

IV.B.7 Ford/BASF SE/UM Activities in Support of the Hydrogen Storage Engineering Center of Excellence

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Subcontractors

- University of Michigan (UM), Ann Arbor, MI
- BASF SE, Ludwigshafen, Germany

Project Start Date: February 1, 2009

Project End Date: June 30, 2015

Overall Objectives

This project addresses three of the key technical obstacles associated with the development of a viable hydrogen storage system for automotive applications:

- (Task 1) Create accurate system models that account for realistic interactions between the fuel system and the vehicle powerplant.
- (Task 2) Develop robust cost projections for various hydrogen storage system configurations.
- (Task 3) Assess and optimize the effective engineering properties of framework-based hydrogen storage media (such as metal-organic frameworks [MOFs]).

Fiscal Year (FY) 2014 Objectives

The project focus during FY 2014 was to complete the following objectives:

- Conduct a scale up of the MOF-5 manufacturing process to deliver >9 kg of material while maintaining

performance, as measured by surface area, particle size, and hydrogen uptake, to within 10% of lab-scale procedure.

- Explore approaches to optimize MOF-5 engineering properties, such as thermal conductivity, mass transport, and safety.

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
- (B) System Cost
- (C) Efficiency
- (D) Durability/Operability
- (E) Charging/Discharging Rates
- (H) Balance-of-Plant (BOP) Components
- (J) Thermal Management

Technical Targets

The outcomes of this project provide input to vehicle and system level models, cost projections, and also contribute to the assessment and optimization of materials properties. Insights gained from these studies are applied towards the engineering of hydrogen storage systems that attempt to meet the DOE 2017 and ultimate hydrogen storage targets, shown in Table 1. As a status based on the cooperative analysis within the HSECoE, the current adsorbent systems are also shown in Table 1 based on powder and compacted MOF-5.

FY 2014 Accomplishments

- Task 1. System Modeling
 - Led the Hydrogen Storage Engineering Center of Excellence (HSECoE) adsorbent system effort by serving as the system architect and provided guidance from an original equipment manufacturer perspective to identify and prioritize the design direction.
 - Contributed to development of the Hydrogen Vehicle Simulation Model based on validated powertrain data and participated in development of the storage system model.

TABLE 1. Technical Targets and Current Adsorbent Systems

Storage Parameter	Units	DOE 2017 Target	DOE Ultimate Target	HexCell MOF-5 powder	MATI MOF-5 compact
System Gravimetric Capacity	kg-H ₂ /kg	0.055	0.075	0.035	0.034
System Volumetric Capacity	kg-H ₂ /L	0.040	0.070	0.018	0.021
Storage System Cost	\$/kWh _{net}	12	8	12.7	15.5
System Fill Time (for 5 kg H ₂)	min	3.3	2.5	3-5	3-5
Minimum Full Flow Rate	(g/s)/kW	0.02	0.02	0.02	0.02
Min/Max Delivery Temperature	°C	-40/85	-40/85	-40/85	-40/85
Min. Delivery Pressure (Fuel Cell)	Atm	5	3	5	5

- Initiated design verification plan to align the failure mode and effects analysis action items with the Phase 3 test results. These activities were aimed at reducing the occurrence of failure modes in the adsorbent system.
- Task 2. Cost Analysis
 - Contributed to trade-off studies and integration analysis of BOP componentry. In collaboration with HSECoE partners, assessed cost-saving opportunities for a full-scale adsorbent storage system.
- Task 3. Assessment/Optimization of Framework-Based Storage Media
 - Delivered 9.3 kg of MOF-5 to HSECoE partners for Phase 3 system testing. Demonstrated successful scale up of material synthesis with delivered material achieving performance levels within 10% of lab-scale material properties.
 - Used high-throughput computational screening to assess the hydrogen storage capacity of ~4,000 porous metal-organic compounds mined from the Cambridge Structural Database. Identified trends in performance, and pinpointed several over-looked, yet promising MOFs that exhibit high volumetric and gravimetric hydrogen densities simultaneously.
 - Demonstrated a 20x improvement in MOF-5 thermal conductivity using an enhanced natural graphite (ENG) layering approach (compared to an equivalent MOF-5/ENG composite with random ENG loading).
 - Initiated degradation MOF-5 impurity cycle testing and conducted additional hydrogen flow parameter testing through powders.
 - Completed the formation of over 50 MATI half pucks using a novel embedded thermocouples technique with high dimensional and density consistency.



