IV.D.1g 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:
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- University of Michigan (UM), Ann Arbor, MI

Project Start Date: February 1, 2009
Project End Date: January 31, 2014

Objectives

This project will address three of the key technical obstacles associated with development of a viable hydrogen storage system for automobile 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).

Technical Barriers

This project addresses the following technical barriers from the Storage section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(B) System Costs
(C) Efficiency
(D) Durability/Operability

Technical Targets

This project is conducting vehicle and system level modeling, cost analysis, and materials property assessment/optimization. Insights gained from these studies will be applied towards the engineering of hydrogen storage systems that meet the following DOE 2010 hydrogen storage targets. We will address the following technical targets from the Hydrogen Storage section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

- Specific energy: 1.5 kWh/kg
- Energy density: 0.9 kWh/L
- Durability (cycle life): 1,000 cycles
- Durability (min. delivery pressure from storage system): 5 bar
- Efficiency (well-to-powerplant): 60%

Accomplishments

Below is a list of accomplishments by-task:

- Task 1. Vehicle Parameter Modeling
  - Determined MATLAB/Simulink as the common platform for building fuel cell and storage system simulation models.
  - Provided key vehicle characteristics parameters to develop the next level of the hydrogen storage simulation model.
  - Initial model and analysis of fuel cell waste heat for initial assessment of target enthalpy.
  - Identified universal modeling framework and interaction assumptions between vehicle, powerplant, and hydrogen storage system models.
  - Evaluated and constructed baseline fuel cell model to support the interaction with the vehicle and hydrogen storage system model.
- Task 2. Manufacturing Cost Modeling
  - Established initial phase of the cost analysis through the pursuit of high level equivalent system studies for the development of a hydrogen storage component cost matrix.

  - Supported the manufacturing and cost analysis technology team in the evaluation of the initial cost assessments for the hydrogen storage systems.
  - Developed the approach using the cost matrix to decompose the key cost drivers for establishing cost sensitivity and trade-offs.
- Task 3. Assessment of Framework-Based Hydrogen Storage Media
  - Completed property screening (e.g. hydrogen capacity, surface area, and pore volume) of five prominent framework powders: MOF-5, MOF-177, IRMOF-8, ZIF-8, HKUST-1.
  - Collected and compiled all requisite materials engineering data for Basolite Z-100H, the semi-commercial version of MOF-5 synthesized by BASF. These include: Dubinin-Astakov (D-A) isotherm parameters, thermal properties (e.g. thermal conductivity, heat capacity, etc.), and bulk properties (e.g., bulk density, specific surface area, etc.).
  - Designed two preliminary sub-scale hydrogen storage modules to be used for framework material assessment and validation of optimized framework concepts.
  - Developed an understanding of, and developed a new measurement protocol which minimizes temperature variation during hydrogen storage experiments at cryogenic temperatures. This allows for more reliable hydrogen capacity measurements and, as a consequence, improved parameterization of adsorption models from experimental data.

Introduction

Widespread adoption of hydrogen as a vehicular fuel depends critically on the development of low-cost, on-board hydrogen storage technologies capable of achieving high energy densities and fast kinetics for hydrogen uptake and release. As present-day technologies -- which rely on physical storage methods such as pressurization or liquefaction -- are unlikely to attain established DOE targets, interest in materials-based approaches for storing hydrogen have garnered increasing attention. To hasten development of these 'hydride' materials, the DOE has established three Centers of Excellence for materials-based hydrogen storage research as part of a "Grand Challenge" to the scientific community. While the Centers have made substantial progress in developing new storage materials, significant challenges associated with the engineering of the storage system around a candidate storage material remain largely unresolved.

Approach

As a partner in the Hydrogen Storage Engineering Center of Excellence (HSECoE), Ford is conducting a multi-faceted research project that addresses three of the key engineering challenges associated with the development of materials-based hydrogen storage systems.

First (Task 1), drawing on our extensive expertise in the engineering of fuel cell (FC) and H_2-internal combustion engine (ICE) vehicles, we are evaluating and developing system engineering technical elements with a focus on hydrogen storage system operating parameters. This effort will result in a set of dynamic operating parameters and a high-level system model describing the interaction of the fuel storage system with the FC (or H_2-ICE) power plant.

Second (Task 2), we are leveraging the unique capabilities of the "Ford/MIT cost model" to develop and perform hydrogen storage manufacturing cost analyses for various candidate system configurations and operating strategies. This analysis will facilitate a technology roadmap for potential cost reductions and manufacturing optimization, while providing important feedback to Go/No-Go decisions on prototype design and construction.

Third (Task 3), we are evaluating and optimizing the "effective engineering properties" of an important class of sorbent materials (metal organic frameworks [MOFs] and other framework-like materials) in order to devise improved packing and processing strategies for their use in a systems context. Various mechanical processing routes are being examined (ranging from powders to pelletization to extrusion) in an effort to simultaneously maximize packing density, heat and mass transfer, and hydrogen uptake characteristics.

