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

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Subcontractor:
University of Michigan (UM), Ann Arbor, MI

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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) 2013 Objectives

The project focus during FY 2013 was to complete the following objectives to achieve a Phase 2 to Phase 3 Go/No-Go decision milestone in support of the Hydrogen Storage Engineering Center of Excellence (HSECoE):

- Report on ability to develop compacted MOF-5 adsorbent media having a total hydrogen material density of greater than or equal to 0.3 g/L, hydrogen density of 11 wt% and 33 g/liter, and thermal conductivity of 0.5 W/m-K at P = 60-5 bar and T = 80-160 K.
- Report on ability to demonstrate composite MOF-5 adsorbent monoliths having hydrogen uptake kinetics allowing for 5.6 kg usable hydrogen storage over a 3-minute fill time, and permeation in packed and powder forms sufficient for a flow rate of 1 m/s superficial velocity and pressure drop of 5 bar.

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 impact vehicle and system level models, cost analysis, and materials property assessment and optimization. Insights gained from these studies are applied towards the engineering of hydrogen storage systems that meet the DOE 2017 and ultimate hydrogen storage targets (Table 1).

TABLE 1. Technical Targets

Storage Parameter	Units	2017	Ultimate
System Gravimetric Capacity	$kg\cdot H_2/kg$	0.055	0.075
System Volumetric Capacity	$kg\cdot H_2/L$	0.040	0.070
Storage System Cost	$\$/kWh_{net}$	12	8
System Fill Time (for 5 kg H_2)	min	3.3	2.5
Minimum Full Flow Rate	(g/s)/kW	0.02	0.02
Min/Max Delivery Temperature	°C	-40/85	-40/85
Min. Delivery Pressure (Fuel Cell)	atm	5	3

FY 2013 Accomplishments

- Task 1. System Modeling
  - Performed the adsorbent system architect role in the HSECoE which coordinated the down-selection of MOF-5 and conducted various design and performance trade-offs.
  - Refined the failure mode and effects analysis (FMEA) for the adsorbent hydrogen storage systems based on the HSECoE team design actions.
- Task 2. Cost Analysis
  - Participated with the HSECoE partners in providing cost projection of the material-based hydrogen storage systems, utilizing the high volume automotive estimating background.
- Task 3. Assessment/Optimization of Framework-Based Storage Media
  - Demonstrated a theoretical total capability of ≥33 g/l for densities of ≥0.3 g/cc and potential for 11 wt% and thermal conductivity of ≥0.5 W/m-K can be approached with 10% enhanced natural graphite (ENG) at ~100 to 150 K.
  - Conducted sub-scale cycle test that provided effective kinetics with the potential for a 3-minute fill. Provided permeation data that indicates a projected pressure drop of 3.6 bar at 77 K for 0.3 g/cc MOF compact.
  - Completed microscopy characterization and assessed the potential to exploit anisotropic properties of densified pellets/pucks. Initiated a design of experiments-based study to quantify effects of humidity exposure. Conducted cycle testing, particle ignition evaluation, internal pressure analysis, and neutron imaging of MOF-5 powders and compacts.

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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 technologies based on compression and liquefaction are unlikely to attain established DOE targets, development in materials-based approaches have 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 three of the key challenges associated with the development of materials-based hydrogen storage systems.

Systems Modeling (Task 1): We are evaluating and developing hydrogen storage system operating models to optimize the storage system operation as it interacts with the fuel cell system.

Cost Analysis (Task 2): We are performing hydrogen storage manufacturing cost analyses for various candidate system configurations and strategies to facilitate potential cost reductions.

Sorbent Media Assessment & Optimization (Task 3): We are characterizing the “effective engineering properties” for MOFs in order to devise optimal strategies for their use in an adsorbent system.

RESULTS

Following is a description of our technical results for each task and how these results relate to achieving the DOE targets.

Task 1. System Modeling

During this past year, the system modeling effort resulted in a utility function for the adsorbent team to utilize in their trade-off studies to optimize the system configuration. The utility function was developed based on the HSECoE Simulink® framework to evaluate the changes in the vehicle attributes due to modifying the 2017 targets by +/- 10% increments. The key system targets that were analyzed were the gravimetric density, volumetric density, and system cost. The vehicle attribute (i.e. driving range, fuel economy, etc.) effects were analyzed while varying the system from the specified target values. Since this was a theoretical exercise rather than based on a particular system, it was assumed that only the specific target being analyzed was changing while the other target value remained consistent, such as for the gravimetric case which assumed volumetric remained constant. The resulting function was an expression that utilized the percent change from the target values, the customer importance factor, and the correlation slope from the models to provide a normalized system ranking and facilitate trade-offs between the key system targets. The modeling team also prepared the HSECoE model framework for a public release using a graphical user interface and conducted a beta trial. In addition, an initial FMEA update was conducted to evaluate the effects of the Phase 2 actions and activities. The potential change is shown in Figure 1 which indicates the original risk priority number in red and revised values in blue.

