IV.B.2 Ford/BASF SE/UM Activities in Support of the Hydrogen Storage Engineering Center of Excellence

Michael Veenstra (Primary Contact, Ford), Justin Purewal (Ford), Jun Yang (Ford), Chunchuan Xu (Ford), Donald Siegel (UM), Yang Ming (UM), Manuela Gaab (BASF SE), Lena Arnold (BASF SE), and Ulrich Müller (BASF SE)

Ford Motor Company
1201 Village Road
Dearborn, MI 48124
Phone: (313) 322-3148
Email: mveenstr@ford.com

DOE Managers

Jesse Adams
Phone: (720) 356-1421
Email: Jesse.Adams@ee.doe.gov

Ned Stetson
Phone: (202) 586-9995
Email: Ned.Stetson@ee.doe.gov

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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 Objective

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 power plant
- (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) 2015 Objectives

The project focus during FY 2015 was to complete the following objectives.

- 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%
- Complete the failure mode and effects analysis (FMEA) associated with real-world operating conditions for a MOF-5-based system, for both HexCell and modular adsorbent tank insert (MATI) concepts based on the Phase 3 test results; report on the ability to reduce the risk priority numbers (RPN) from the Phase 2 peak/mean and identify key failure modes
- Update the cryo-adsorbent system model with Phase 3 performance data, integrate into the framework; document and release models to the public
- Explore approaches to optimize MOF-5 engineering properties, such as thermal conductivity and compaction effects

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)
(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 2020 and ultimate hydrogen storage targets, shown in Table 1. As a status based on the cooperative analysis within the Hydrogen Storage Engineering Center of Excellence (HSECoE), the current adsorbent systems are also shown in Table 1 based on powder and compacted MOF-5.

TABLE 1. Technical Targets and Current Adsorbent Systems

Storage Parameter	Units	DOE 2020 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	0.035
System Volumetric Capacity	kg·H_2/L	0.040	0.070	0.0185	0.0213
Storage System Cost	\$/kWh_{net}	10	8	14.5	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	ºC	-40/85	-40/85	-40/85	-40/85
Min. Delivery Pressure (Fuel Cell)	atm	5	5	5	5

FY 2015 Accomplishments

- Completed impurity gas cycle tests that indicate low or no degradation from the exposure
- Updated FMEA action items and reduced the RPN from Phase 2 values
- Supported the Simulink framework release and model testing through development in the modeling group
- Coordinated adsorbent system design activities within the HSECoE as the System Architect
- Provided an original equipment manufacturer perspective and outlook for the development of the adsorbent system
- Demonstrated improvement in puck density results using filtering and other techniques
- Developed alternative materials and approaches to increase thermal conductivity beyond expanded natural graphite (ENG) mixtures

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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 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, a significant amount of 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 conducted impurity gas cycling degradation testing and refined the failure modes and effects analysis for the adsorbent storage system, and further explored approaches for optimization of MOF-5 adsorbent media using various novel compaction and thermal conductivity approaches. Additional details are provided in the following section.

RESULTS

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

Impurity Gas Cycling Degradation Testing

The robustness of adsorbents with respect to repeated exposure to impurities in the hydrogen gas stream is an important performance metric for hydrogen storage applications. To meet the 2015 objective, we completed a comprehensive series of impurity-induced degradation tests using MOF-5 as the test material. We studied contaminant types and levels that were consistent with the SAE J2719 standard, using an extrinsic pressure cycling test method analogous to the actual operational cycles of a cryo-adsorption hydrogen storage system (see Figure 1). The objective required the MOF-5 capacity loss after 300 adsorption/desorption cycles with impure hydrogen gas to not degrade below 10%.

