IV.D.8 Ford/BASF SE/UM Activities in Support of the Hydrogen Storage Engineering Center of Excellence

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Contract Number: DE-FC36-GO19002

Subcontractors:

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

Project Start Date: February 1, 2009
Project End Date: June 30, 2014

Fiscal Year (FY) 2012 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]).

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

Technical Targets

The outcomes of this project affect vehicle and system level models, cost analysis, and materials property assessment/optimization. Insights gained from these studies are applied towards the engineering of hydrogen storage systems that meet the following DOE 2010 and ultimately 2017 hydrogen storage targets (Table 1).

TABLE 1. Technical Targets

Storage Parameter	Units	2010	2017
System Gravimetric Capacity	$kg{\cdot}H_2/kg$	0.045	0.055
System Volumetric Capacity	$kg{\cdot}H_2/L$	0.028	0.040
Storage System Cost	$\$/kWh_{net}$	TBD	TBD
System Fill Time (for 5 kg H_2)	min	4.2	3.3
Minimum Full Flow Rate	(g/s)/kW	0.02	0.02
Min/Max Delivery Temperature	ºC	-40/85	-40/85
Min. Delivery Pressure (Fuel Cell)	Atm	5	5

TBD – to be determined

FY 2012 Accomplishments

- Task 1. System Modeling
  - Benchmarked the system modeling results in comparison to other hydrogen vehicle and storage analyses by Argonne National Lab (ANL) and identified the areas of differing assumptions or modeling approaches.
  - Enhanced the framework and validated the elements of the universal Hydrogen Storage Engineering Center of Excellence (HSECoE) Simulink® model with further refinement to the fuel cell model to ensure the waste heat and temperature polarization effects appropriately represent integration with the hydrogen storage system.

  - Completed a detailed failure mode and effects analysis (FMEA) for the adsorbent and chemical hydrogen storage systems with the respective design teams.
- Task 2. Cost Analysis
  - Supported the benchmarking and development of the HSECoE material-based hydrogen storage system cost projection models.
  - Decomposed the pressure vessel for the purpose of adsorbent system design trade-offs and sensitivity cost assessments.
  - Developed initial estimator tool and references to be utilized for cost manufacturing models with projection capability based on a set of key cost drivers.
- Task 3. Assessment/Optimization of Framework-Based Storage Media
  - Led the HSECoE adsorbent efforts as the system architect through the identification of research gaps, development of SMART (specific, measurable, attainable, relevant, timely) milestones, completed material selection, and coordinated team.
  - Validated powder MOF-5 isotherm model parameters at higher pressure (i.e. up to 200 bar), and at temperatures within the anticipated operating window.
  - Assessed the impact of thermal conductivity aids on principal hydrogen storage engineering properties (e.g., gravimetric capacity, gas permeability, crush strength, etc.).
  - Established relationship between density and gas transport through permeation and diffusivity.

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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. As present-day technologies are unlikely to attain established DOE targets for onboard hydrogen storage technologies, interest in materials-based approaches have garnered increasing attention. To hasten development of these 'hydride' materials, the DOE 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 remain largely unresolved.

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 system engineering technical elements with a focus on hydrogen storage system operating models which will result in a set of dynamic parameters for optimizing the storage system 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 operating strategies to facilitate potential cost reductions and manufacturing optimization for the storage system designs.

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

Below 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 Team focused on the key tasks that were necessary to ensure robustness in the models and system designs. First, Ford led a benchmarking analysis and facilitated a face-to-face design review at United States Council for Automotive Research with ANL and the HSECoE. The review provided an excellent assessment of the commonalities and differences between the ANL and HSECoE modeling assumptions for various material-based hydrogen storage systems. As part of the benchmarking analysis, an evaluation matrix was completed to compile the model results from ANL and HSECoE for each of the baseline systems as identified at the phase 1 milestone: sodium alanate, liquid ammonia borane, and adsorbent MOF-5. The matrix included a summary comparison to the DOE storage system technical targets, a system bill of material with weights and volumes, and a schematic for the system. The HSECoE architects were able to use the results of this effort to reconfirm and/or improve their model assumptions based on the independent comparative assessment. In addition, the modeling effort continued with further refinement in the fuel cell model to ensure the waste heat was correctly represented for the integration with the hydrogen storage systems. In particular, the idle and dynamic UA (overall heat transfer coefficient x heat transfer surface area) values in the fuel cell stack model were modified and verified against vehicle test data.

