IV.B.1 Hydrogen Storage Engineering Center of Excellence

Donald L. Anton (Primary Contact), Theodore Motyka, Bruce J. Hardy, David A. Tamburello, Claudio Corgnale, and Martin Sulic Savannah River National Laboratory (SRNL) Bldg. 999-2W Aiken, SC 29808 Phone: (803) 507-8551 Email: Donald.Anton@srnl.doe.gov

DOE Managers

Ned Stetson Phone: (202) 586-9995 Email: Ned.Stetson@ee.doe.gov Jesse Adams Phone: (720) 356-1421 Email: Jesse.Adams@ee.doe.gov

Subcontractors

- Pacific Northwest National Laboratory (PNNL), Richland, WA
- United Technologies Research Center (UTRC), East Hartford, CT
- General Motors Company (GM), Warren, MI
- Ford Motor Company (FMC), Dearborn, MI
- National Renewable Energy Laboratory (NREL), Golden, CO
- Los Alamos National Laboratory (LANL), Los Almaos, NM
- Jet Propulsion Laboratory (JPL), Pasadena, CA
- University of Michigan (UM), Ann Arbor, MI
- California Institute of Technology (CalTech), Pasadena, CA
- Oregon State University (OSU), Corvallis, OR
- Hexagon Lincoln LLC, Lincoln, NE
- Université du Québec à Trois-Rivières (UQTR), Trois-Rivières, QC, Canada

Project Start Date: February 1, 2009 Project End Date: December 31, 2015

Overall 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 hydrogen, and adsorption materialsbased 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 materialsbased technology (adsorbents, metal hydrides, and chemical hydrogen storage materials)

Fiscal Year (FY) 2015 Objectives

- Coordination and facilitation of partner's activities
- Designed and fabricated a 2-L adsorbent subscale prototype utilizing a hexagonal aluminum honeycomb structure (HexCell) heat exchange system
- Completed validation of the hydrogen cryo-adsorbent test station
- Demonstrate performance of a flow through adsorbent subscale prototype system
- Demonstrate performance of a modular adsorbent tank insert (MATI) adsorbent subscale system

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells, and Infrastructure 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

The projected performance of the two adsorption systems, HexCell and MATI, being evaluated are given in Table 1 in comparison to the technical targets.

FY 2015 Accomplishments

- Completed assembly of the flow through subscale prototype system and began initial characterization experiments
- Completed validation of the hydrogen cryo-adsorbent test station for evaluating the performance of the 2-L MATI prototype
- Completed a slide package describing the adsorbent acceptability envelope and accompanying hydrogen storage applications for the DOE Materials-Based Hydrogen Storage Summit
- Completed assembly of MATI subscale prototype and completed charging and discharging characterization experiments

INTRODUCTION

The Hydrogen Storage Engineering Center of Excellence (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 balance of plant requirements, storage system components, and materials engineering efforts. These data and models will then be used to design components and subscale prototypes of hydrogen storage systems which will be evaluated and tested to determine the status of potential systems against the DOE 2020 and ultimate 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/or privately sponsored programs has been assembled to study and analyze the engineering aspects of condensed phase hydrogen storage as applied to automotive applications. The technical activities of HSECoE are divided into three system architectures, adsorbent, chemical hydrogen, 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 program 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.