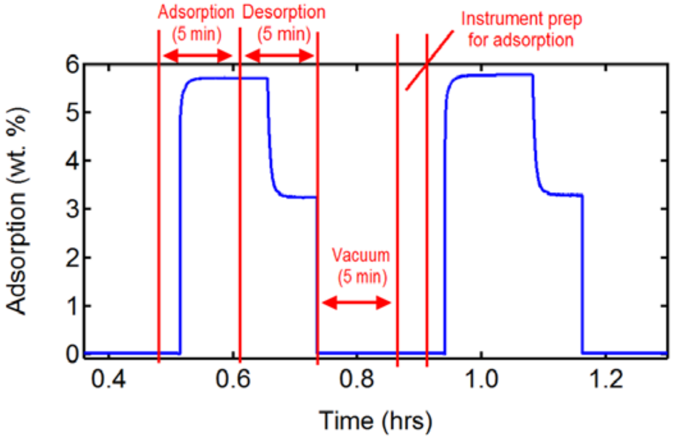


FIGURE 1. Test procedure used for pressure cycling of the impurity mixture test gas with a pressure swing during a single cycle depicted

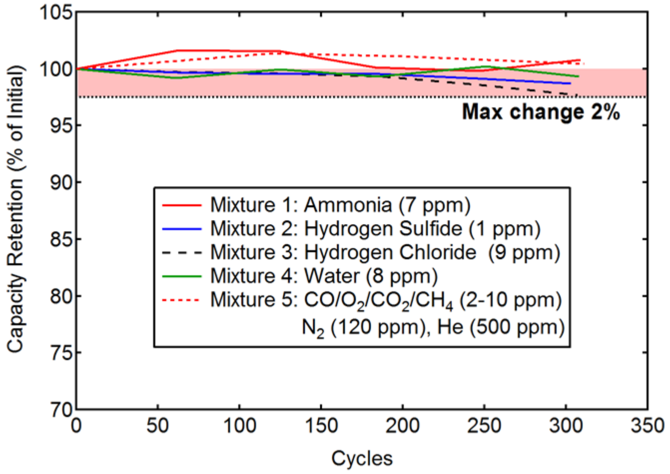


FIGURE 2. Summary of MOF-5 hydrogen storage capacity at 77 K during pressure cycling with impurity gas mixtures

Based on the SAE J2719 gas quality requirement for fueling stations, the following mixtures were independently cycled to analyze the effect of each impurity (1) ammonia (NH_3) at 7 ppm; (2) hydrogen sulfide (H_2S) at 1 ppm; (3) hydrogen chloride (HCl) at 9 ppm; (4) water (H_2O) at 8 ppm; and (5) carbon monoxide (CO) at 2 ppm, carbon dioxide (CO_2) at 6 ppm, methane (CH_4) at 8 ppm; oxygen (O_2) at 10 ppm, nitrogen (N_2) at 120 ppm, helium (He) at 500 ppm. The majority of these levels exceed the impurity limits defined in J2719 due to ability to qualify the concentration which results in a more stringent test of MOF-5 robustness. The impact on MOF-5 capacity was evaluated by measuring isotherms at 60 cycle increments until the test achieved 300 cycles with the impurity mixture. Figure 2 provides a summary of the hydrogen capacity measured during pressure cycling tests for all five impurity gas mixtures. The hydrogen capacity retention is shown in terms of the maximum excess adsorption at 77 K as a percentage of the initial capacity measured at the beginning of the cycle testing (i.e., capacity at cycle 0). For all five of the impurity gases tested, the capacity retention met the objective with a negligible change of only 2% after 300 cycles.

