IV.D.7 Thermal Management of Onboard Cryogenic Hydrogen Storage Systems

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Fiscal Year (FY) 2012 Objectives

Main objectives of this project are:

- To develop system models and detailed transport models for onboard hydrogen storage systems using adsorbent materials, and to determine system compliance with the DOE technical targets.
- To develop storage media structures with optimized engineering properties for use in storage systems.
- To design and build an experimental vessel for validation of cryo-adsorption models.

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
(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 potential to meet 2017 technical target for onboard hydrogen storage as shown Table 1.

TABLE 1. 2017 Technical Targets for Onboard Hydrogen Storage

Storage Parameter	2017 Target (system)	MOF-5 (material)
System Gravimetric Capacity	0.055	0.187
System Volumetric Capacity[1]	0.040	0.028

[1] Volumetric capacity is based on powdered MOF5

FY 2012 Accomplishments

- Developed a two-dimensional (2-D) model of refueling of MOF-5 pellet with Dubinin-Ashtakohov (D-A) adsorption isotherm that includes effects of expanded natural graphite (ENG) additive and anisotropic thermal conductivity.
- Demonstrated that over 96% of the hydrogen from MOF-5 bed can be extracted.
- Completed the design, built, and installation of a cryo-vessel with automated control instrumentation.
- Designed an effective helical coil heat exchanger for hydrogen desorption process to be used in an MOF-5 bed with a hydrogen supplying rate of 1 g/s.
- Completed low temperature thermal conductivity measurements of MOF-5 pellets with density of 0.3 and 0.5 g/cm^3 respectively, and with 0, 5 and 10 wt% ENG for improved thermal conductivity.

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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 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 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 the cryo-absorbent fuel tank.

Over FY 2012, models have been developed for the MOF adsorbent material, MOF-5, with a focus on optimization of heat exchanger design with the objective of minimizing the heat exchanger mass while meeting DOE targets. In addition, models for MOF-5 intra-pellet hydrogen transport to optimize pellet shape and pellet permeability and thermal conductivity for refueling have been developed. Examination of the low density and thermal conductivity properties of MOF-5 lead to compaction of the adsorbent with addition of a thermal enhancer by up to 10 wt%. Samples of various densities and thermal enhancement were studied over a large temperature range.

Approach

Based on the previous work done with AX-21 system, continued modeling effort was carried out for the design of an optimized heat exchanger to be used in the MOF-5 system. The goal of this design is to extract 5,600 g of hydrogen during a 5,600 s time discharge period with a maximum hydrogen flow rate of 1 g/s to supply the fuel cell stack. All the required heat for achieving this goal should be supplied by the internal element in a helical coil shape. Two scenarios were studied in details, in which the initial bed pressure was set to 60 and 200 bars respectively, for systems with a thermal conductivity of 0.3 and 0.5 W/mK respectively. For each system, two contact heat fluxes, 919 and 1,546 W/m^2, were also examed. For all the case studies, the final bed pressure was set to 4 bars. The optimal pellet size was calculated through modeling based on previously reported excess adsorption data on neat MOF-5 pellets [1,2]. Parameters used for the baseline case study are: isotropic thermal conductivity of a MOF-5 pellet with 10 wt% ENG, permeability of 1.2 x 10^{-14} m^2, D-A adsorption isotherm parameters for neat MOF-5 and pellet dimensions of h=d=1 cm. MOF-5 pellets with densities of 0.3 and 0.5 g/cm^3 respectively were used for the permeability modeling study. The anistropic thermal conductivity modeling of MOF-5 + ENG pellets was aimed to examine the effect on refueling time across the radial and axial direction of the pellet. Low temperature thermal conductivity experiments were also carried out on a series of MOF-5 pellets, with the densities of 0.3 and 0.5 g/cm^3 respectively, each one of them contains 0, 5 and 10 wt% ENG respectively for the thermal enhancement. The ENG were introduced into the system by mixing MOF-5 and ENG with a shaker mill with no additional mixing medium. Pellets were primarily prepared by Ford and supplied to GM for measurement; additional pellets were also prepared by GM for validation purpose. The thermal conductivity of pellet was measured with a P670 Thermal Transport System from Quantum Design, over a range of 4–350 K.