INTRODUCTION

Widespread adoption of hydrogen as a vehicular fuel depends critically on the development of low-cost, onboard hydrogen storage technologies capable of achieving high energy densities and fast kinetics for hydrogen uptake and release. Since present-day technology based on compression and liquefaction is unlikely to attain established DOE targets, development of materials-based storage approaches has garnered increasing attention. To hasten development of these ‘hydride’ materials, the DOE previously established three centers of excellence for materials-based hydrogen storage research. While the centers have made substantial progress in developing new storage materials, challenges associated with the engineering of the storage system around a candidate storage material have received much less attention.

APPROACH

Ford-UM-BASF is conducting a multi-faceted research project that addresses the key challenges associated with the development of materials-based hydrogen storage systems. As in previous years, we continue to be engaged in system modeling (Task 1), with the objective of a public release of the HSECoE Hydrogen Vehicle Simulation Model. Work also continues in the system cost analysis effort (Task 2). During the past year, the majority of our effort has been focused on sorbent media (Task 3), with the primary goal of characterizing the “effective engineering properties” of MOFs in order to guide the development of optimal strategies for their use in an adsorbent system. In particular, we projected the performance for several thousand sorbent materials, conducted scale up of the MOF-5 synthesis process, and explored approaches for optimization of MOF-5 adsorbent media. Additional details are provided in the following section.

RESULTS

Following is a description of our technical results for certain key accomplishments and how these results relate to achieving the DOE targets.

Sorbent Media Performance Potential

As a response to project reviewers, we performed an analysis to determine the performance potential of sorbent media. Rather than considering theoretical MOF structures, we sought to identify promising known MOFs whose crystal structures reside within the Cambridge Structural Database. Many of these compounds have not been assessed as hydrogen storage materials. We developed an approach based on data mining and automated structure analysis to identify, “cleanup,” and rapidly predict the hydrogen storage properties of these compounds. Approximately 20,000 candidate compounds were generated from the Cambridge Structural Database using an algorithm that removes solvent/guest molecules. These compounds were then characterized with respect to their surface area and porosity. Employing the empirical relationship between excess hydrogen uptake and surface area, we predict the theoretical total hydrogen storage capacity for the subset of ~4,000 compounds exhibiting nontrivial internal porosity (see Figure 1).

Our screening identified several overlooked compounds having high volumetric and gravimetric hydrogen capacities simultaneously; these compounds are suggested as targets of opportunity for additional experimental characterization. More importantly, our screening revealed that the relationship between gravimetric and volumetric hydrogen density is concave downward, Figure 1, with maximal volumetric performance occurring for surface areas of 3,100–4,800 m²/g. We conclude that hydrogen storage in MOFs will not benefit from further improvements in surface area alone. Rather, discovery efforts should aim to achieve

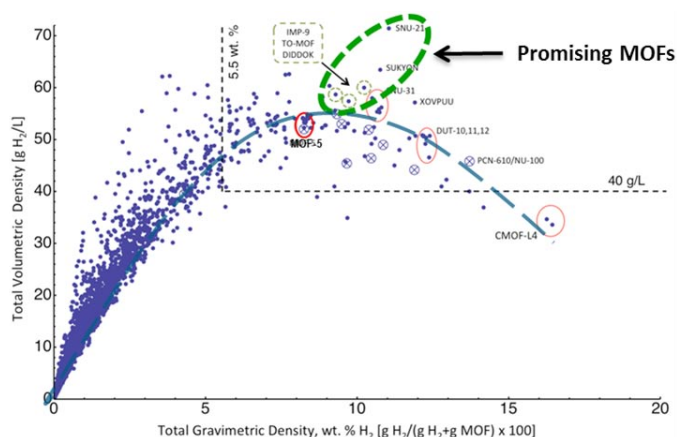


FIGURE 1. Theoretical Total (adsorbed + gas phase hydrogen at 77 K and 35 bar) Volumetric and Gravimetric Density of Stored Hydrogen in ~4,000 MOFs Mined from the Cambridge Structural Database.

moderate mass densities and surface areas simultaneously, while ensuring framework stability upon solvent removal.