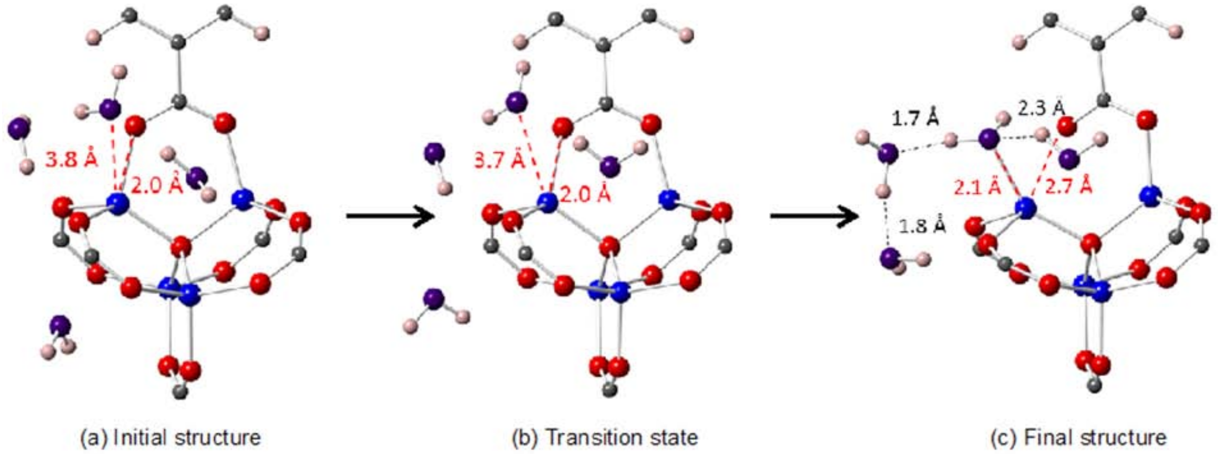
In addition, we also tested the practical consideration of the MOF being exposed to hydrogen fuel impurities for an extended period of time (1 week) and at higher storage temperature of 25°C. The test exposed MOF-5 powders under hydrogen gas with single impurity of 1 ppm H_2S and 8 ppm H_2O respectively with negligible change in the excess hydrogen adsorption isotherm, X-ray diffraction and Fourier transform infrared spectrum. We also further studied the impact of humid air exposure on MOF-5 properties and determined for humidity levels below ~50% threshold only minor degradation is observed for exposure times up to several hours, suggesting that MOF-5 is more stable than generally assumed under moderately humid conditions. In contrast, irreversible degradation occurs in a matter of minutes for exposures above the 50% threshold. In order to understand this mechanism, we used van der Waals-augmented density functional theory and transition state finding techniques to predict the thermodynamics and kinetics of water adsorption/insertion into the MOF-5 (see Figure 3). The calculations suggest that the thermodynamics of MOF hydrolysis are coverage dependent; water insertion into the framework becomes exothermic only after a sufficient number of H_2O molecules are adsorbed on a Zn-O cluster.

Failure Modes and Effects Analysis (FMEA)

As part of the 2015 objectives, the FMEA ratings were modified based on the HSECoE Phase 3 activities by the adsorbent team. Some of the key actions that facilitated the reduction in the RPN include the following.

- Completed testing to reduce occurrence ratings associated with hydrogen impurity concerns
- Assessed tank robustness with adsorbent material and cryogenic operating conditions
- Conducted thermal management evaluation testing to assess performance in adsorbent bed
- Performed system testing to assess material variability and effects of non-homogenous bed

The design verification plan updates from the key organizations involved in the testing—Université du Québec à Trois-Rivières, Oregon State University, Savannah River National Laboratory, United Technologies Research Center, Hexagon Lincoln, and Ford—were incorporated into the FMEA modified occurrence and detection ratings. The result achieved the 2015 objective by reducing the Phase 2 RPN mean from 513 to 288 and RPN mean from 157 to 114 based



(a) Initial structure (b) Transition state (c) Final structure

FIGURE 3. Water insertion process in MOF-5: (a) magnification of MOF-5 structure with 4 water molecules physically adsorbed near the Zn-O cluster; (b) transition state; (c) final MOF-5 structure containing a Zn-O bond broken via the insertion of a single water molecule

on the Phase 3 advancements of the original 109 potential failure modes identified by the team. The key outcome of the FMEA provides the potential top failure modes that should be considered in further research efforts for adsorbent storage systems. These top failure modes include: non-homogenous adsorbent bed, leaks at cold temperature, insulation performance, and degradation of the thermal management system over the system life.

Sorbent Media Optimization

The hydrogen storage media in the MATI system consists of densified "pucks" of MOF-5. These pucks have been compacted to a nominal density of 0.4 g/cc, which is two to three times the density of tapped powder. The best performance of these pucks will be achieved when the density variation is small. We utilized micro-computed tomography to characterize density variations (see Figure 4) and optimized the homogenous density of the puck with pre-meshed powders. The pucks had a diameter of 3 cm and height of 1 cm while mesh sized ranged from 2 mm to 0.8 mm.