The modeling team also initiated a target sensitivity study to assess the effects of the storage system gravimetric and volumetric ratios on the vehicle fuel economy and driving range using the HSECoE framework. These results provide a quantitative correlation between the storage targets and vehicle effects which will guide the optimization of the system design. Another key accomplishment was the leading and completion of the FMEA for the adsorbent and chemical hydride systems. The HSECoE team recognized the FMEA as tool that can be used to evaluate risk, reduce failure modes, and guide the validation test plan. The functions within the FMEA were directly aligned with the DOE system targets and the effects along with the severity were completed based on prior original equipment manufacturer assessments. The result of the FMEA was the development of the risk priority number (RPN) which is the product of the severity, occurrence, and detection ratings. The RPN number allows the team to identify the key causes of high risk failures. Figure 1 provides a graphical Pareto summary of the adsorbent system RPN ratings. The team will utilize the FMEA to take action on the high RPN items and then reevaluate the rating after the action has been taken which should reduce the system risk and increase the probability of successfully achieving the desired functions. The same process was accomplished for the chemical hydrogen system based on liquid ammonia borane media.

Task 2. Cost Analysis

The Manufacturing and Cost Analysis Team during the past year developed the initial cost projections for the leading material-based storage systems within the HSECoE and conducted a cost workshop to evaluate the assumptions. As conducted with the system modeling review, an evaluation matrix was constructed to understand the key differences between the TIAX and HSECoE cost structure and assumptions. For the adsorbent system, a Pareto analysis

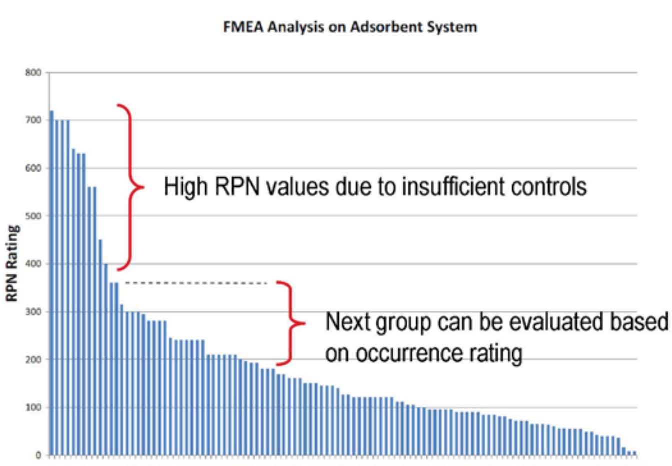

FIGURE 1. Adsorbent FMEA Pareto Chart of RPNs

identified the following key cost differences: pressure vessel fiber carbon fiber, MOF media, balance-of-plant design requirements and quantities. The overall cost results for the MOF system was similar at a cost of $3,019 ($16.18/kWh) for TIAX and $2,871 ($15.4/kWh) for HSECoE. As part of this cost task, a detailed break-down of the tank manufacturing process was formulated in a cost model based on input from Lincoln Composites and other tank suppliers. The activity-based process steps were developed for different tank types including the effects of the MOF integration into the tank. Material estimating models were also developed to assess the system effects from pressure and temperature for the adsorbent system operating condition trade-off studies.