TABLE 1. System Status vs	. Technical Targets for the Crvo-Adsorbent System

				HexCell		MATI	
		2020 Technical Targets	End of Phase 1	End of Phase 2	Projected End of Phase 3	End of Phase 2	Projected End of Phase 3
Gravimetric Density	(kg H ₂ /kg sys)	0.055	0.0312	0.0352	0.0384	0.0341	0.0385
Min. Delivery Temp.	(°C)	-40	-40	-40	-40	-40	-40
Max Delivery Temp.	(°C)	85	85	85	85	85	85
Min. Delivery Pressure	(b ar)	5	5	5	5	5	5
Max. Operating Temp.	(°C)	60	60	60	60	60	60
Min. Operating Temp.	(°C)	-40	-40	-40	-40	-40	-40
Max. Delivery Pressure	(b ar)	12	12	12	12	12	12
Min. Full Flow Rate	([g/s]/kW)	0.02	0.02	0.02	0.02	0.02	0.02
System Cost	(\$/k Wh net)	\$10	\$18.30	\$12.73	\$14.79	\$15.45	\$16.32
Onboard Efficiency	(%)	90%	90%	90%	90%	97%	97%
Volumetric Density	(kg H ₂ /liter)	0.040	0.01938	0.01749	0.02059	0.02072	0.02363
Cycle Life (1/4 - full)	(N)	1500	1500	1500	1500	1500	1500
Fuel Cost	(\$/gge)	4	6.00	6.00	6.00	6.00	6.00
Loss of Useable H_2	$([g/hr]/kgH_2)$	0.05	0.4451	0.2670	0.8065	0.2670	0.6916
Wells-to-Power Plant Efficency	(%)	60%	40%	40%	40%	40%	40%
Fuel Purity	(%)	99.97%	99.99%	99.99%	99.99%	99.99%	99.99%
Transient Response	(sec)	0.75	0.75	0.75	0.75	0.75	0.75
Start Time to Full Flow (-20°C)	(sec)	15	15	15	15	15	15
Fill Time (5kg H ₂)	(min)	3.3	3.3	3.3	3.3	3.3	3.3
Start Time to Full Flow (20°C)	(sec)	5	5	5	5	5	5

RESULTS

The 2-L HexCell prototype has been designed at SRNL and fabricated at UQTR. UQTR has been successful in sealing the domed 2-L vessel and have not had to switch to the new 2-L flanged vessel provided by Hexagon Lincoln. With the leak issue resolved, the following experimental efforts have been completed to date.

- Dead volume measurements with and without the HexCell internal heat exchanger structure within the 2-L vessel
- Room temperature isotherms for varying operating pressures in the fully instrumented 2-L prototype (powder MOF-5 [metal-organic framework] packed to a density of 160 kg/m³)
- Initial isotherm measurements at 77 K for varying operating pressures; note that there have been some H₂ flow rate inconsistencies that UQTR is working to resolve

Much of the last year has been spent attempting to seal the 2-L vessels designed by Hexagon Lincoln. The newest vessel, a 2-L stainless steel flanged vessel, appears to have solved the leak issues that plagued the collared design. In addition, once a sealable vessel solution was built and in the hands of the team members, OSU has had several complications during the assembly and proof testing of the 2-L MATI prototype, including a cracked endcap and leaking through several thermocouple (TC) penetration locations. Thus, a six-month no-cost extension was requested and granted in order to complete the experimental phase of the project. The 2-L MATI prototype was completed at OSU and shipped to SRNL on March 6, 2015. During shipping, significant damage to the system was identified, requiring full disassembly, re-instrumentation and reassembly. Images of the assembly process and the newly assembled prototype vessel are shown in Figure 1. The final 2-L MATI prototype assembly includes the following.

- 16 MOF-5 pucks
- 30 internal TCs
- One pressure transducer tap
- One gas inlet/outlet tap
- Two MATI pass-throughs

Once assembled, the prototype was pressure tested at room temperature up to 100 bar, and then in liquid nitrogen up to 100 bar as shown in Figure 2.

An acceptable leak rate is assumed to be no more than 0.100% of the full tank gas storage during an experimental run. Based on the initial models of the 2-L MATI prototype, 0.100% of the gas storage at 80 K and 100 bar (60 bar) is 0.0624 g (0.0510 g). Translating this into a drop in pressure, this corresponds to a maximum allowable pressure drop from 100 bar (60 bar) of 0.262 bar (0.147 bar). Assuming a 30 min drive cycle experiment, this corresponds to a leak rate of 0.0087 bar/min at 100 bar (0.0049 bar/min at 60 bar). The 2-L MATI prototype vessel as it is currently sealed has leak rates below 0.0033 bar/min, below the minimum acceptable rate.

