

## IV.C.15 Hydrogen Adsorbents with High Volumetric Density: New Materials and System Projections

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- Demonstrate at least one MOF with hydrogen capacities exceeding baseline MOF-5 by 15%.

### 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 MOF-5 and compares against the best adsorbents identified by this project to-date, IRMOF-20 and SNU-70.

### FY 2017 Accomplishments

- Demonstrated that IRMOF-20 surpasses the usable capacity of MOF-5 and therefore meets the project's first go/no-go milestone.
- Nearly 500,000 MOFs were assessed computationally; more than 2,000 compounds identified that can surpass MOF-5 by 15%.
- Several promising MOFs were synthesized and evaluated with respect to their H<sub>2</sub> uptake; demonstrated that the

### 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) 2017 Objectives

- Estimate system level performance of selected high-capacity MOFs using HSECoE system models parameterized from isotherm measurements.

**TABLE 1.** System-level technical targets compared to materials-level performance of the baseline MOF-5 adsorbent and the highest-performing MOFs identified by this project to date, IRMOF-20 and SNU-70. 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)	Project Status: SNU-70 (materials level, total/usable)
Gravimetric Capacity	wt%	4.5	6.5	8.0 / 4.5	9.3 / 5.7	10.7 / 7.3
Volumetric Capacity	g-H <sub>2</sub> /L	30	50	53 / 31	52 / 33	49 / 34

usable volumetric capacity of SNU-70 exceed that of IRMOF-20.

- Estimated system level performance of IRMOF-20 and DUT-23(Co) using HSECoE system models parameterized from isotherm measurements.



## 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 interaction. Therefore, distinct approaches are needed to address these independent issues. While some effort has previously been devoted to increasing  $\Delta H$  (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 focus of this effort is to demonstrate MOFs whose hydrogen density surpass 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 solvent/reactants have been removed). Toward this goal, our FY 2016 effort demonstrated IRMOF-20, a MOF whose capacities slightly surpassed that of MOF-5 (see Table 1). In FY 2017 we aimed to improve performance further, by identifying and demonstrating MOFs that surpass the usable capacity of MOF-5 by 15%.

The first step in this search involved an expansion of our computational screening protocol. In FY 2016 approximately 2,000 known MOFs were screened for their usable H<sub>2</sub> capacities. In FY 2017 we dramatically enlarged our catalogue of screened compounds to include 5,109 known MOFs and approximately 464,600 hypothetical compounds. In total, 469,741 MOFs were examined from seven databases. A summary of this screening effort is provided in Table 2. Importantly, more than 2,000 MOFs were identified whose capacities can theoretically surpass that of MOF-5 by 15%.