Sorbent Media Scale Up

The scale up MOF-5 synthesis from a small-scale reactor (60 liters) to series-production representative reactors (200 liters) was successfully demonstrated. A total of 9.3 kg of MOF-5 powder was synthesized and subsequently characterized to ensure the scaled-up material could achieve a level of performance—as measured by surface area and particle size—to within 10% of lab-scale procedure. As shown in Table 1, the scaled-up material mix (GP0378) achieved the desired 10% of lab-scale material (GP0326). In fact, the Brunauer-Emmett-Teller (BET) surface area of the scaled-up material was increased by about 1% relative to the 60-liter (lab-scale) batch. The crystal size comparison between batches was found to be comparable using scanning electron microscopy analysis. The microscopy evaluation provided an assessment of the MOF-5 crystal attributes (i.e., roughness) as an effect from the scale-up synthesis steps (i.e., washing time). The particle size was extensively evaluated using laser diffraction based on International Organization for Standardization technical specification ISO 13320. The cumulative distribution measurement of particle size indicates a consistent particle size among the batches, with the particle size of the scaled-up material within 7% of the lab-scale batch.

TABLE 1. Surface Area, Crystal Size, and Particle Size Comparison of 200 Liter Scale-Up Material (GP0378) to 60 Liter Lab-Scale Material (GP0326)

Batch Code	Reactor Size (L)	Amount (kg)	BET (m ² /g)	Zn (wt%)	C (wt%)	Crystal size (μm)	Particle size (mm)
GP0372	200	3.1	2937	32	37	0.2-2.0	
GP0374	200	3.5	2870	34	37	0.2-2.0	
GP0375	200	3.2	2955	34	37	0.2-2.0	
GP0378	Mix of above	9.3	2937	30	37	0.2-2.6	0.1-1.3
GP0326	60	1	2905	34	37	0.2-3.0	0.1-1.4

In addition to comparing physical properties of the powders produced by different synthesis methods, the hydrogen uptake was also compared. As shown in Figure 2, the 200-liter batch provides the same excess adsorption as the 60-liter material, consistent with their similar surface areas. Multiple measurements were taken for both powder and 0.5 g/cc compacted pellets, and the good agreement between batches was maintained across these systems.

Sorbent Media Assessment and Optimization

MOF-5 has an extremely low thermal conductivity, suggesting that enhancement strategies may be needed to enable efficient heat exchange designs within the adsorbent system. To increase the thermal conductivity of MOF-5 we explored the addition of ENG to MOF-5 pellets. In this

Isotherm Comparison

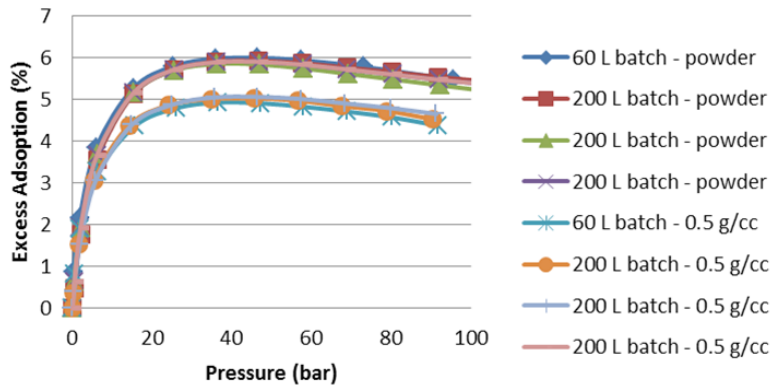


FIGURE 2. Excess Adsorption Comparison of the 200 Liter Scaled-Up Material versus 60 Liter Lab-Scale Material Synthesis

approach the ENG is typically mixed randomly into the MOF-5 powder. For cylindrical pellets, the ENG particles tend to lie perpendicular to the press direction, resulting in anisotropic thermal conductivity in the radial vs. axial directions. In previous work we determined that the thermal conductivity along directions parallel to the ENG alignment is two to three times higher than that in the perpendicular direction.

Our more recent work has demonstrated that additional improvement to thermal conductivity can be achieved by layering the ENG within the MOF-5 pellet. The pellet in Figure 3 (left) was formed by filling the die with alternating layers of MOF-5 and ENG. The die was tapped after each new layer was added. When all the layers were filled the pellet was pressed. The ENG appears to form a series of connected layers across the pellet. The resulting thermal conductivity as shown in Figure 3 (right) has 20 times improvement over the thermal conductivity measured in a pellet of comparable density and random ENG loading.

As a follow-up to the previous permeation flow testing with compacted pellets, we conducted flow testing through a bed of MOF-5 powder. The results align with the trend of an exponential increase in permeation with decrease of the sample density. The conclusion is that the hydrogen permeability of MOF-5 with density at 0.20 g/ml is over 100 times higher than that with density of 0.30g/ml. The testing was repeated with powders that were slightly compacted in the holder at a density of 0.25 g/cc and 0.29 g/cc which follow the expected trend.

