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

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Overall Objectives

Main objectives of this project are:

- 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) 2013 Objectives

- Demonstrate 3-minute scaled refueling by an internal flow-through cooling system based on powder media

- Validate metal-organic framework (MOF)-5 powder bed capable of 0.15 g H_2/(g MOF) and 20 g H_2/(liter MOF)

- 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)

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 MOF-5-based storage media with optimized engineering properties. This material has the potential to meet the 2017 technical targets for onboard hydrogen storage as shown in the following table:

Storage Parameter	2017 Target (system)	MOF-5 (material)
System Gravimetric Capacity	0.055	0.187
System Volumetric Capacity	0.040	0.028

FY 2013 Accomplishments

- Completed the installation and testing of the cryo-vessel with automated control instrumentation

- Obtained performance and operational data of MOF-5 powder/heat exchanger system

- Installed and tested helical coil heat exchanger in the cryo-vessel, reaching targeted H_2 release rate

- Validated adsorption and desorption models with cryo-vessel experiments

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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 Hydrogen Storage Engineering Center of Excellence (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 (Figure 1) 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. 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 temperature devices (RTDs) and associated data acquisition channels are used to measure temperatures throughout the system and in the adsorption bed. Twenty-two of the RTDs are devoted to measuring temperatures throughout the bed and at the inlet and outlet ports. The remaining ten 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 Multiphysics® 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
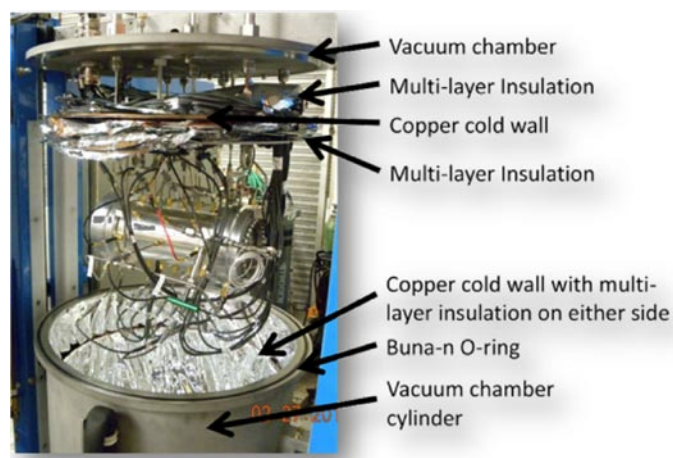

FIGURE 1. 3-liter vessel mounted to instrument with RTDs attached prior to closing vacuum chamber.

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

Various adsorptions were performed on the MOF-5 powder bed to examine our 3-minute refueling milestone within the parameters of 5–60 bar and 150–80 K. A pressure of 60 bar can be reached within one minute, thus leaving more than 2 minutes for flow-through cooling. However, with an initial bed temperature of 150 K, the lowest bed temperature at 3 minutes during our testing was still above 100 K. The slow cooling effect seen in the MOF-5 powder bed is attributed to the test vessel itself and the interaction of the incoming cold gas with the warm gas inside the vessel. The large thermal mass of the stainless steel pressure vessel, approximately 25 lbs, coupled with the limited intimate contact the cold hydrogen gas has with the internal vessel wall result in only a small decrease in vessel body temperature. The body temperature has a significant effect on the overall bed temperature. When flow-through cooling is halted, the bed and vessel wall quickly reach a temperature equilibrium close to that of the vessel wall's initial state. To drive the vessel temperature down during an adsorption, external cooling would be required. Unfortunately, while our apparatus does have liquid nitrogen flow control to the vessel end caps, it was not designed for a rapid cooling process. The larger factor for the slow flow-through cooling is the mixing of the incoming cold hydrogen with the warm bed hydrogen. In an ideal case, the cold gas would move through the bed while pushing the warm gas out like two immiscible liquids. This would allow for higher inlet flow rates compared to the outlet due to the higher density of the incoming gas. Unfortunately this is not the case. The cold gas moves throughout the vessel, therefore the hydrogen gas that is removed is not necessarily the warmest gas within the bed. This is apparent in Figure 2. The temperature profiles shown are center points moving away from the inlet as they get closer to the outlet. While it is expected that the exothermic heat of adsorption onset should be a progression from inlet to outlet, it is clear from Figure 2 that the further a point is away from the inlet the slower is the cooling effect, indicating that the incoming cold hydrogen is not progressing through the bed by pushing the warm gas out. A vessel design to improve
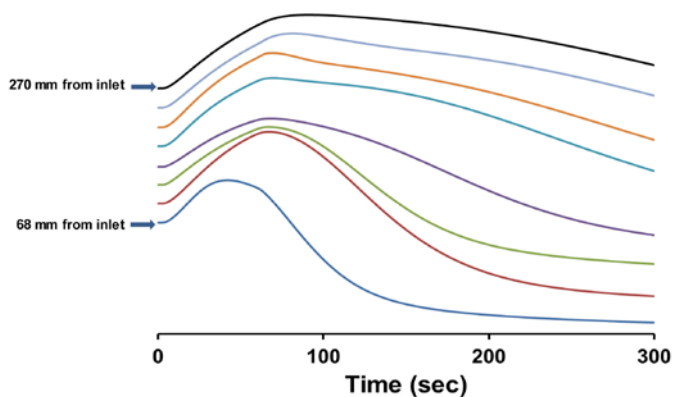
FIGURE 2. Experimental temperature profiles shown are center points moving away from the inlet as they get closer to the outlet. The further a point is away from the inlet the slower is the cooling effect.