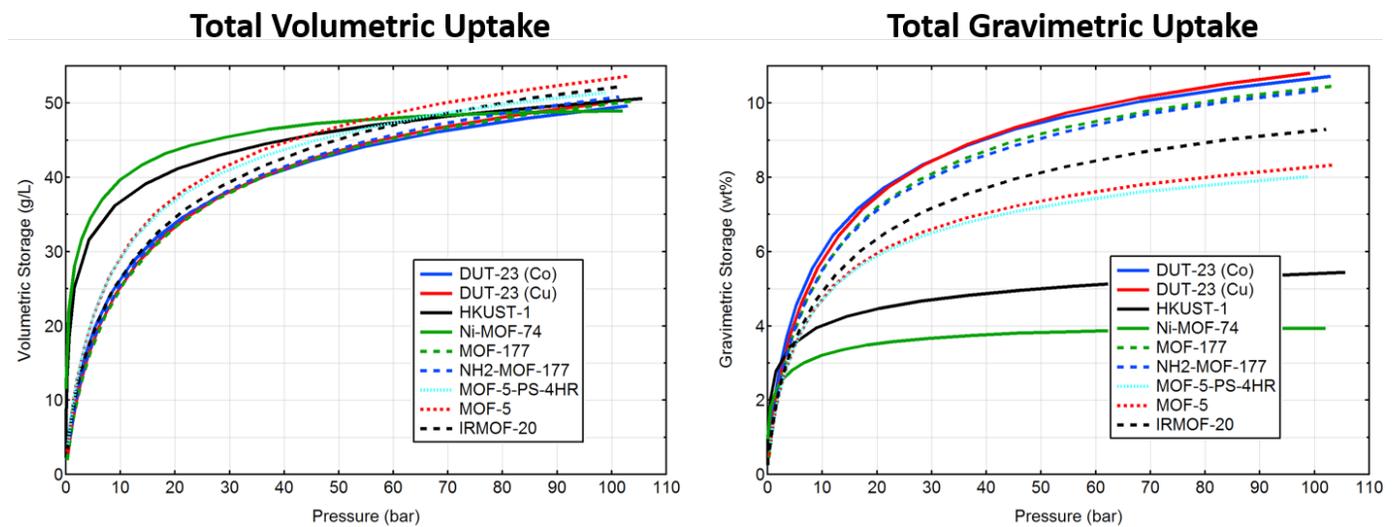
Based on these computational predictions, several MOFs were examined experimentally. A partial list of compounds evaluated includes: ZJU-32 [8], MOF-143 [9], DUT-12 [10], DUT-10(Co) [10], MOF-177-NH<sub>2</sub> [11], DUT-23(Co) [12], DUT-23(Cu) [12], ZELROZ [13], EDUVOO [14], GAGZEV [15,16], and SNU-70. Hydrogen uptake isotherms for a subset of these compounds is shown in Figure 1 (based on single crystal densities). Based on these calculations and measurements, it was demonstrated that SNU-70 can out-perform both MOF-5 and IRMOF-20 (last year's top-performing compound). A list of the total and usable capacities of SNU-70 is shown in Table 1, and compared against the performance of MOF-5 and IRMOF-20.

Another accomplishment of FY 2017 was the demonstration of the Hydrogen Adsorbent System Model to project system level performance of two promising MOFs identified in the present program, IRMOF-20 and DUT-23(Co). The system model was developed by the Hydrogen Storage Engineering Center of Excellence, and previously applied to model MOF-5 based systems. Figure 2 illustrates the projected performance of these systems, demonstrating that a 3% improvement in gravimetric performance and 11% improvement in volumetric performance can be achieved using a DUT-23(Co)-based storage system.

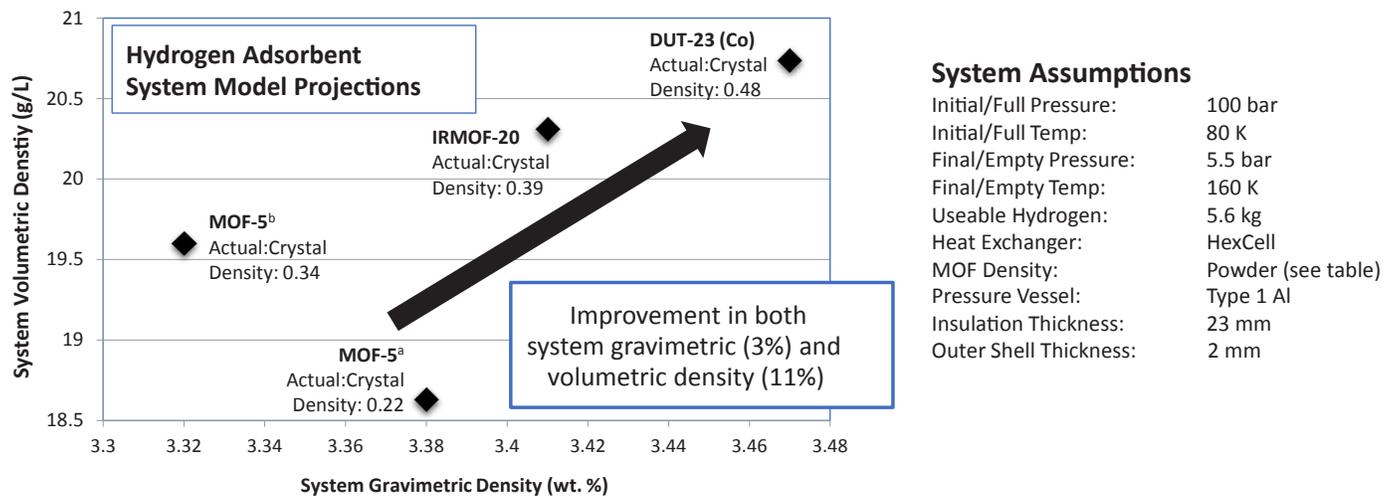
**TABLE 2.** Summary of Screening of MOFs for Usable H<sub>2</sub> Capacities

