IV.B.6 Thermal Management of Onboard Cryogenic Hydrogen Storage Systems

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Overall Objectives

- Develop system simulation models and detailed transport models for onboard hydrogen storage systems using adsorbent materials, and to determine system compliance with the DOE technical targets
- Design, build, and test an experimental vessel for validation of cryo-adsorption models and determine the fast-fill and discharge dynamics of cryo-adsorbent storage systems

Fiscal Year (FY) 2014 Objectives

- Demonstrate 3-minute scaled refueling by an internal flow-through cooling system based on powder media
- Demonstrate scaled H_2 release rate of 0.02 (g H_2/s)/kW by an internal heating system (<6.5 kg and 6 L)
- Participate in Phase III of the project as an original equipment manufacturer consultant in face-to-face meetings and coordinating council telecons; indicate technical or programmatic areas the Hydrogen Storage Engineering Center of Excellence (HSECoE) should be pursuing with more emphasis

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:

(A) System Weight and Volume

(C) Efficiency

(E) Charging/Discharging Rates

(J) Thermal Management

Technical Targets

In this project, studies are being conducted to develop metal-organic framework (MOF)-5-based storage media with optimized engineering properties. This material has the potential to meet the 2017 technical targets for onboard hydrogen storage shown in Table 1.

TABLE 1. Project Technical Targets

Storage Parameter	2017 Target
System Gravimetric Capacity	0.055 (kg H_2/kg system)
System Volumetric Capacity	0.040 (kg H_2/L system)

FY 2014 Accomplishments

- Completed work on the experimental verification of the fast-fill and discharge dynamics of a cryo-adsorbent bed. The experimental data obtained with the cryo-apparatus enabled GM and the HSECoE to validate the transport models for these processes.
- Conducted additional experiments and model simulations while varying several operating conditions to improve upon the flow-through method of cooling the MOF-5 bed.
- The helical coil electric resistance heater design was tested successfully in the experimental program, reaching the targeted H_2 release rate.
- Obtained performance and operational data of MOF-5 powder/heat exchanger system.

INTRODUCTION

The DOE is supporting research to demonstrate viable materials for onboard hydrogen storage. Onboard hydrogen storage systems based on cryo-adsorbents are of particular interest due to the high gravimetric hydrogen capacity and fast kinetics of the sorbent materials at low temperatures and moderate pressure. However, cryo-adsorbents are generally characterized by low density and unsatisfactory thermal properties. As part of the HSECoE team, the GM team is building system models and detailed transport models to optimize a cryo-absorbent fuel tank. A laboratory-scale cryogenic vessel was designed, built, and tested to determine the charging and discharging capabilities of an actual, operational system.

APPROACH

The 3-liter stainless steel cryogenic test vessel is sealed in an evacuated chamber that is temperature controlled down to cryogenic temperatures to best establish adiabatic conditions. Approximately 525 g of pure MOF-5 powder is packed into the 3-liter test vessel resulting in an adsorbent bed density of 0.18 g/cm^3. When pressurized to 60 bar, the adsorbent bed contains 96 g of hydrogen resulting in a weight fraction of 0.16 kg H_2/(kg MOF + H_2) and a volumetric density of 0.032 kg H_2/L of MOF. Mass flow rates in and out of the adsorption vessel are measured with a number of selectable orifice meters to allow accurate measurement over a large range of flow rates (0.005 to 0.75 g/s). A GM-designed helical coil heater with a center heating element is installed in the vessel to supply heat to the adsorbent bed during discharge. The vessel can be pressurized by either controlling the outlet flow rate or closing the outlet. A total of 32 high precision resistive temperatures devices and associated data acquisition channels are used to measure temperatures throughout the system and in the adsorption bed. Twenty-two of the resistive temperatures devices are devoted to measuring temperatures throughout the bed and at the inlet and outlet ports. The remaining 10 are associated with monitoring thermal conditions of hydrogen gas flow throughout the apparatus.