Task 3. Sorbent Media Assessment & Optimization

System Architect Role: During the previous year, the HSECoE adsorbent system architect position transitioned to Don Siegel along with the additional responsibilities of coordinating the design and research priorities for the adsorbent team. In particular, SMART milestones and GANTT charts were developed for each HSECoE partner within the adsorbent team. The official material selection of MOF-5 for the HSECoE was completed and documented. The system design status was progressed using several face-to-face meetings, monthly teleconferences, and individualized modeling reviews.

Materials Engineering: We had previously collected several isotherms between 77 and 295 K and 0 to 100 bar for powder MOF-5, and fit this data to the Dubinin-Astakov model. Using this same approach, we have determined the isotherm parameters for a series of MOF-5 compacts with varying density and expanded natural graphite (ENG) content. In particular, we have collected adsorption isotherms at no less than three different temperatures including 77, 200, and 298 K for 0.3 or 0.5 gcm^{-3} compacts with 0, 5, or 10 wt% ENG. Here, we describe data for 0.3 gcm^{-3} MOF-5, however, the same process was applied for the determination of 0.5 gcm^{-3} MOF-5 data. The excess gravimetric hydrogen uptake (n_{ex}) for 0.3 gcm^{-3} compacted MOF-5 with 0, 5, or 10 wt% ENG additive as a function of temperature (77 to 295 K) and pressure (0 to 100 bar) is shown in Figure 2. The excess gravimetric capacity data for neat 0.3 gcm^{-3} MOF-5 at 77 K (Figure 2, top) shows a maximum uptake of approximately 6 wt% at 40 bar. This value is the same as the (uncompacted) powder MOF-5. The excess volumetric capacity based on the bulk density for the MOF-5 compact (ρ=0.30 gcm^{-3}) is 18 $g \cdot H_2/L$, 225% larger than for powder MOF-5 (ρ=0.13 gcm^{-3}). Therefore, densification of MOF-5 is indeed beneficial for improving the volumetric capacity of MOF-5 without significantly reducing gravimetric capacity. The addition of 5 or 10 wt% ENG (Figure 2, middle for the 5 wt% case) results in a small decrease in excess gravimetric capacity. In particular, the maximum excess adsorption values for 0.3 gcm^{-3} MOF-5 with 5 or 10 wt% ENG is 5.2 or

