

## IV.C.10 Hydrogen Adsorbents with High Volumetric Density: New Materials and System Projections

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Contract Number: DE-EE0007046

Subcontractor:  
Ford Motor Company, Dearborn, MI

Project Start Date: August 1, 2015  
Project End Date: July 31, 2018

- Drawing from established MOF crystal structure databases, predict the hydrogen capacity of several thousand candidate MOFs computationally.
- Demonstrate experimentally at least one MOF with >90% of the projected surface area, >3,000 m<sup>2</sup>/g, and with a hydrogen capacity at least matching the MOF-5 baseline compound.

### 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

### Technical Targets

The outcomes of this project contribute to the optimization and assessment of hydrogen storage materials, and also provide input to models that project the performance of these materials at the system level. Insights gained from this study can be applied towards the development of materials that attempt to meet the DOE 2020 and ultimate hydrogen storage targets, which are summarized in Table 1. The ultimate success of this project rests upon developing MOFs that out-perform the baseline MOF-5 adsorbent. Therefore, Table 1 also summarizes the materials-level hydrogen capacity of single-crystal MOF-5 and compares against the best adsorbent identified by this project to-date, isoreticular metal organic framework (IRMOF)-20.

### Overall Objectives

- Demonstrate metal-organic frameworks (MOFs) that exhibit high volumetric and gravimetric hydrogen densities simultaneously, and that exceed the performance of the benchmark adsorbent, MOF-5, at cryogenic conditions.
- Project the performance of most promising compounds to the system level by parameterizing models developed by the Hydrogen Storage Engineering Center of Excellence (HSECoE).

### Fiscal Year (FY) 2016 Objectives

- Quantify the usable and total hydrogen capacity of the benchmark adsorbent, MOF-5.

### FY 2016 Accomplishments

- Characterized the hydrogen capacity of the benchmark adsorbent MOF-5 (on a usable and total basis) by performing air-free synthesis and hydrogen isotherm measurements.

**TABLE 1.** System-Level Technical Targets Compared to Materials-Level Performance of the Baseline MOF-5 Adsorbent and the Highest-Performing MOF Identified by this Project To-Date, IRMOF-20. Total capacities are reported at 77 K and 100 bar. Usable capacities are determined assuming an isothermal pressure swing at 77 K between 100 bar and 5 bar. All materials-level capacities are based on single-crystal densities.

Storage Parameter	Units	DOE 2020 Target (System Level, Usable)	DOE Ultimate Target (System Level, Usable)	MOF-5 Baseline (Materials Level, Total/Usable)	Project Status: IRMOF-20 (Materials Level, Total/Usable)
Gravimetric Capacity	wt%	5.5	7.5	8.0/4.5	9.3/5.7
Volumetric Capacity	g-H <sub>2</sub> /L	40	70	53/31	52/33

- Screened more than 2,000 known MOFs using Grand Canonical Monte Carlo and semi-empirical computational methods; identified several promising compounds.
- Synthesized and characterized seven candidate MOFs.
- Demonstrated IRMOF-20 as capable of surpassing the usable capacity of MOF-5.



## INTRODUCTION

A high-capacity, low-cost method for storing hydrogen remains one of the primary barriers to the widespread commercialization of fuel cell vehicles. Although many storage technologies have been proposed, storage via adsorption remains one of the more promising approaches due to its fast kinetics, facile reversibility, and high gravimetric densities. Adsorbents struggle, however, in two key measures: volumetric density and operating temperature. For example, it is well known that high surface area adsorbents such as MOFs can achieve high gravimetric densities. Nevertheless, high volumetric densities are uncommon in these materials, and it has recently been suggested that total volumetric density and gravimetric density are inversely related beyond a threshold surface area [1]. In the case of operating temperatures, the relatively weak enthalpy of H<sub>2</sub> adsorption implies that high hydrogen densities are possible only at cryogenic temperatures.

Although an ideal adsorbent would overcome both of these shortcomings, it is important to recognize that volumetric density and operating temperature are controlled by different factors: the former depends upon the adsorbent's *structure*, whereas the latter depends on the *chemistry* of the H<sub>2</sub>-adsorbent bond. Therefore, distinct approaches are needed to address these independent issues. While some effort has previously been devoted to increasing DH (e.g., MOFs with open metal sites), attempts to increase volumetric densities have received much less attention. This is unfortunate, as analysis by the HSECoE has indicated that vehicle range is highly sensitive to volumetric density. Consequently, the development of adsorbents that simultaneously achieve high volumetric and gravimetric hydrogen densities – while maintaining reversibility and fast kinetics – would constitute a significant advance. Moreover, these materials would serve as logical starting points for follow-on efforts aimed at increasing the operating temperature.