Representative results from the desorption experiments from 60 bar to 1 bar while submerged in the liquid nitrogen (LN_2) bath are shown in Figure 3 for a gaseous nitrogen



FIGURE 1. 2-L MATI prototype in various stages of assembly



FIGURE 2. MATI prototype pressure test in liquid nitrogen

 (GN_2) flow of 150 SLPM through the MATI. Due to cooling effects within the lines, the GN_2 enters the MATI at approximately 250 K, which is still more than enough heat to aid in desorption. Note that, even with the cooling effects of the LN, bath, the average puck temperature at 8 min is 150 K.

A MATI-only cool down experiment was also performed to cool the 2-L prototype assembly from room temperature without the aid of the LN_2 bath, with its results shown in Figure 4. The final length of LN_2 supply tubing would normally run through the LN_2 bath to maintain a near 80 K temperature prior to entering the MATI. Without the LN_2 bath, the LN_2 supply to the MATI remains >100 K at the MATI inlet. Even with this limitation, the average puck temperature drops from 285 K to 141 K after 6 min, 134 K after 9 min, and 129 K after 18 min. Thus, the MATI's design has shown to be quite capable of cooling the adsorbent pucks.

Several updates have been made to the adsorbent storage system to reflect the latest experimental data and detailed model simulations. Additional updates will be performed after the graphical user interface evaluation is complete and the Phase III results are available.

CONCLUSIONS AND FUTURE DIRECTIONS

Adsorbent system efforts are concentrated on Phase III prototype design, assembly, testing, and modeling, including test station design, construction, and capabilities verification. Two prototypes are being tested and modeled: (1) powder MOF-5 in a hexagonal heat exchanger (HexCell) that utilizes



FIGURE 3. Temperature profiles for desorption of MATI system from 60 bar to 1 bar, initialized at 80 K, with a GN, flow at 150 SLPM



FIGURE 4. Temperature profiles for a closed-vessel cool down operation using only the MATI starting from room temperature

flow-through cooling during refueling and resistance heating during discharge is being tested at UQTR and modeled at SRNL, and (2) compacted MOF-5 in a MATI utilizing isolated LN_2 during refueling and isolated H_2 during discharge is being tested at SRNL and modeled at OSU. Initial tests on both systems have been concluded and both are working as anticipated, illustrating that adsorbent systems are capable of meeting many of the DOE technical targets for hydrogen storage.

Future technical work will include:

- Continue validation experiments on the 2-L MATI prototype assembly to include testing at pressures greater than 60 bar, cycling for a minimum of 50 cycles, and validation of thermal and mass flow models against experimental data
- Continued validation experiments on the 2-L HexCell prototype assembly to include cryogenic charging and discharging experiments, cycle testing to a minimum of 50 cycles, and validation of thermal and mass flow models against experimental data
- Update Simulink cryo-adsorbent system models to predict full-scale system performance

FY 2014/2015 PUBLICATIONS/ PRESENTATIONS BY SRNL/UQTR

1. Hardy, B., Corgnale, C., Tamburello, D., Anton, D. "Acceptability envelope for adsorption based hydrogen storage," Invited presentation at MCARE 2014, Clearwater (FL), USA.

2. C. Corgnale, B. Hardy, D. Tamburello, R. Chahine, and D. Anton, "Simulation of hydrogen adsorption systems adopting the flow through cooling concept," International Journal of Hydrogen Energy (2014), 39, 17083–17091.

FY 2014/2015 PATENTS BY SRNL/UQTR

1. Tamburello et al., Heat Transfer Unit Method for Prefabricated Vessel, 61/905,557, 12/12/2013.