Results

A. Three-Dimensional (3-D) Modeling for Hydrogen Desorption on MOF-5

Figure 1 demonstrates the bed temperature profile and amount of extracted hydrogen during the discharge with an initial bed pressure of 200 bars and bed thermal conductivity of 0.5 W/mK. Figure 1A shows that the average final bed temperature remains in an acceptable range of 150-160 K whereas maximum bed temperature lies below 240 K. Minimum bed temperature lies in between 80-105 K. Further investigation confirmed that there is uniform temperature distribution throughout the bed which significantly affects the desorption efficiency. Figure 1B indicates the amount of extracted total hydrogen (gas phase + adsorbed phase)

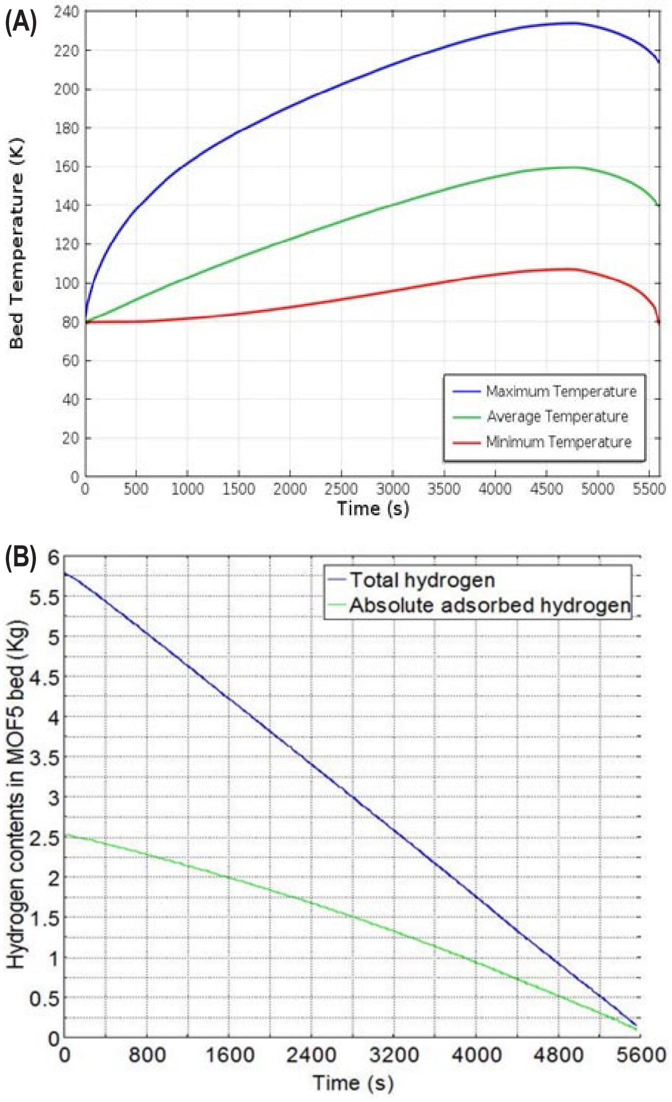

FIGURE 1. (A) Temperature profiles; and (B) amount of hydrogen extraction in MOF-5 bed.

and absolute adsorbed hydrogen during the time period. It is evident that the system can effectively extract over 96% of hydrogen from the bed. Table 2 further shows the comparison of hydrogen extraction process in two models for AX-21 and MOF-5. Both models are proven to be efficient and accurate since the modeled desorption efficiencies are very close to that of the theoretical values. The total hydrogen desorption efficiency of MOF-5 is significantly higher than that of AX-21 (>96% vs. >92%). Another important aspect is that the heat applied into the discharging is comparatively lower in MOF-5 system than that in AX-21 system. Furthermore, the results indicate that the bed volume with higher initial pressure is comparatively lower in MOF-5 than that of AX-21. There are also significant design alterations in the heating coil with the exception for a 60 bar system. A significant decrease in coil length and turns were also observed for the MOF-5 system with higher initial pressure of 200 bars, compared to AX-21 system.

TABLE 2. Comparison of Simulation and Theoretical Results for 5.6 kg of Deliverable H_2

	60 bar and 80K		200 bar and 80K	
	AX-21 bed	**MOF-5 Bed**	**AX-21 bed**	**MOF-5 Bed**
THEORETICAL (D-A METHOD) HYDROGEN AVAILABILITY FOR EXTRACTION				
% extracted H_2	92.1	96.7	94.1	98.4
RESULTS FROM SIMULATION				
% extracted H_2	**91.8**	**96.6**	**92.6**	**97.5**
Required Heat (W)	**1,760**	**1,546**	**1,374**	**919**
Mass of the bed (kg)	59	30	36	16
Total bed volume (L)	212.52	217.23	140.08	125.24
HEATING ELEMENT SPECIFICATION				
Turn of the coil	12.13	12.40	8	6.63
Length of the coil (m)	13.33	13.63	8.80	7.30

B. 2-D Modeling of Pellet Size, Permeability, and Thermal Conductivity Effect on Refueling

Various pellet sizes were studied for the effect of refueling time. Stick like pellets with aspect ratios of *h/d* >>2 were found to be the most suitable size to achieve the fast refueling time at a relatively high storage volume. Likewise, flat "hockey puck" pellets are also likely to provide low refueling time. Conversely, short pellets (*h/d* ≈0.5) show the longest refueling times. In addition, a random packed bed of such pellets is not recommended based on simulation studies.