## APPROACH

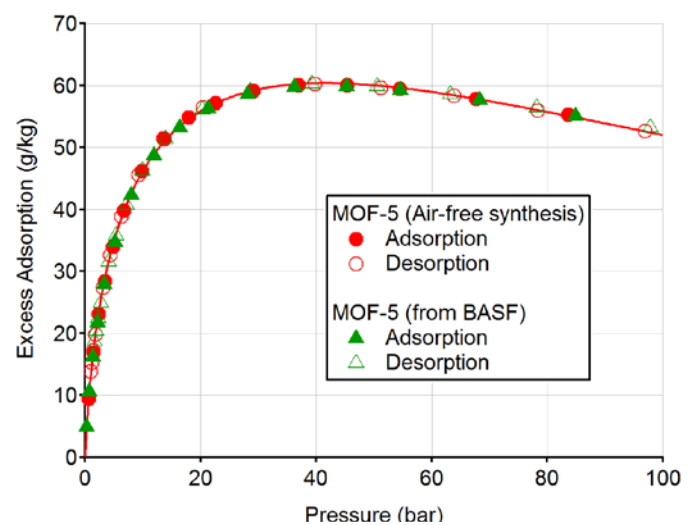
This project aims to circumvent the tradeoff between total volumetric and gravimetric hydrogen densities typical of most hydrogen adsorbents. This will be accomplished

by combining computational screening for promising compounds with experimental synthesis and measurement of hydrogen storage densities within those compounds. The ultimate goal is to demonstrate materials having balanced gravimetric and volumetric performance that can surpass the storage density of the benchmark compound, MOF-5. The performance of the most promising compounds will be projected to the system level by parameterizing system models developed by the HSECoE.

## RESULTS

As described above, a major milestone for this effort is to demonstrate MOFs whose hydrogen density surpasses that of MOF-5 in its optimal or “pristine” form (i.e., MOF-5 which has not been exposed to air, and from which all solvents and reactants have been removed). Synthesis efforts following the air-free procedure described by Kaye et al. [2] were performed to establish unambiguously the usable capacity of pristine MOF-5. Modifications to this protocol were also explored; nevertheless, the resulting materials performed identically. The surface area of the as-synthesized material, 3,512 m<sup>2</sup>/g, was found to be in very good agreement with our calculated value, 3,563 m<sup>2</sup>/g.

Figure 1 presents a comparison of the H<sub>2</sub> isotherms for as-synthesized MOF-5 and pre-commercial MOF-5 supplied by BASF. These measurements revealed that hydrogen uptake is essentially identical in both compounds. Table 2 tabulates the measured usable and total uptake in as-synthesized MOF-5 as a function of pressure. Assuming isothermal (T = 77 K) pressure swing operation between 100 bar and 5 bar, the usable capacity was measured to be 31.1 g H<sub>2</sub>/L and 4.5 wt%.



**FIGURE 1.** Measured excess H<sub>2</sub> isotherms in as-synthesized MOF-5 and in a pre-commercial version of MOF-5 supplied by BASF

**TABLE 2.** Total and usable hydrogen uptake in as-synthesized MOF-5 as a function of pressure

P (bar)	Total		Usable (P-swing)	
	Vol. (g/L)	Grav. (wt%)	Vol. (g/L)	Grav. (wt%)
5	22.2	3.5	-	-
35	44.4	6.8	22.2	3.3
50	47.8	7.3	25.6	3.8
100	53.3	8.0	31.1	4.5

Computational screening was performed to identify MOFs that could meet or exceed the performance of MOF-5. Figure 2 shows total and usable capacities for approximately 2,000 MOFs whose crystal structures were extracted from our own “Michigan MOF” database [1], from the CoRE database [3], and for MOFs suggested by chemical intuition. These predictions were based on Grand Canonical Monte Carlo calculations employing two different interatomic potentials: the so-called pseudo-FH model [4] and MGS model [5].