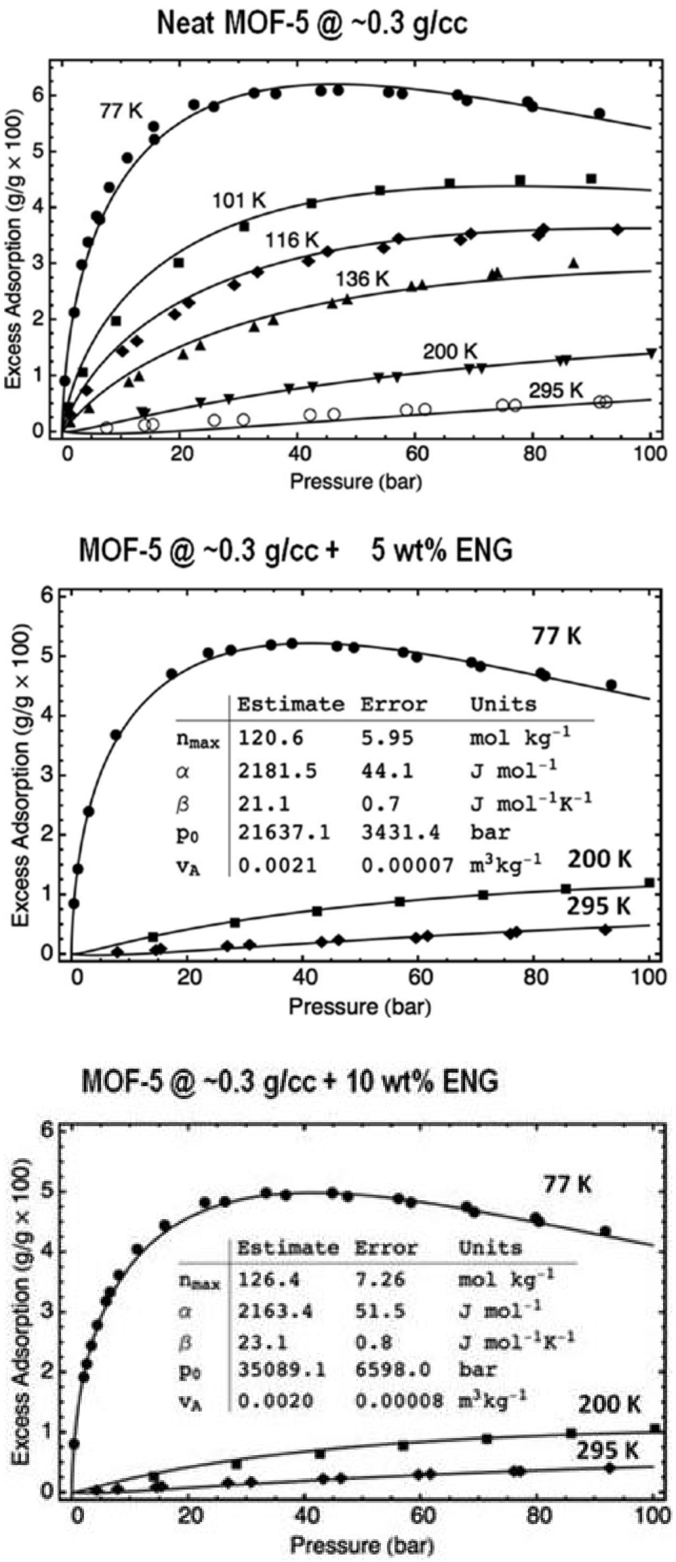

FIGURE 2. Excess hydrogen adsorption isotherms for compacted MOF-5 (ρ=0.3 gcm^{-3})

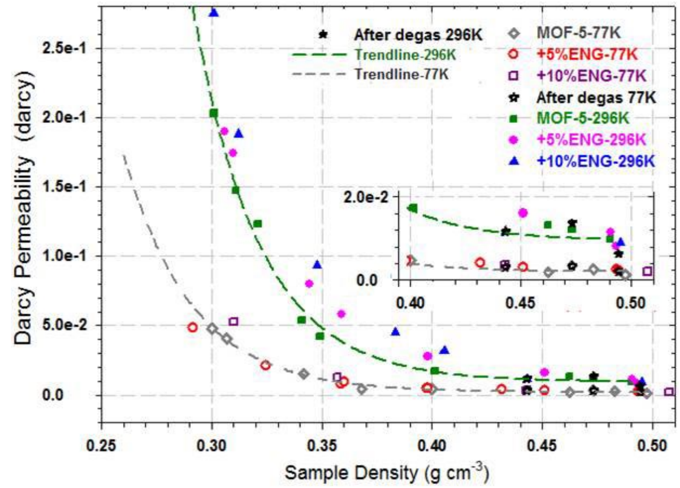

FIGURE 3. Darcy permeability of hydrogen versus sample density

5.0 wt%, a 13% or 17% decrease relative to the neat 0.3 gcm^{-3} (or powder) MOF-5. Despite this decrease in gravimetric capacity, we have previously shown that the thermal conductivity for 0.3 gcm^{-3} MOF-5 can be improved by 200% or 500% with the addition of 5 or 10 wt% ENG (Figure 2, bottom for 10 wt% ENG).

Permeation Measurements: Hydrogen permeation testing was conducted on MOF-5 pellets using the incompressible gas approach and the Darcy equation. The Darcy permeability (κ) of neat MOF-5, MOF-5 + 5 wt% ENG and MOF-5 + 10 wt% ENG samples was determined for various densities at 77 K and 296 K as shown in Figure 3. The results indicate the permeability decreases exponentially with the density of the pellet. In addition, the permeability measured at 296 K is higher than that measured at 77 K for the same sample. At 77 K, the permeability of neat MOF-5, MOF-5 + 5 wt% ENG, and MOF-5 + 10 wt% ENG samples are not significantly different.