This work is expected to impact the broader goals for the DOE and FreedomCAR, leading to a significant advance in the engineering of materials-based hydrogen storage systems, refinement in our understanding of the performance targets of hydride materials, and ultimately, the development of commercially-viable hydrogen storage systems.

Results

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

Task 1. Vehicle Parameter Modeling

The Integrated Power Plant/Storage System Modeling Technology Area modeling approach focused on a MATLAB/Simulink platform with a common structure to assist in the exchangeability and interaction

of models within the Center. A modeling interface matrix was further refined and utilized in constructing the top-level HSECoE Simulink model structure (Figure 1).

In support of the HSECoE modeling structure, a fuel cell model was developed to provide the linkage between the vehicle model and hydrogen storage model. The fuel cell model as indicated by the interface matrix for the translation of the vehicle power demand to the hydrogen storage flow requirement. It is also needed to characterize the waste heat available for the hydrogen storage system to avoid the need for external heating devices. The original FC model in the Hydrogen Storage SIMulator (HSSIM) vehicle model was based on a simple polarization curve from Kartha and Grimes in *Fuel Cells: Energy Conversion For The Next Century*, Physics Today (1994). The desire of the team was to refine the FC model to allow for ambient temperature effects and potentially pressure effects. Therefore, a search was conducted to assess available fuel cell models to be utilized in the Simulink framework. The FC performance equations developed by Stefanopoulou (et al. 2004) in *Control-oriented modeling and analysis for automotive fuel cell systems* had the desired thermal term and appeared appropriate for the initial phase of the model.

Task 2. Manufacturing Cost Modeling

The hydrogen storage manufacturing cost analysis is included in the Performance Analysis workstream. In particular, the Manufacturing and Cost Analysis Technology Team is being lead by M. Weimar from the Pacific Northwest National Laboratory. A benchmark study was conducted to assess hydrogen storage cost analysis approaches and progress a tool for decomposing the hydrogen storage system into critical elements. The cost modeling effort has evaluated the assumptions of the HSSIM vehicle modeling and approaches to integrate the cost analysis with the performance modeling, which result in consumer preferences based on both performance and cost. The integration assessment allows the HSECoE team to trade-off vehicle architectures (i.e. hybridization levels) and parameters to optimize the hydrogen storage characteristics.

The initial phase of the cost analysis was established through the pursuit of high-level equivalent system studies that support the development of a hydrogen storage component cost matrix. The draft and the approach of the component cost matrix were presented to the HSECoE partners that reinforced the need for the matrix to serve as a foundation for the system architects. The matrix would include the functions to scale the appropriate components. The team developed the cost strategy to provide the matrix of components and then to decompose the key cost drivers to establish cost sensitivity and trade-offs for the system architects.

Task 3. Assessment of Framework-Based Hydrogen Storage Media

As a first step we assessed several key properties a series of benchmark framework materials. This was conducted via a brief property screening study, wherein the hydrogen capacity, surface area, and pore volume data for the following powders were measured in our laboratory using a cryogenic Sievert's apparatus. The compounds studied included: Basolite Z100H (MOF-5), Basolite Z377 (MOF-177), Basolite Z200 (IRMOF-8), Basolite Z1200 (ZIF-8), Basolite C300 (HKUST-1).