Three-dimensional adsorption and desorption models of the 3-liter cryogenic test vessel were developed using COMSOL Multiphysics® software. COMSOL contains application modes allowing for fluid flow through a porous media. The porous and fluid media are treated as a single medium having volume-averaged variables such as the flow velocity, pressure, and density. The gas and the solid bed are assumed to be in thermal equilibrium. Real gas properties of hydrogen are calculated using equations for a compressibility factor. Properties that are temperature or pressure dependent (and time-varying), such as the heat capacity of the MOF-5 bed and the heat of adsorption, are calculated at each time step. The amount of adsorbed hydrogen was quantified by employing a Dubinin-Astakhov isotherm. Model simulations were performed for the charging and discharging processes for the 3-liter cryogenic vessel. The flow in the system was modeled with Free and Porous Media Flow physics, and the heat transfer process was modeled with Heat Transfer with Porous Media. Pressure drop and flow velocity fields can be calculated with the former physics, and the process of heat transfer in the solids, fluids, and porous media can be investigated with the latter one.

RESULTS

A. Cryogenic Test Vessel – Charging Tests

During hydrogen charging, the exothermic adsorption process will produce heat as the hydrogen is introduced into the vessel. For fast hydrogen charging, this adsorption heat must be removed from the storage vessel as quickly and efficiently as possible or the rate of adsorption will decrease significantly. Experiments were performed to control the heat removal by varying the hydrogen outlet flow rate during flow-through cooling. Outlet flow rates of 0.4 and 0.52 g/s were used to determine if the faster rate would be more efficient at cooling the MOF-5 bed. For the 0.4 g/s case, the outlet flow rate had to be increased to 0.58 g/s at time 160 or the target pressure of 60 bar would have been exceeded. The initial bed temperature was approximately 102 K. Pressure was ramped from 5 bar to 60 bar within 60 seconds. The inlet hydrogen temperature was maintained at 82 K and the inlet flow rate was 0.65 g/s. The effect of the outlet flow rate on the average bed temperature profile is shown in Figure 1. After an initial rapid increase in temperature due to the heat produced by adsorption, the run with the faster outlet flow rate of 0.52 g/s maintains a lower temperature for the majority of the run until the temperatures eventually converge. The faster outlet flow rate helps to speed up the removal of the heated hydrogen gas. However, the final temperature of 104 K is still well above the desired temperature of 82 K.

The flow-through cooling method tested previously was found to have several inefficiencies. For example, the mass flow rate required to bring the 150 K MOF-5 bed to a temperature of 80 K would require an extremely large amount of hydrogen to pass through the vessel. Cooling the bed from an initial temperature of 150 K to 80 K by flowing hydrogen that is at the target temperature is also inefficient. Another issue with flow-through cooling is that

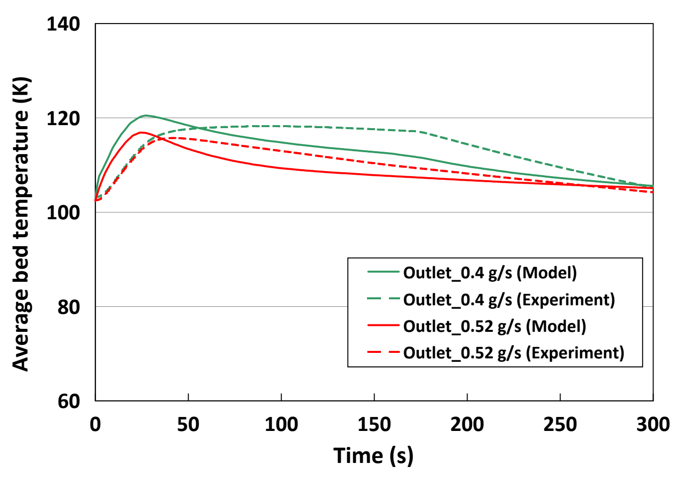

FIGURE 1. Effect of Outlet Flow Rate on Average Bed Temperature during Flow-Through Cooling

its effectiveness could suffer from possible channeling in the MOF-5 powder bed. This could cause some areas of the bed to be bypassed by the cold stream of hydrogen, making it very difficult to cool down these regions.