CONCLUSIONS AND FUTURE DIRECTIONS

- Task 1. System Modeling
 - Evaluate the cryo-adsorbent system model based on Phase 3 performance data; support the integration into the framework; and document and release models to the public.

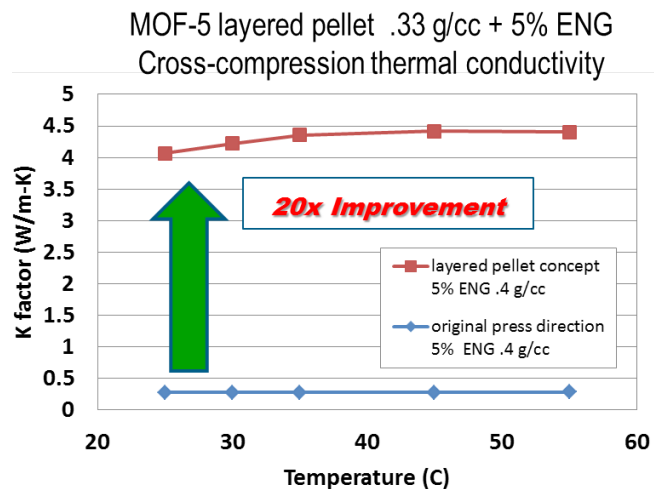
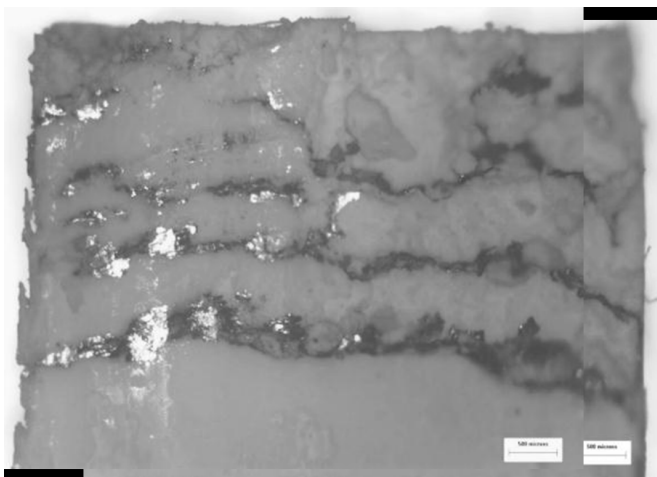


FIGURE 3. Layered Pellet Micrograph (Left) and Thermal Conductivity Measurement (Right)

- Complete the failure mode and effects analysis associated with real-world operating conditions for a MOF-5-based system, for both HexCell and Modular Adsorbent Tank Insert concepts based on the Phase 3 test results. Reduce the risk priority numbers from the Phase 2 peak/mean and identify key failure modes.
- Task 2. Cost Analysis
 - Support further integration of the system BOP components for the cost analysis, and prepare for HSECoE project summary documentation to guide material researchers.
- Task 3. Sorbent Media Assessment and Optimization
 - Complete MOF-5 degradation cycle testing based on impurity levels as stated in SAE International technical specification SAE J2719 and report on the ability to mitigate to less than 10%.
 - Complete the optimization approaches to enhance thermal conductivity, mass transport, and density variations in formed pucks.

FY 2014 PUBLICATIONS/PRESENTATIONS

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2. Y. Ming, J. Purewal, D. Liu, A. Sudik, C. Xu, J. Yang, M. Veenstra, K. Rodes, R. Soltis, J. Warner, M. Gaab, U. Muller, and D.J. Siegel, *Thermophysical Properties of MOF-5 Powders*, *Microporous Mesoporous Mater.*, **185**, 235 (2014). DOI:10.1016/j.micromeso.2013.11.015
3. Y. Ming, H. Chi, R. Blaser, C. Xu, J. Yang, M. Veenstra, M. Gaab, U. Müller, C. Uher, and D. Siegel, *Anisotropic Thermal Transport in MOF-5 Composites*, *International Journal of Heat and Mass Transfer*, submitted.
4. M. Veenstra. “MOF-5 Development in Support of the Hydrogen Storage Engineering Center of Excellence,” USDRIVE Hydrogen Storage Technical Team, March 19, 2014.
5. D.J. Siegel. “Adsorbent System Overview,” Phase 3 Go/No-Go Milestone Review, March 19, 2014.
6. M. Veenstra, “Ford/BASF/UM Activities in Support of the Hydrogen Storage Engineering Center of Excellence”, 2013 DOE Hydrogen Program Annual Merit Review Meeting, Washington, June 18, 2014.