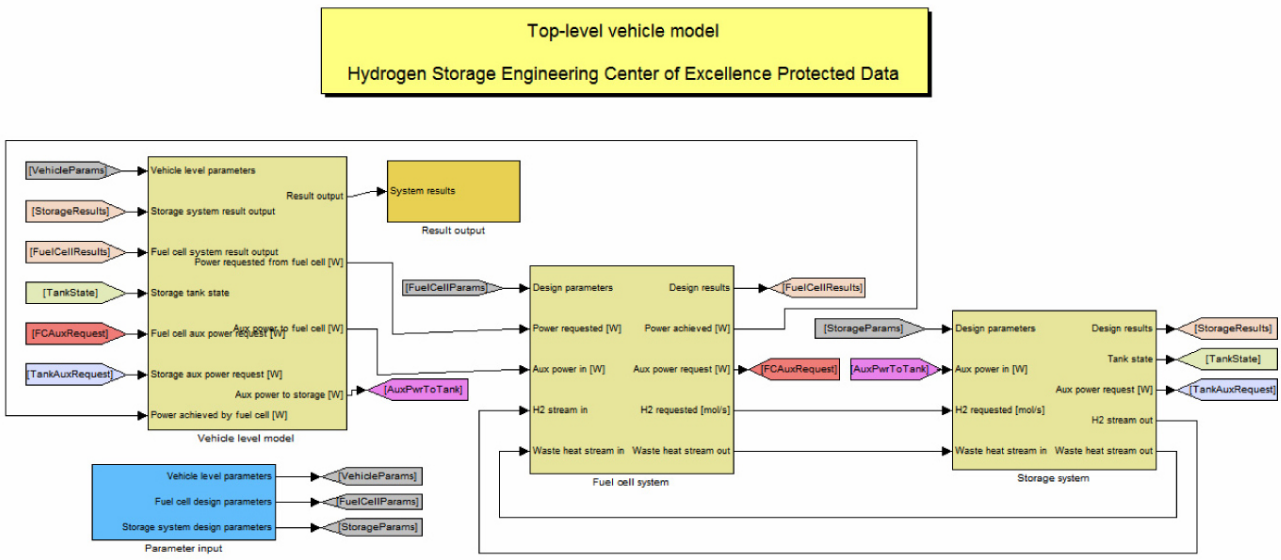


FIGURE 1. HSECoE High-Level Universal Simulink Model Structure and Interfaces

The data from these measurements are summarized in Figure 2.

The objective for this phase of our work is to gather existing literature data, and, as appropriate, collect new physical, thermal, and isotherm data to facilitate creation of a materials property "data set." The contents of the data set are important as they serve as inputs for the HSECoE's modeling activities. The three primary categories of the data set for an adsorbent material include: Dubinin-Astakov isotherm parameters, thermal properties (e.g. thermal conductivity, heat capacity, etc.), and bulk properties (e.g., bulk density, specific surface area, particle diameter, etc.). Subsequently, MOF-5 was selected by the Center as an initial framework material of interest and thus a complete set of its fundamental and engineering material properties is required. Our experiments were conducted using the semi-commercial form of MOF-5 (Basolite Z100H), synthesized by BASF.

Generation of the Dubinin-Astakov parameters for Basolite Z-100H requires collection of isotherms at several different temperatures (e.g., between -196°C and room temperature). Modification of Ford's existing sorption instrument (Sievert's apparatus) to include variable-temperature cryogenic capability was necessary. Upon instrument validation, isotherm data for Basolite Z-100H was collected at five different temperatures, -196°, -190°, -178°, -167°, and -151°C, toward determination of the desired Dubinin-Astakov parameters which fully describe an isotherm and can be used for material modeling. These data are shown in Figure 3 as the filled data points.

A modified version of the Dubinin-Astakov equation (Equation 1) [1], was subsequently used as the model for a non-linear regression analysis on the corrected empirical data.

$$n_{ex} = n_{max} \exp[-[\frac{RT}{\alpha + \beta T}]^2 \ln^2(\frac{P_0}{P})] - \rho_g V_a \quad (1)$$

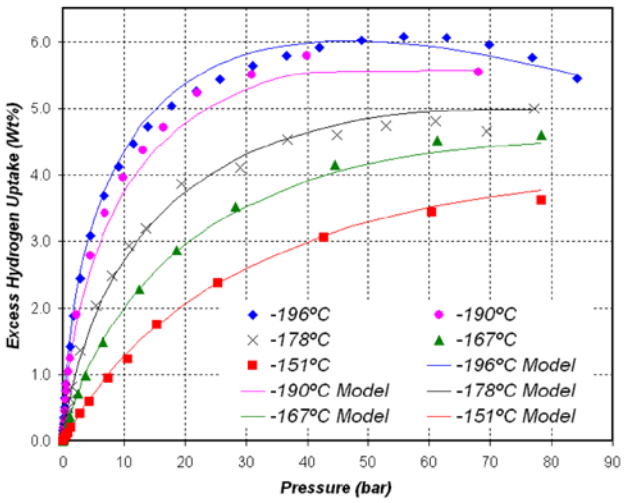
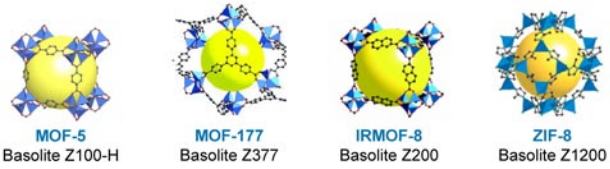


FIGURE 3. Modified Dubinin-Astakov model fit (*solid lines*) to experimental excess hydrogen adsorption isotherm (*symbols*) for Basolite Z-100H at -196°C (blue), -190°C (pink), -178°C (black), -167°C (green), and -151°C (red).

In particular, the empirical data from all five isotherms was simultaneously fit to the above model using five fitted parameters from Equation 1: n_{max} (max. uptake), α (enthalpic factor), β (entropic factor), ρ_g (gas phase density), and V_a (adsorbed volume). The values for these parameters, which result in a minimization of the error between model and observed data, are given in Table 1.