Task 2. Cost Analysis

The cost analysis effort during this past year produced several key results that assisted in significant progress of the system cost assessment. First, the team established baseline raw material cost values and aligned these assumptions with other related projects within the DOE portfolio through a benchmarking effort. Second, the cost projections in conjunction with PNNL included a sensitivity assessment of adsorbent systems with different types of tank technologies (I, III, IV), MOF-5 densities (powder, 0.32 g/cc, 0.52 g/cc), ENG levels (neat, 5%, 10%) along with a combination of MOF-5 pellets and AX-21 powders. Based on this analysis, the system cost for the adsorbent system was reduced due to the decrease in operating pressure from 200 bar to 100 bar and use of a Type I tank. Finally, deep-dive design reviews provided an effective method to determine the required components within the system and further reduce cost.

Task 3. Sorbent Media Assessment and Optimization

Isotherm data was collected to evaluate the working capacity of the MOF-5 material between 5 and 60 bar. For gravimetric density, the performance decreased from 12 wt% (total) for a powder form (80 K) to 7% for a 0.3 g/cc compact. This value can be increased to 9 wt% and then 12 wt% when both temperature swing and a 60% packing efficiency is included. For volumetric density, a similar assessment was made but the performance increases from 20 g/l for a powder (80 K) to 22 g/l for a 0.3 g/cc compact (5% ENG) and further increase to 34 g/l for a 0.5 g/cc compact (5% ENG) with a temperature swing but will be reduced if a packing efficiency (60%) is included.

MOF-5 has an extremely low thermal conductivity and will likely require enhancement of its thermal transport properties to allow for efficient heat exchange designs at the system level. ENG at 10 wt% loading has been shown to significantly improve (~4x to 6x) the thermal conductivity of MOF-5, achieving ≥0.5 W/m-K at ~100 to 150 K. Figure 2 provides images of MOF-5 pellets containing 5% ENG. The single pellet image in Figure 2 appears to have an ENG gradient from top to bottom.

Microscopy analysis confirmed that the ENG gradient was superficial. However, this analysis also revealed a preferred or anisotropic orientation of the ENG within the material. Figure 2 (right) demonstrates this anisotropic orientation of the ENG as highlighted with yellow lines from the imaging analyzer. Based on this discovery, we proceeded to characterize the anisotropic performance of the MOF-5 to pursue potential optimization of the cross-compression oriented ENG particles and crystallites within the pellets. The alignment of ENG leads to an improved thermal conductivity in the radial direction, Figure 3. In other words, thermal conductivity is improved (~3x) in the cross-compression direction (red line), which is perpendicular to the press direction, compared to that along the press direction (blue line). Permeation was also slightly higher in the cross-compression direction (~2x) due to the ENG channels formed within the MOF compacts. As shown in Figure 3, a unique pellet was developed to evaluate the cross-compression anisotropic properties.

A key concern regarding the use of MOF-5 in onboard storage applications is the potential sensitivity to air and/or impurities in the hydrogen stream. During this past

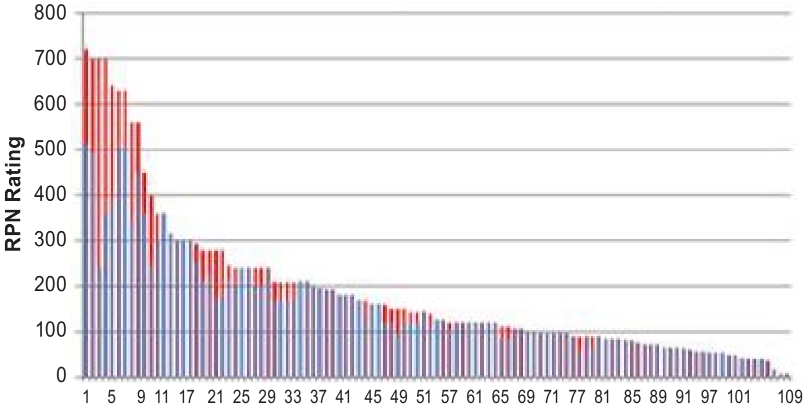

FIGURE 1. Updated Adsorbent FMEA Pareto Chart of Risk Priority Numbers with Phase 2 Results