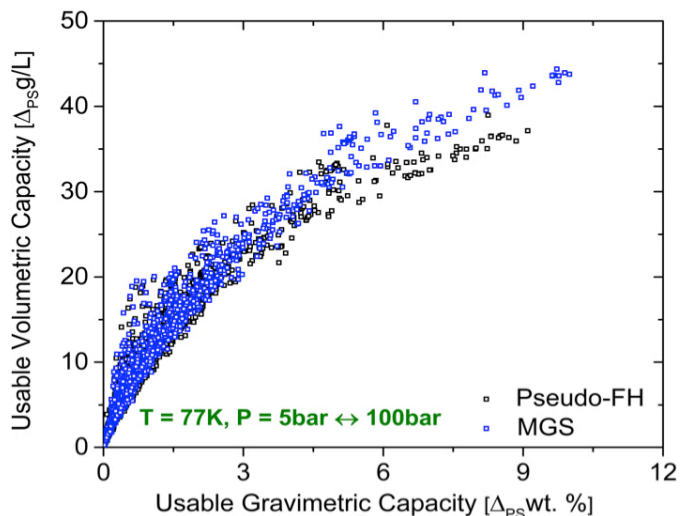
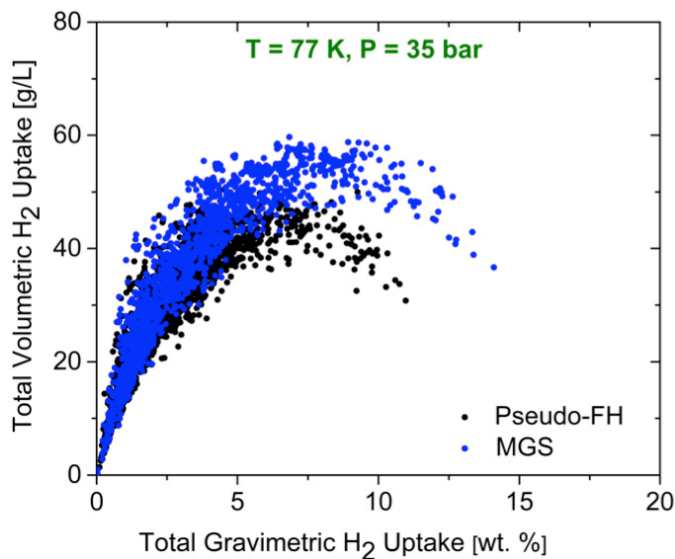
These calculations identified IRMOF-20 [6] as a promising, high-capacity compound. This compound was synthesized, and demonstrated a surface area of 4,073 m<sup>2</sup>/g. This value is in very good agreement with (i.e., within 94% of) the calculated surface area, 4,324 m<sup>2</sup>/g. Pressure-composition-temperature measurements were used to evaluate the gravimetric and volumetric capacity of IRMOF-20 at 77 K. Figure 3 illustrates the hydrogen isotherms for this compound, which are reported on a

total basis and assuming single crystal density. To place this performance in context, isotherms for MOF-5 are also plotted.