Based on these values, the standard error between model and experimental data is 0.46 mol/kg or 0.094 wt%. The residual squared value is 0.998. Using these parameters enables one to determine excess uptake at a variety of temperatures and pressures of interest. Additionally, absolute (or total) uptake and heat



Material	Langmuir Surface Area (m^2/g)	Measured Max Excess Uptake (Wt·% H_2)	Literature Max Excess Uptake (Wt ·% H_2)	Measured Max Excess Uptake (g·H_2/L)	Measured Absolute Uptake @ 70 bar (Wt·%H_2) | (g·H_2/L)	DOE Targets (2015)
MOF-177	**5000**	**7.0**	**7.0-7.2**	**30 (SC) 13 (LP)**	**12.0 | 51 (SC) , 22 (LP)**	**Volumetric**
MOF-5	**3500**	**6.0**	**5.2-6.0**	**37 (SC) 6 (LP)**	**10.0 | 62 (SC), 10 (LP)**	**40 g·H_2/L**
IRMOF-8	**1700**	**3.3**	**3.5**	**15 (SC) 10 (LP)**	**4.3 | 19 (SC), 13 (LP)**	**Gravimetric**
ZIF-8	**1650**	**2.7**	**3.0-3.3**	**25 (SC) 6 (LP)**	**4.1 | 38 (SC), 9 (LP)**	**5.5 wt%·H_2**

'SC' and 'LP' indicate whether the volumetric capacities are based on single crystal (SC) or loose powder (LP) density, These values help by providing upper and lower bounds to volumetric uptake.

FIGURE 2. Baseline Property Data for Select Framework Materials

TABLE 1. Modified Dubinin-Astakov Isotherm Property Data for Basolite Z-100H (MOF-5)

Modified D.-A. Isotherm Parameters	
α (Jmol^{-1})	2490
β (Jmol^{-1}K^{-1})	10.5
n_{max} (wt%)	16.61
P_o (MPa)	296
V_a (ml g^{-1})	1.75

of adsorption behavior can also be calculated. For example, based on the Basolite Z-100H parameters in Table 1 an absolute uptake of approximately 10 wt% is projected at 70 bar and -196ºC. This finalized thermal, bulk property, and Dubinin-Astakov data for powder Basolite Z100H were submitted and distributed to the HSECoE. This established process of compiling and generating all relevant data (i.e. "data set") for a given framework will be extended to future frameworks of interested as well as extension to compacted/processed forms of a given framework of interest.

Lastly, we have initiated and completed the design work for two preliminary hydrogen storage modules which are necessary for anticipated Phase II framework materials testing. The requirements and specifications for both designs were formulated based on a variety of criteria including von Mises yield stresses at the operating temperatures and pressures, material compatibilities, heat transfer, safety, and data acquisition.

Conclusions and Future Directions

- Task 1. Vehicle Parameter Modeling
  - Complete the integration of the FC stack waste heat model and enhance the FC polarization model at sub-zero temperatures with validation of empirical data.
  - Determine the appropriate integration of static parameters (i.e. cost, weight, volume) within the dynamic performance modeling framework.
  - Support the development of the vehicle and storage system modeling, including the implementation of the waste heat interaction, refinement of the weighting coefficients for the viability index, and confirming the vehicle characteristics parameters for current and projected future levels.
- Task 2. Manufacturing Cost Modeling
  - Support the completion of the hydrogen storage system component cost matrix for the system architects to use as a common reference.
  - Evaluate the key components in order to establish their cost functions in relation to the performance model variables.
  - Decompose the key components into their direct and indirect cost elements for the purpose of assessing cost drivers and opportunities.
- Task 3. Framework-Based Hydrogen Storage Media Properties
  - Continue to monitor and experimentally screen the properties of existing and newly discovered powder framework materials which show promise for hydrogen storage.
  - Pursue detailed densification studies of Basolite Z100H (and other framework materials as appropriate) which includes investigation of the impact of the following processing parameters on the resulting hydrogen storage properties: binder (and/or lubricant), compaction conditions, pellet and particle size, ancillary additives.
  - Continue development of lab-scale testing module including the assembly of the test-bench and data acquisition system.

FY 2010 Publications/Presentations

1. Hydrogen Storage Materials Research at Ford Motor Company, Andrea Sudik, Invited Presentation, Northwestern University Materials Science & Engineering Department Symposium, February 2010.

2. Hydrogen Storage Materials Research at Ford Motor Company, Andrea Sudik, Invited Presentation, Canadian Society for Chemistry Conference, June 2010.

3. Presentation at 2010 Hydrogen Program Annual Merit Review, A. Sudik and M. Veenstra, June 2010.

References

M. –A. Richard, P. Bénard, R. Chahine, *Adsorption,* **2009**, *15*, 43.