FIGURE 3. Effect of MOF density on H_2 storage increase rate.

flow-through cooling would require directional channels for the gas.

To decrease the mixing of the gases we added more adsorbent to the inlet side of the test vessel. Prior to adding more adsorbent the existing bed was compacted as much as possible. The new MOF-5 powder (7.78 g), was also compacted before the vessel was sealed. By compacting and adding more powder to the inlet side of the test vessel it was our intention to slow down diffusion of the incoming cryogenic hydrogen through the initial section of the bed, thereby displacing the warm gas more effectively. The compaction increased the bed density of MOF in the system from 164 kg/m^3 to 174 kg/m^3. Experimental and modeling results from the two cases are shown in Figure 3. The data in Figure 3 indicates that the density of MOF has an effect on the H_2 charging rate per unit mass of MOF. The H_2 charging rate per unit mass of MOF increases with the density of MOF in the vessel. The key factor for successful fast H_2 charging is to remove the heat from the vessel as soon as possible. To optimize the fast removal of heat from the system, preventing the back mixing of cold H_2 and hot H_2 is crucial. As the density of MOF in the system increases, the intensity of back mixing among hot and cold H_2 in the system can be reduced. Therefore, the heat removal efficiency can increase, which leads to lower average bed temperatures and higher efficiency of H_2 charging. The improved efficiency due to the compacted MOF was not sufficient to counteract the heat of adsorption and attain the target refueling time of 3 minutes.

B. Modeling of the Ideal Charging Process

During charging, the adsorbent vessel and the bed must be cooled for effective hydrogen adsorption. In addition, since hydrogen adsorption is an exothermic process, the heat of adsorption must also be removed. An ideal charging case was modeled that aimed to cool the system within 3 minutes without considering the limits on peak mass flow
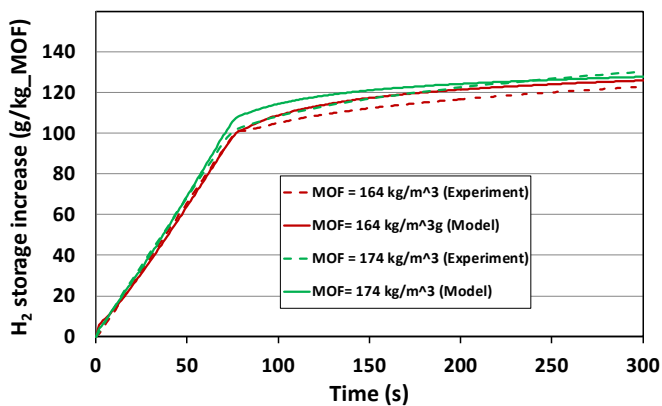
rate inherent in the 3-liter cryogenic vessel's equipment configuration. For the ideal case, the pressure was ramped from 5 bar to 60 bar within 1 minute, and the outlet was opened gradually at the beginning of the pressure ramp and fully opened in 20 seconds. The inlet H_2 temperature was set to 80 K. Operations with two different initial system temperatures (150 K and 80 K) were investigated. Due to the impact of the initial system temperature, profiles of both the inlet and outlet mass flow rates and the amount of H_2 accumulation in the vessel were different in the two cases, even though the outlet velocity profiles were set to the same value. For the 150 K case, the inlet mass flow rate was approximately 0.4 g/s after the pressure ramp and the outlet mass flow rate was about 0.18 g/s. At the end of 3 minutes of charging, slightly more than 40 grams of H_2 was accumulated in the vessel. The final average bed temperature was 137 K. With this outlet velocity, the vessel could not be refueled within 3 minutes. For the case with an initial system temperature of 80 K, a lot more H_2 can be added into the vessel during the first 60 seconds. At the end of 3 minutes of charging, around 87 grams of H_2 was accumulated in the vessel and the final average bed temperature was 82 K, very close to the desired value. It is more difficult to flow a high volume of cold H_2 into a hot vessel than into a cold vessel. The impact of initial temperature on the process of charging is twofold. The hot system needs a larger quantity of cold H_2 to cool down, and it also results in having a lower inlet mass flow rate than the cooler system.