In order to address the issues associated with the flow-through cooling method, an alternative experimental method was devised for cooling the MOF-5 bed during charging. In this rapid charge/discharge method, the outlet of the cryogenic test vessel was initially closed while hydrogen flowed into the vessel. After a rapid temperature increase due to the adsorption heat, the outlet was opened to discharge the heated gas and depressurize the vessel. After a pressure of 5 bar was reached, along with a corresponding drop in temperature, the outlet was then closed and a new charge/discharge cycle was begun. For the first experiment a series of five charge/discharge cycles was performed with an initial bed temperature of 150 K. While each subsequent cycle achieved lower temperatures, the average bed temperature failed to reach the 80 K target, although it did decrease approximately 45 K from the initial temperature. For a second experiment, an initial bed temperature of 115 K was used. The results of this experiment are shown in Figure 2. The minimum temperature reached was 73 K, well below the inlet hydrogen temperature of 80 K. This shows that the cycling method can cool certain regions of the bed to a temperature lower than that of the inlet hydrogen, making it possible to store more hydrogen. This is a definite improvement over the flow-through cooling method, which could not achieve these low temperatures.

The cryogenic test vessel had been situated for horizontal gas flow for the entire set of experiments performed with it. This was the logical orientation for testing, since a full-size storage vessel would have to be placed horizontally in a vehicle. In order to test the effect of the vessel orientation on the experimental results, a run was performed in which the vessel was placed in the vertical position. The temperature profiles along the center line of the vessel matched closely for comparable charging tests performed with the vessel in the horizontal and vertical positions. The repeatability of the temperature profiles indicates that the orientation of the vessel had a negligible effect on the results.

B. Cryogenic Test Vessel: Discharging Experiments and Modeling

Previous discharge experiments with the cryogenic vessel demonstrated that a continuously running helical coil heater supplies adequate heat to maintain desorption and release hydrogen at the desired target rate of 0.02 g H_2/sec. Energy savings might be attained if it is possible to avoid powering the heater continuously when driving the vehicle. To test this hypothesis, the effect of delaying the introduction of heating power to the helical coil was investigated for the discharge process. The initial pressure of 60 bar can be used to extract hydrogen from the vessel without supplying heat. However, due to the endothermic effect of hydrogen desorption, the bed temperature will decrease. Extra heat must eventually be provided to warm up the bed. There are potential benefits to this mode of operation. If hydrogen in the vessel is not going to be used in a short period of time, the temperature drop in the vessel can be helpful for prolonging the dormancy period. If the hydrogen that remains in the tank can be warmed up by heat transfer from the warmer ambient air during parking time, less heating power is needed for the discharge and energy can be saved.

Figure 3 shows the change of average bed temperature in the vessel when heat is not provided until 2,160 s. The discharge rate was 0.02 g/s, supplied heating power 39 W, and heat flux 978 W/m^2. It can be seen that the average bed temperature drops during the discharge process. The lowest average bed temperature reached was 75 K. The

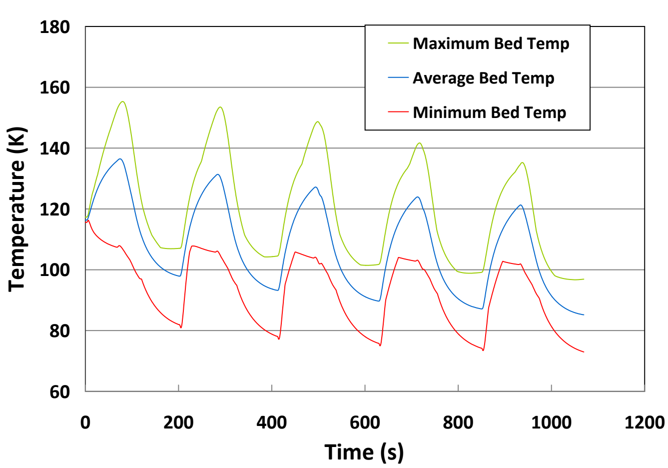

FIGURE 2. Rapid Cooling for the Charging Process with Initial Bed Temperature of 115 K