Based on previous study, pellet compaction to 0.51 gm/cm^3 provides a good compromise between the volumetric and gravimetric capacities [1]. Permeability was measured for MOF-5 pellets at different compaction levels (0.3 to 0.5 gm/cm^3). Three values were modeled: a baseline of 1.2×10^{-14} m^2 (corresponding to 0.51 g/cm^3 MOF-5 pellet), a high value of 2.1×10-13 m^2 (0.301 g/cm^3 pellet), and a low value of 5.1×10^{-16} m^2. The results showed that pellet permeability had a negligible impact on the amount of hydrogen adsorbed and the volume-averaged temperature. Even for the lowest value of permeability, the pressure equilibrates within 0.1 seconds. We conclude that the pellet permeability does not have any impact on the refueling behavior of a single pellet with quiescent boundary conditions. These results may not be extrapolated to refueling of an adsorbent bed because pressure drop and flow rate through the bed may depend on the bed permeability.

Anisotropic thermal conductivity of MOF-5 pellets with 10 wt% ENG was also modeled. Figure 2 shows the effect of radial thermal conductivity λ_r on the refueling. The axial conductivity was kept at the nominal value of λ_z while two cases of $\lambda_r = \{2, 4\} \times \lambda_z$ were studied. The results show that increasing the radial thermal conductivity decreases the refueling time from 15.7 seconds in the base case to 9.3 and 5.1 seconds, respectively. We consider the refueling time here to be the point at which 95% of the pellet's volumetric storage capacity has been reached.

C. Low Temperature Thermal Conductivity Measurements

Figure 3 shows improvement in thermal conductivity while increasing the amount of ENG and the pellet density. In this study, pellets with 0.3 g/cm^3 are proven not strong for handling, which resulted in limited data collection. In addition, structural integrity of 0.3 g/cm^3 pellets decreased with increasing wt% ENG. Noticeable variances in the thermal conductivity profile were observed over the temperature range studied, indicating there is a lack of the consistency between pellets. These variances are attributed

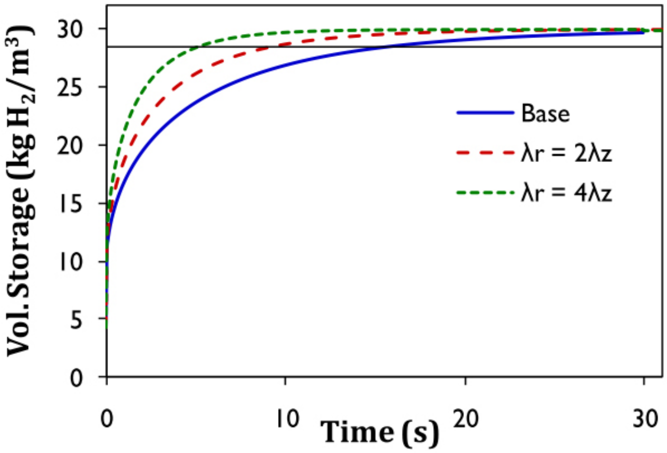

FIGURE 2. Effect of radial thermal conductivity on pellet refueling. The solid line corresponds to $\lambda_r = \lambda_z$; the axial thermal conductivity is kept at a nominal value of λ_z and the radial value is increased in the two dashed lines.