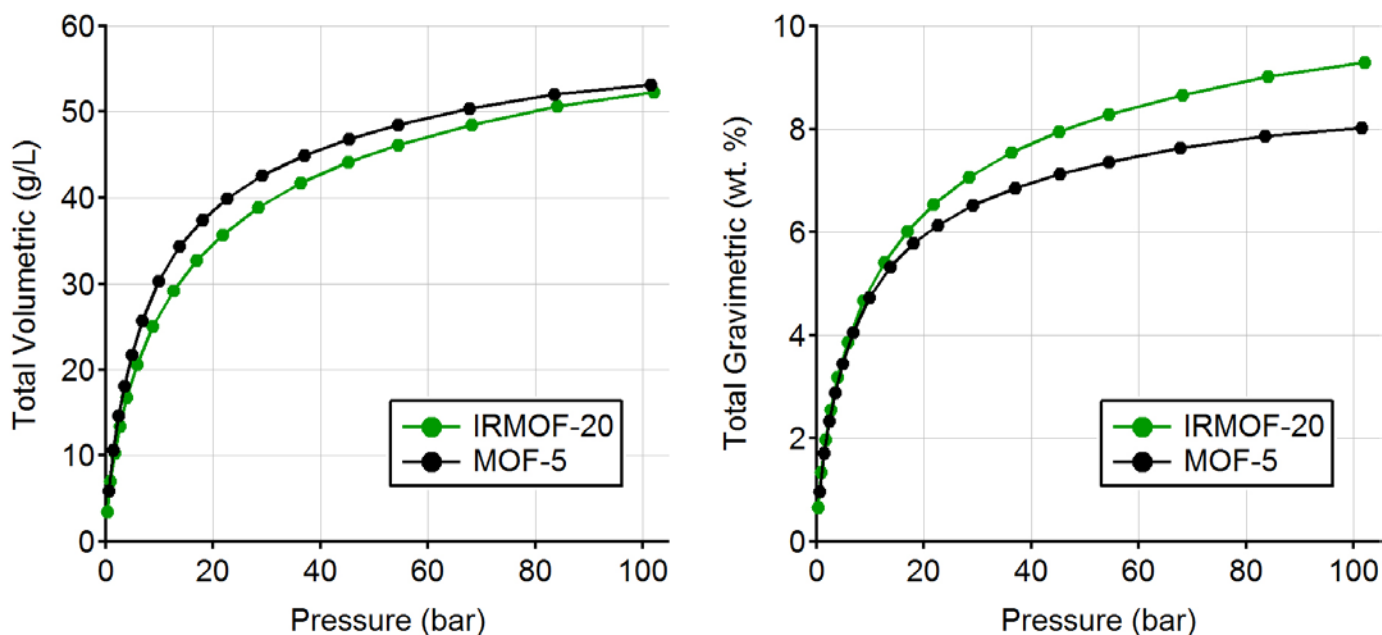
The isotherms show that the total gravimetric capacity of IRMOF-20 exceeds that of MOF-5 for all pressures measured (up to 100 bar). On the other hand, total volumetric performance is slightly lower for IRMOF-20 up to approximately 100 bar.

The measured total hydrogen capacities were converted into usable capacities assuming operation via an isothermal pressure swing at 77 K. The minimum pressure (“empty vessel”) was set to 5 bar, in accordance with the DOE targets. Three maximum “full vessel” pressures,  $P_{\max}$ , were examined: 35 bar, 50 bar, and 100 bar. The usable capacity of IRMOF-20 was measured to match or exceed that of MOF-5 for all values of  $P_{\max}$ . The HSECoE previously demonstrated MOF-5 based storage systems operating at  $P_{\max} = 100$  bar. Under these same conditions the usable, materials-only capacity of IRMOF-20 is 33.1 g H<sub>2</sub>/L and 5.7 wt%. These values are, respectively, 6% and 27% larger than the corresponding values for MOF-5 (Table 2).

In addition to MOF-5 and IRMOF-20, six additional MOFs were synthesized and characterized with regard to their hydrogen capacity. Of these, the compounds with Cambridge Structure Database identifiers SUKYNON, EPOTAF, and DIDDOK, exhibited surface areas far below the calculated values. This was attributed to pore collapse and/or incomplete activation. The other three compounds included UMCM-4 and two MOF-5 variants with modified linkers. Although these compounds did achieve reasonably



**FIGURE 2.** Total (left) and usable (right) capacities predicted by Grand Canonical Monte Carlo for approximately 2,000 MOFs. Crystal structures are primarily drawn from the UM and CoRE MOF databases; MOFs suggested by intuition are shown with red data points. Two forms of the H<sub>2</sub>-MOF interatomic potential (Pseudo-FH and MGS) are examined. The performance of MOF-5 is depicted with a blue symbol. All calculations assume T = 77 K and single crystal MOF densities.



**FIGURE 3.** Total measured volumetric (left) and gravimetric (right) hydrogen capacity of IRMOF-20 compared to MOF-5

high surface areas, they did not surpass MOF-5 in both volumetric and gravimetric hydrogen uptake.

## CONCLUSIONS AND FUTURE DIRECTIONS

Computational screening and experimental synthesis/ characterization revealed IRMOF-20 as a hydrogen adsorbent which can surpass the usable capacity of the benchmark compound MOF-5 under cryogenic conditions. Future directions for this effort will focus on screening additional compounds with the goal of identifying MOFs that can surpass the performance of MOF-5 by 15%.

## FY 2016 PUBLICATIONS/PRESENTATIONS

1. D.J. Siegel, "Hydrogen Adsorbents with High Volumetric Density: New Materials and System Projections," 2016 DOE Hydrogen and Fuel Cells Program Annual Merit Review Meeting, Washington, June 8, 2016.

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