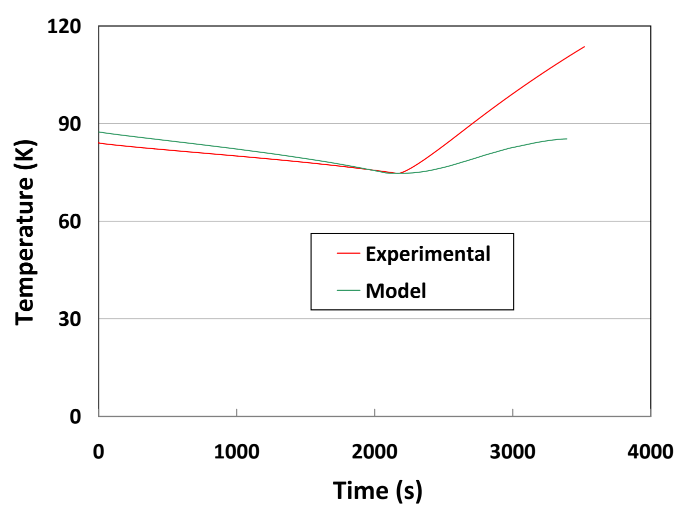

FIGURE 3. Effect of Delayed Heat Supply during Discharge on Average Bed Temperatures

inconsistency in average bed temperatures between the experiment and the model at the latter part of discharge is mainly due to the fact that the temperatures beyond the ends of the heating element were not detected and recorded. In the discharge process, temperatures in those two regions tend to be lower due to the endothermic effect of desorption. The average bed temperature in the model is integrated over the entire volume of the bed; thus, it tends to be lower than the values obtained in the experiment. The corresponding pressures in the vessel are shown in Figure 4. Delaying the supply of heating power to the helical coil causes the pressure to drop far more rapidly than the case with a continuously running heater. Although the delayed heating case runs for a slightly shorter amount of time, most likely due to additional hydrogen remaining adsorbed, the experiments show that leaving the heating power off for certain periods may be beneficial. With the use of better electronics controlling the system during driving, it may be possible to obtain significant energy savings.

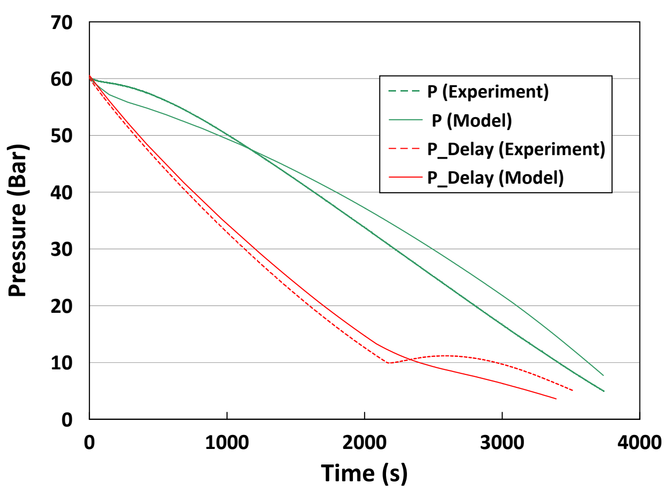

FIGURE 4. Effect of Delayed Heat Supply during Discharge on Pressure

CONCLUSIONS AND FUTURE DIRECTION

- The GM team completed its Phase II work on the experimental verification of the fast-fill and discharge dynamics of a cryo-adsorbent bed. The experimental data obtained with the cryo-apparatus enabled GM and the HSECoE to validate the transport models for these processes.
- The flow-through cooling concept for removal of heat during charging was validated experimentally, within the limits of the test apparatus. In addition, the helical coil electric resistance heater design was tested successfully in the experimental project.
- GM will continue to participate in Phase III as an original equipment manufacturer consultant to the HSECoE team. No additional experimental work is planned for Phase III.

FY 2014 PUBLICATIONS/PRESENTATIONS

1. M. Cai, et al. (2014), Testing and Modeling of a Cryogenic Hydrogen Storage System with a Helical Coil Electric Heater, presented at the 2014 DOE Hydrogen Program Annual Merit Review Meeting, Washington, D.C.

2. P. Hou, J.P. Ortmann, M. Sulic, A. Chakraborty, M. Cai, Experimental and numerical investigation of the cryogenic hydrogen storage processes over MOF-5, submitted to IJHE.