C. Modeling of the Experimental Discharging Experiments

The objective of the discharge experiments is to demonstrate that an internal heating element is capable of supplying the heat required to desorb enough H_2 to maintain a desired release rate (0.02 g H_2/sec). The adsorbent bed initially contained a total of 96 g of H_2 at a temperature of approximately 80 K and a pressure of 60 bar. In order to fully discharge the usable H_2, the final state of the bed should be 150 K and 5 bar. Two levels of power (39 W and 58 W)

for the helical coil heater were used in the experiments and modeled with COMSOL. For the first experiment 39 W was supplied to the heater, and the resulting heat flux of 678 W/m^2 raised the average bed temperature to only 123 K at the end of the experiment. The H$_2$ in the bed was not fully desorbed, which resulted in a total of 11 grams of H$_2$ (adsorbed plus gas) remaining in the vessel. Increasing the supplied power to 58 W for the second experiment produced a heat flux of 978 W/m^2 from the heating element surface and raised the bed's average temperature to a final value of 150 K. Figure 4 shows the amount of H$_2$ remaining in the bed during the course of this experiment and the modeling simulation. The initial amount of adsorbed H$_2$ was calculated using the Dubinin-Asthakov model with a temperature of 84 K and pressure of 61 bar. The experimental value for the total amount of adsorbed plus gaseous H$_2$ (ntotal) was estimated using the outlet flow rate of 0.02 grams/sec. The temperatures in the vessel at the end of discharging were not uniform. Therefore, to estimate the total amount of H$_2$ remaining in the bed (ntotal) at the end of discharging, the temperature of the system was equilibrated after closing the outlet. The revised value of ntotal in Figure 4 was then calculated by using the Dubinin-Asthakov model with the equilibrated temperature and pressure. As the revised ntotal value of 6 grams of H$_2$ is close to the modeled value, the prediction of the Dubinin-Asthakov model over the experimental range, i.e., 4 bar, 150 K to 60 bar, 80 K, appears to be consistent. The discharge experiment with the cryogenic vessel shows that the helical coil heater supplies adequate heat to maintain desorption and release H$_2$ at the desired target rate. However, the heater's weight and volume targets could not be met.
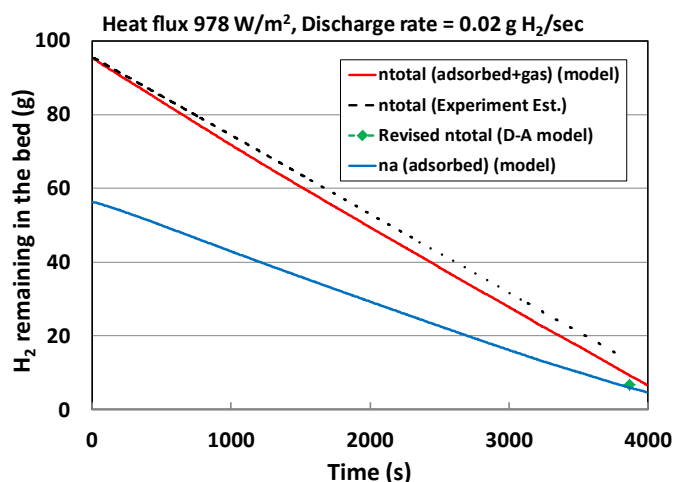
While the discharge experiments validate the accuracy of the model in simulating the desorption process, some differences between experimental and modeled results should be noted. For the discharge process there was a brief pressure increase in the vessel near the beginning of the experiments which was not captured in the model simulations. This may be attributed to the possibility that the intensity of convection in the experiment is better than that in the model. Therefore, the gas in the real system can be heated up faster than that in the model and the pressure increase is more evident in the real system. As mass transport in the real system is better than that in the model, gases could be released more easily and the pressure then drops faster in the real system. Temperature comparisons between the experiments and the model simulations are useful, but they are limited by the fact that the RTDs measure temperatures at a finite set of points, whereas the model can integrate the temperatures over the entire volume of the storage bed. However, we found that the average temperatures of the RTD measurements agreed reasonably well with the model's values.

FUTURE DIRECTION

GM will participate in Phase 3 as an advisor to the HSECoE team. No experimental work is planned for Phase 3.

FY 2013 PUBLICATIONS/PRESENTATIONS

1. M. Cai, et al. (2013), Thermal Management of On-Board Cryogenic Hydrogen Storage Systems, presented at the 2013 DOE Hydrogen Program Annual Merit Review Meeting, Washington, D.C.

2. J.P. Ortmann, and N.S. Kaisare, Modeling of Cryo-adsorption of Hydrogen on MOF-5 pellets: Effect of pellet properties on moderate pressure refueling, International Journal of Hydrogen Energy, manuscript submitted, 2013.

3. P. Hou, J.P. Ortmann, M. Sulic, M. Cai, Experimental and numerical study of the discharging process of a MOF-5 hydrogen storage system, GM Internal Report, 2013.

4. P. Hou, J.P. Ortmann, M. Sulic, M. Cai, Experimental and numerical study of the charging process of a MOF-5 hydrogen storage system, GM Internal Report, 2013.

FIGURE 4. Total and adsorbed hydrogen in the bed for desorption run.