydride materials with selection of fluid phase material.
- Completed down-select of chemical hydride materials with selection of exothermic materials.
- Completed failure modes and effects analysis for both adsorbent and chemical hydride systems identifying potential failure modes not previously considered including adsorbent bed packing and impurity effects and chemical hydride settling/flocculation and balance of plant (BOP) compatibility issues.
- Identified primary technical barriers limiting advancement of materials based hydrogen storage systems as:
  - Metal Hydrides (heat transfer design, media compaction, media thermal conductivity, lowered mass of BOP components).
  - Chemical Hydrides (media slurry agent/solvent with 50 wt% capacity, media kinetics, novel impurity trapping) .
  - Adsorbents (Type 4 vessels at cryogenic temperatures, media thermal conductivity improvement, flow through cooling, media compaction, minimized tank outgassing, potential low pressure Type 1 tank).
- Identified Phase 3 Go/No-Go targets
- Initiated Phase 3 testing requirements system sizing analysis.
- Upgraded HSECoE.org website and added metal hydride models for public download and use.

SRNL Technical Accomplishments

- Completed a demonstration of a flow through cooling system and validated detailed models for super activated carbon.
- Developed external, publically accessible, website and disseminated the metal hydride acceptability envelope and the metal hydride heat transfer model.
- Designed and evaluated heat transfer technologies for cooling the adsorbent during the charging phase and heating it during the discharge phase.
- Evaluated detailed and system level performance for modified forms of MOF-5. These modified forms include pellets at different levels of compaction and amended MOF-5 which contained additives to enhance thermal conductivity.
- Used system models to identify suitable hydrogen refueling and desorption schemes for cryo-adsorbent systems.
- Used system models to design adsorbent systems.
- Identified optimal operation conditions for adsorbent system using MOF-5 or MaxSorb (including compacted forms).

- Evaluated media and gas thermodynamic properties required for modeling framework.

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Introduction

The HSECoE brings together all of the materials and hydrogen storage technology efforts to address onboard hydrogen storage in light-duty vehicle applications. The effort began with a heavy emphasis on modeling and data gathering to determine the state of the art in hydrogen storage systems. This effort spanned the design space of vehicle requirements, power plant and BOP requirements, storage system components, and materials engineering efforts. These data and models will then be used to design components and sub-scale prototypes of hydrogen storage systems which will be evaluated and tested to determine the status of potential system against the DOE 2010 and 2015 technical Targets for hydrogen Storage Systems for Light-Duty Vehicles.

Approach

A team of leading North American national laboratories, universities, and industrial laboratories, each with a high degree of hydrogen storage engineering expertise cultivated through prior DOE, international, and privately sponsored projects has been assembled to study and analyze the engineering aspects of condensed phase hydrogen storage as applied to automotive applications. The technical activities of the Center are divided into three system architectures: adsorbent, chemical hydride and metal hydride matrixed with six technologies areas: Performance Analysis, Integrated Power Plant/Storage System Analysis, Materials Operating Requirements, Transport Phenomena, Enabling Technologies and Subscale Prototype Construction, Testing and Evaluation. The project is divided into three phases; Phase 1: System Requirements and Novel Concepts, Phase 2: Novel Concept Modeling Design and Evaluation and Phase 3: Subscale System Design, Testing and Evaluation.

SRNL Technical Results

SRNL and its sub-recipient UQTR to date have met and or exceeded their FY 2012 objectives for all of their major technical goals within the HSECoE. These objectives fall within the areas of: Transport Phenomena, Adsorbent System Level Modeling, Material Operating Requirements and System Architecture. Transport Phenomena and Adsorbent System Modeling results are shown below for adsorbent systems.

Transport Phenomena

- Numerical models were validated against data from the UQTR flow-through cooling experiments. The predicted and measured volume average temperatures compared well, see Figure 1. Discrepancies are due to experimental error and modeling assumptions about the homogeneity of the adsorbent bed.
- New test facilities are being prepared at UQTR to conduct flow-through tests at higher gas flowrates.
- A vessel for flow-through cooling experiments with a structured adsorbent is being constructed at UQTR. The adsorbent will be in the form of pellets stacked in a honeycomb array, see Figure 2.
- In conjunction with the UQTR structured adsorbent experiments, a numerical model that represents the charging and discharging process is being developed by SRNL.
- UQTR produced 17 kg of activated carbon for experimental usage within the HSECoE.
- A numerical model has been developed for non-conductive heating of the adsorbent bed. Experiments are being designed and necessary property measurements are being made. This technique has the potential to