ENG has been the additive included in MOF-5 compacts to enhance the thermal conduction. A potential drawback of ENG is the anisotropy of the heat conduction properties of MOF+ENG pucks formed by uniaxial compaction. As an alternative to ENG, we identified other thermal conductive additives such as graphene platelets which have a particle size that can completely coat the MOF-5 aggregates. The result was a formation of a continuous network of conductive carbon that improved the improved isotropic thermal conductivity in the axial direction by 62% in comparison to ENG at the same loading of 5%.

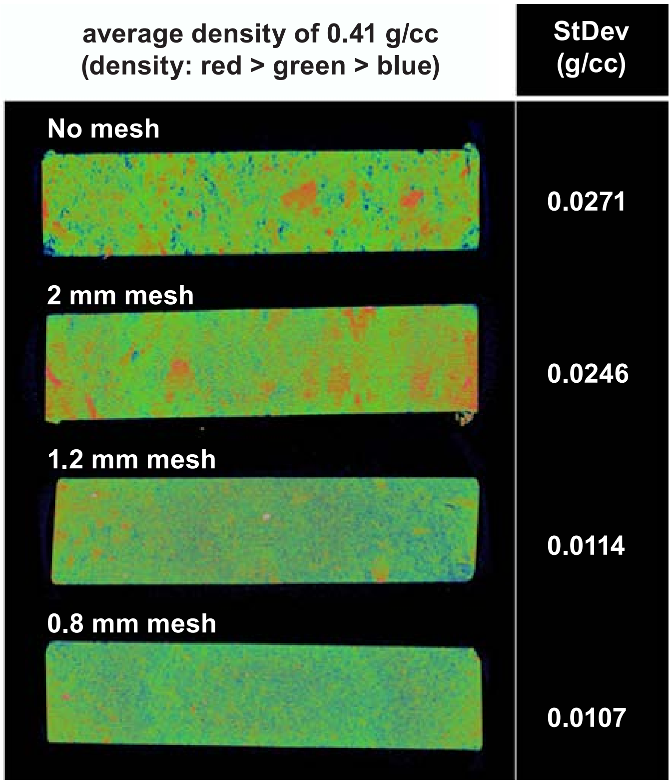


FIGURE 4. The micro CT images for pure MOF-5 pucks with pre-mesh powder prior to compaction along with standard deviation of density variation within the puck

CONCLUSIONS AND FUTURE DIRECTIONS

To ensure a successful conclusion of our HSECoE project, we plan to document our final results by completing the following publications:

- Stability of MOF-5 in a hydrogen gas environment with expected fueling station impurities
- Molecular scale water insertion mechanism in MOF-5
- Neutron and X-ray imaging studies of MOF-5 kinetics and tomography
- HSECoE Ford/UM/BASF final project report.

SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

1. R. Blaser, M. Veenstra, and C. Xu, "Adsorbent material with anisotropic layering," U.S. Patent 9 006 137, April 14, 2015.

FY 2015 PUBLICATIONS/PRESENTATIONS

1. Y. Ming, H. Chi, R. Blaser, C. Xu, J. Yang, M. Veenstra, M. Gaab, U. Müller, C. Uher, D.J. Siegel, "Anisotropic Thermal Transport in MOF-5 Composites," International Journal of Heat and Mass Transfer, 82, 250 (2015). DOI: 10.1016/j.ijheatmasstransfer.2014.11.053.

2. Y. Ming, J. Purewal, J. Yang, C. Xu, R. Soltis, J. Warner, M. Veenstra, M. Gaab, U. Muller, and D.J. Siegel, "Kinetic Stability of MOF-5 in Humid Environments: Impact of Powder Densification, Humidity Level, and Exposure Time," Langmuir, 2015, 31 (17), pp. 4988–4995, DOI: 10.1021/acs.langmuir.5b00833.

3. M. Veenstra. "Onboard Automotive Targets: An OEM Perspective," DOE Materials-based Hydrogen Storage Summit, January 27, 2015.

4. D.J. Siegel. "Engineering and Adsorbent-based Hydrogen Storage System: What Have We Learned?" DOE Materials-based Hydrogen Storage Summit, January 27, 2015.

5. M. Veenstra, "Ford/BASF/UM Activities in Support of the Hydrogen Storage Engineering Center of Excellence," 2015 DOE Hydrogen Program Annual Merit Review Meeting, Washington, June 9, 2015.