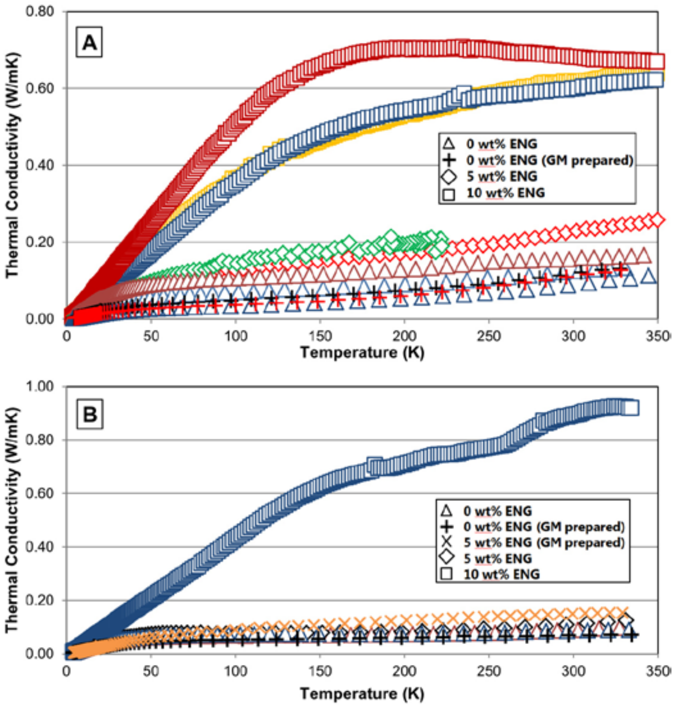

FIGURE 3. MOF-5 pellets (A) 0.5 g/cm^3 series; (B) 0.3 g/cm^3 series with 0, 5, and 10 wt% expanded natural graphite (ENG).

to slight difference in density or wt% ENG or orientation of ENG within each pellet. Typically, the lowest density pellet within a series exhibited the lowest *k* value, as expected. As shown in Figure 3, one interesting observation is that the pellets with 0.3 g/cm^3 did not improve in *k* value as significantly as the pellets with 0.5 g/cm^3 over the range of 0 to 5 wt% ENG. However, the difference between 0.3 and 0.5 g/cm^3 pellets is only slight at ENG levels of 10 wt%. This is mainly due to the graphite which plays a more significant role in the thermal conductivity over the temperatures studied.

Future Directions

- Include D-A adsorption isotherm parameters for MOF-5 pellet with 10% ENG in pellet model; obtain improved measurement of pellet permeablility for model.
- Modeling of a 3-D flow through hydrogen charging system in MOF-5 bed for a 3-L vessel.
- Design and fabrication of a 3-L vessel for MOF-5 charging and discharge experiments – model validation with simulation results.
- Design and modeling of heat exchangers – liquid N_2 cooling during adsorption and fuel cell waste heat for desorption.
- Experimental validation of flow-through and heat exchanger models.

FY 2012 Publications/Presentations

1. S Kumar et al. Thermal Management of On-Board Cryogenic Hydrogen Storage Systems, DOE Annual Merit Review, 2012, Washington, D.C.

2. A Chakraborty; S Kumar. Heat Exchanger Design for Adsorbent Systems : Model and Results, HSE CoE face to face meeting, Santa Fe,NM, November, 2011.

3. A Chakraborty; S Kumar. Thermal Management and Desorption Modeling of a Cryo-adsorbent Hydrogen Storage System, International Journal of Hydrogen Energy, manuscript submitted, 2012.

4. M Sulic; S Kumar; M Cai. Cycling and Engineering Properties of Highly Compacted Sodium Alanate Pellets, International Journal of Hydrogen Energy, manuscript submitted, 2012.

5. M Sulic; S Kumar; M Cai. Controlled Degradation of Highly Compacted Sodium Alanate Pellets, International Journal of Hydrogen Economy, manuscript submitted, 2012.

6. M. Raju; S. Kumar. Optimization of Heat Exchanger Designs in Metal Hydride based Hydrogen Storage Systems, International Journal of Hydrogen Economy, 37, 2767, 2012.

7. S Kumar; M Raju; VS Kumar. System Simulation Models for On-board Hydrogen Storage Systems, International Journal of Hydrogen Economy, 37, 2862, 2012.

8. N Kaisare. Modeling of Cryo-adsorption of Hydrogen on MOF-5 Pellets: effect of pellet properties on moderate pressure refueling, Internal GM report, 2012.

9. VS Kumar. 2-D Model for Non-isothermal Adsorption of Hydrogen in Cylindrical Adsorbent Pellets, Internal GM report, 2011.

10. S Kumar. Metal Hydride Material Requirements for Hydrogen Storage in Fuel Cell Vehicles, Internal GM report, 2012.

References

1. Purewal, J.J.; Liu, D.; Yang, J.; Sudik, A.; Siegel, D.J.; Maurer, S.; Muller, U., Increased volumetric hydrogen uptake of MOF-5 by powder densification. International Journal of Hydrogen Energy 2012, 37, (3), 2723-2727.

2. Sudik, A.; Veenstra, M.; Müller, U.; Maurer, S.; Gaab, M.; Purewal, J.; Liu, D.a.; Xu, C.; Siegel, D.; Ni, J., Adsorbent Materials for HSECoE, In Hydrogen Storage Technical Team Review, 2012.