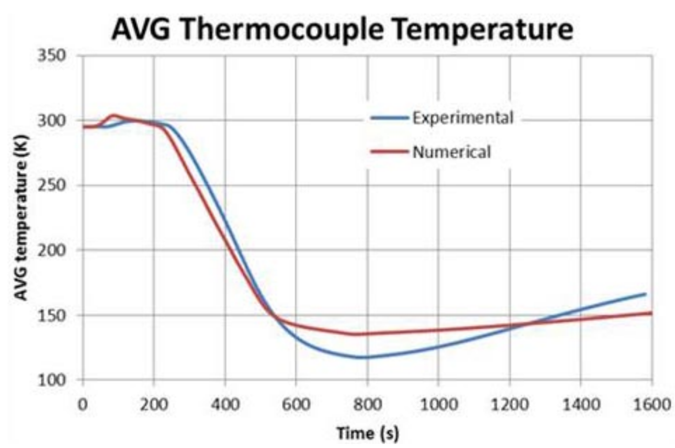

FIGURE 1. Average temperatures for hydrogen charging of the flow-through system predicted by the detailed numerical model and those measured in experiments performed at UQTR.

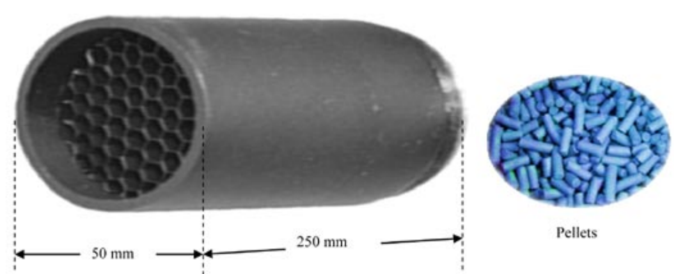

FIGURE 2. Honeycomb insert for stacking MOF-5 pellets for structured bed. The diameter and length of the pellets is 6 mm.

affect rapid hydrogen discharge even for low bed thermal conductivities.

- Development of the Modular Adsorption Tank Insert (MATI) concept for adsorbent bed heat exchangers continues as a joint effort between UQTR, OSU and SRNL. The effort includes design, optimization and planned experiments.
- Continued evaluation, fitting and incorporation of Ford data for compacted forms of MOF-5.

Adsorbent System Level Modeling

- The Matlab®-version of the cryo-adsorbent system models has been updated to include the following design options, with additional testing and debugging extending into the next quarter. All subroutines have expansion capabilities should additional options be needed. (Figures 3 and 4 show just two examples [MOF-5 in Type I tanks] out of dozens of modeling comparisons that were analyzed using the system models):
  - Dubinin-Astakhov (D-A) Parameters for hydrogen storage within several cryo-adsorbents.

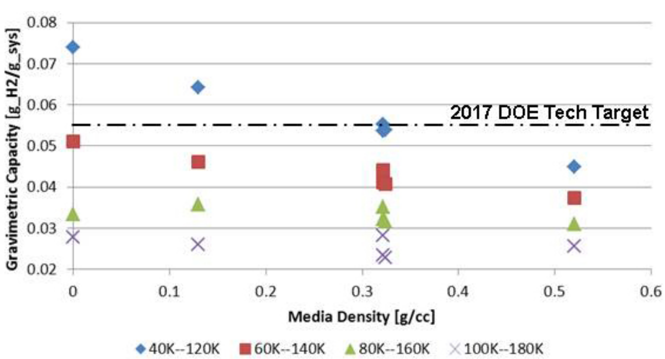

FIGURE 3. System model gravimetric capacity trends for compacted MOF-5 in an aluminum Type I tank at P_{full_tank} = 60 bar. Zero density corresponds to comparable cryo-compressed systems.

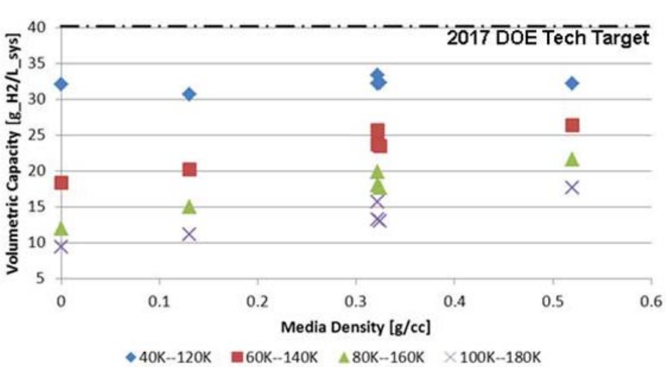

FIGURE 4. System model volumetric capacity trends for compacted MOF-5 in an aluminum Type I tank at P_{full_tank} = 60 bar. Zero density corresponds to comparable cryo-compressed systems.