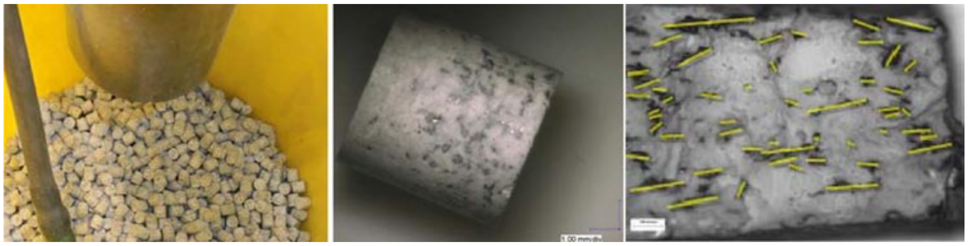

FIGURE 2. Images of MOF-5 Pellets with 5% ENG and Anisotropic Imaging Analysis

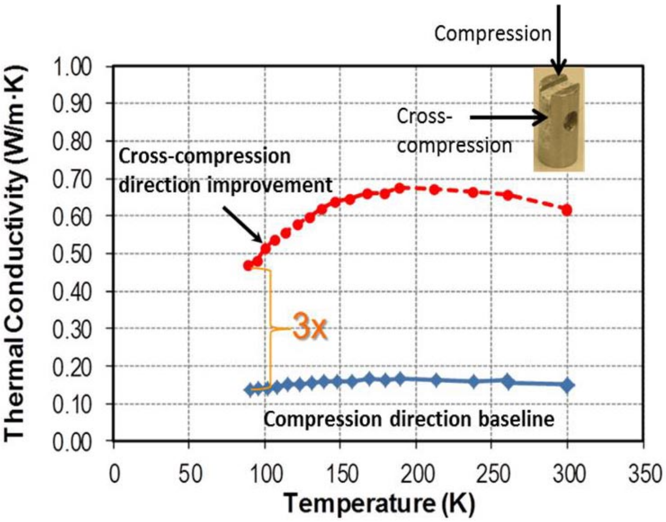

FIGURE 3. Thermal Conductivity Test Results to Compare the Anisotropic Effects

year, we have conducted tests to assess the impact of exposing MOF-5 powders to humidified air. Initial testing was conducted in the lab with approximately 45% relative humidity and a temperature of ~22°C. A 12 minute exposure was found to result in a 1.2% to 1.5% decrease in hydrogen uptake capacity. A 1.5 hour exposure had an additional, yet small, decrease to 3.5% to 3.7% compared to the unexposed sample. X-ray diffraction patterns were measured for samples exposed for different durations and were found to be in agreement with the update data. We also completed Hartman tube and 20-L sphere dust ignition tests on MOF-5, along with degradation cycle testing (>390 cycles) to confirm the robustness of the MOF-5 for practical onboard storage systems.

CONCLUSIONS AND FUTURE DIRECTIONS

- Task 1. System Modeling
  - Update the cryo-adsorbent system model with Phase 3 performance data, validate alignment within +/- 10%, integrate into the framework; document and release models to the public.
  - Complete the FMEA associated with real-world operating conditions for a MOF-5-based system, for both Hexcel and Modular Adsorption Tank Insert concepts based on the Phase 3 test results. Report on the ability to reduce the risk priority numbers from the Phase 2 peak/mean and identify key failure modes.
- Task 2. Cost Analysis
  - Conduct analysis of various adsorbed hydrogen storage systems in order to recommend design revisions and direction based on high volume automotive cost projections.
  - Provide hydrogen storage cost reductions for achieving the DOE targets with the other HSECoE project partners (with a focus on part integration and reduction).
- Task 3. Sorbent Media Assessment and Optimization
  - Conduct a scale-up of the MOF-5 manufacturing process to deliver >9 kg of material while maintaining performance, as measured by surface area and particle size, to within 10% of lab-scale procedure.
  - Based on the scaled-up material, characterize practical media-level properties via microscopy, imaging, and other empirical studies to improve performance of adsorbent materials within the prototype systems.
  - Evaluate MOF-5 degradation beyond 300 cycles based on maximum allowable impurity levels as stated in SAE J2719 and report on the ability to mitigate to less than 10%.

SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

1. **Michael Veenstra** was a recipient of a United States Council for Automotive Research special recognition award on May 8, 2013 for his work on the Hydrogen Storage Tech Team and for his guidance with system design requirements for sorbent-based storage systems in the HSECoE. DOE Leadership recognized that his contributions will translate to improved solicitations and research direction in the future.

FY 2013 PUBLICATIONS/PRESENTATIONS

1. J.J. Purewal, D. Liu, J. Yang, A. Sudik, M. Veenstra, J. Yang, S. Maurer, U. Müller, and D.J. Siegel "Improved Hydrogen Storage and Thermal Conductivity in High-Density MOF-5 Composites," Journal of Physical Chemistry C, 116 (38), pp 20199–20212, September 2012.

2. C. Xu, J. Yang, M. Veenstra, A, Sudik, J.J. Purewal, B.J. Hardy, J. Warner, S. Maurer, U. Müller, and D.J. Siegel "Hydrogen Permeation and Diffusion in Densified MOF-5 Pellets," International Journal of Hydrogen Energy, 2012, February 2013.

3. M. Veenstra. "MOF-5 Development in Support of the Hydrogen Storage Engineering Center of Excellence," USDRIVE Hydrogen Storage Technical Team, March 20, 2013.

4. D.J. Siegel. "Adsorbent System Go/No-Go Discussion," Phase 3 Go/No-Go Milestone Review, March 22, 2013.

5. M. Veenstra, "Ford/BASF/UM Activities in Support of the Hydrogen Storage Engineering Center of Excellence", 2013 DOE Hydrogen Program Annual Merit Review Meeting, Arlington, VA, May 14, 2013.