Conclusions and Future Directions

- Task 1. System Modeling
  - Complete storage system and powerplant model validation and framework refinement based on component bench tests within the Phase 2 testing.
  - Provide the necessary system model results and optimization studies for the Phase 3 prototype design and scalability evaluation to correlate with the onboard design.
- Task 2. Cost Analysis
  - Develop complete set of material assumptions and predictive usage cost model for the critical components within the adsorbent and chemical hydride systems.

 - Establish comprehensive activity-based manufacturing cost models for the storage system materials and components with the HSECoE systems.
- Task 3. Sorbent Media Assessment and Optimization
 - Complete any required material property characterization such as high-pressure and/or low-temperature measurements to support modeling efforts.
 - Continue to assess impact of thermal conductivity aids on material properties and system attributes.
 - Investigate mechanical stability of compacts with respect to cycling and/or mechanical vibration along with subsequent effects on the material properties.
 - Develop tank assembly feasibility and MOF-5 integration concepts.
 - Study degradation effects of MOF-5 upon exposure to air/moisture, and identify the extent to which these can be reversed by various activation procedures.
 - Evaluate uptake robustness by analyzing pellet variations and impurities.
 - Select material and operating conditions for Phase 3 design and sub-scale testing.
 - Pursue experimental validation of sorbent bed and system models through neutron imaging and/or other experimental characterization efforts.

Special Recognitions & Awards/Patents Issued

Matthew Thornton, National Renewable Energy Laboratory; **Michael Veenstra**, Ford Motor Company; and **José Miguel Pasini**, United Technologies Research Center were recognized with a DOE Hydrogen and Fuel Cells Program R&D Award at the 2012 AMR for their outstanding contributions to the development of the integrated modeling framework for the Hydrogen Storage Engineering Center of Excellence (HSECoE).

FY 2012 Publications/Presentations

1. J.J. Purewal, D. Liu, J. Yang, A. Sudik, D.J. Siegel, S. Maurer, U. Müller, "Increased volumetric hydrogen uptake of MOF-5 by powder densification," International Journal of Hydrogen Energy, v 37, n 3, p 2723-2727, February 2012.

2. J.M. Pasini, B. Van Hassel, D. Mosher, and M. Veenstra, "System modeling methodology and analyses for materials-based hydrogen storage," International Journal of Hydrogen Energy, v 37, n 3, p 2874-2884, February 2012.

3. D. Liu, J. Purewal, J. Yang, A. Sudik, S. Maurer, U. Mueller, J. Ni, D. Siegel, "MOF-5 Composites Exhibiting Improved Thermal Conductivity", International Journal of Hydrogen Energy, v 37, n 7, p 6109-6117, April 2012.

4. M. Thornton, M. Veenstra, JM. Pasini, "Development of a Vehicle Level Simulation Model for Evaluating the Trade-off between Various Advanced On-board Hydrogen Storage Technologies for Fuel Cell Vehicles", 2012 SAE World Congress, April 2012.

5. M. Veenstra, Ford/BASF/UM "Activities in Support of the Hydrogen Storage Engineering Center of Excellence," 2012 DOE Hydrogen Program Annual Merit Review Meeting, Arlington VA, May 2012.

6. D.J. Siegel, "Development of an Advanced Hydrogen Storage System Based on Adsorbent Media," 2012 World Hydrogen Energy Conference, June 2012, Toronto, Canada.

7. 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, submitted for final review.

8. 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, 2012, submitted for review.

9. Justin Purewal, Dongan Liu, Andrea Sudik, Stefan Maurer, Ulrich Mueller, Don Siegel. "Improved Hydrogen Storage and Thermal Conductivity in High-density MOF-5 Composites". 2012 MRS Spring Meeting & Exhibit- Symposium P: Advanced Materials and Nanoframeworks for Hydrogen Storage and Carbon Capture, April 2012, San Francisco, California.