  - Internal tank heat exchanger concepts, where the mass and volume of the heat exchanger is adaptable based on the properties of the cryo-adsorbent.
  - Expanded tank sizing estimator with a wide range of dimensional options and design types.
- The system model have been extended to include thermo-physical property correlations for 0.1 bar <P<450 bar and 20 K<T<450.
  - Included para-ortho conversion correlations based on temperature.
  - Provides for direct system level comparisons between cryo-compression of gas-only storage and cryo-adsorbent based storage.
- Ongoing collaborative efforts:
  - Working with UQTR, GM, and Ford to update the D-A Parameter estimates and proof-of-concept tank designs.
  - Working with PNNL to update the tank sizing estimator and improve on its accuracy for multiple tank types.
  - Working with OSU to improve the accuracy of the MATI design subroutine within the system model analysis.
  - Working with JPL to redesign the hydrogen conditioning heat exchanger for multiple passes to work with the warm hydrogen stream leaving the MATI for use in the desorption loop.
  - Working with PNNL to decrease the mass and volume of the system BOP components.
  - Working with NREL and PNNL to add costing estimates to the system model analyses.

Conclusions and Future Directions

Metal hydride efforts were terminated based on the judgment that no known material was near capable of meeting either the 2017 or ultimate targets in a system configuration. Ultimately, a metal hydride is needed which will have a capacity of 10-11 wt% hydrogen and an enthalpy of 25-27 KJ/mole H_2 to avoid the requirement of consuming a significant portion of the stored hydrogen. No metal hydride is foreseen to meet this very demanding target.

Chemical hydride efforts centered on slurry/solvent ammonia-borane materials development and utilizing flow through reactor development with dynamic temperature control, high flow gas liquid separation and impurity trapping. Further studies were conducted on endothermic vs. exothermic chemical hydrides with the identification of various start stop cycles deeply inhibiting attainment of the onboard efficiency target.

Adsorbent system efforts centered on compaction and thermal management during both fill and discharge segments

of operation. Identification of flow through cooling during fueling and resistive heating during discharge were identified and verified numerically. The overall system operating temperature and pressure ranges were analyzed with various options for optimum system performance identified. Cryogenic pressure vessel designs were developed and materials and tank testing equipment constructed and used to design potential tank concepts.

Future technical work by SRNL in the adsorbent area will include:

- Examining the performance of the MATI using the system models.
- Validating, tuning and refining the detailed models to make them applicable for scale up and alternative applications of hydrogen storage technology.
- Continuing the flow-through cooling experiments, investigating MOF-5 in powder and compacted forms, as applicable.
- Optimizing the adsorbent system with respect to pressure work, enthalpy of hydrogen discharge flow, dormancy conditions and thermal interaction with the container wall.
- Selecting an adsorbent, and form thereof, for use in the prototype.
- Designing the prototype and develop an experimental test matrix.

FY 2012 Publications/Presentations

1. B. Hardy, C. Corgnale, R. Chahine, M-A Richard, S. Garrison, D. Tamburello, D. Cossement and D. Anton. "*Modeling of adsorbent based hydrogen storage systems*." International Journal of Hydrogen Energy, Volume 37, Issue 7, April 2012, Pages 5691-5705.

2. C. Corgnale, B. Hardy, S. Garrison, D. Tamburello, D. Anton. "*Acceptability envelope for metal hydride-based hydrogen storage systems*." International Journal of Hydrogen Energy, Volume 37, Issue 3, February 2012, Pages 2812-2824.

3. S. Garrison, M. Gorbounov, D. Tamburello, B. Hardy, C. Corgnale, B. vanHassel, D. Mosher and D. Anton. "*Optimization of internal heat exchangers for hydrogen storage tanks using metal hydrides*." International Journal of Hydrogen Energy, International Journal of Hydrogen Energy, Volume 37, Issue 3, February 2012, Pages 2850-2861.

4. M. Bhouri, J. Goyette, B. Hardy, D. Anton. "*Numerical modeling and performance evaluation of multi-tubular sodium alanate hydride finned reactor*." International Journal of Hydrogen Energy, Volume 37, Issue 2, January 2012, Pages 1551-1567.

5. B. Hardy, C. Corgnale. "*Adsorbent Based Hydrogen Storage System Models*." Invited presentation at the 2012 World Hydrogen Energy Conference, Toronto, Canada, June 4, 2012.