Database	Number of MOFs				Calc. Usable Capacity	
	Available in database	Zero surface area	H <sub>2</sub> capacity evaluated empirically	H <sub>2</sub> capacity evaluated w/GCMC	At least equals MOF-5	Exceeds MOF-5 by 15%
Real MOFs [1,2]	5,109	1,978	3,131	3,131	90	20
Mail-Order MOFs [3]	112	4	108	112	32	15
<i>In Silico</i> MOFs [4]	2,816	154	2,662	466	21	1
NW Hypothetical MOFs [5]	137,000	30,160	106,840	12,374	4,437	768
Zr-MOFs [6]	204	0	204	204	126	35
UO Hypothetical MOFs [7]	324,500	32,993	291,507	16,372	7,768	1,209
<b>Total</b>	<b>469,741</b>	<b>65,289</b>	<b>404,452</b>	<b>32,659</b>	<b>12,474</b>	<b>2,048</b>

GCMC – Grand Canonical Monte Carlo



**FIGURE 1.** H<sub>2</sub> isotherms of several promising MOFs measured at T = 77 K



**FIGURE 2.** Application of the HSECoE System Model to project the performance of IRMOF-20 and DUT-23(Co)-based systems

## CONCLUSIONS AND UPCOMING ACTIVITIES

Computational screening and experimental synthesis/characterization revealed SNU-70 as a hydrogen adsorbent which can surpass the usable capacity of the benchmark compounds MOF-5 and IRMOF-20 under cryogenic conditions. Upcoming activities will focus on evaluating additional compounds with the goal of identifying MOFs that can surpass the performance of MOF-5 by 15%.

## FY 2017 PUBLICATIONS/PRESENTATIONS

1. D.J. Siegel, “Hydrogen Adsorbents with High Volumetric Density: New Materials and System Projections,” 2017 DOE Hydrogen Program Annual Merit Review Meeting, Washington, June 8, 2017.
2. D.J. Siegel, “Metal-Organic Frameworks for Gas Capture and Storage: Computational Discovery and Experimental Validation,” TMS 2017 Annual Meeting & Exhibition, Symposium on “Computational Materials Discovery and Optimization—From Bulk to Materials Interfaces and 2D Materials,” San Diego, CA, February 26–March 2, 2017.

## REFERENCES

1. Goldsmith, J., A.G. Wong-Foy, M.J. Cafarella, and D.J. Siegel, *Chem. Mater.*, 2013. **25**: p. 3373–3382.
2. Chung, Y.G., J. Camp, M. Haranczyk, B.J. Sikora, et al., *Chem. Mater.*, 2014. **26**: 6185–6192.
3. Martin, R.L., L.-C. Lin, K. Jariwala, B. Smit, and M. Haranczyk, *J. Phys. Chem C*, 2013. **117**: p. 12159–12167.
4. Bao, Y., R.L. Martin, C.M. Simon, M. Haranczyk, B. Smit, et al., *J. Phys. Chem. C*, 2015. **119**: 186–195.
5. Wilmer, C.E., M. Leaf, C.Y. Lee, O.K. Farha, B.G. Hauser, et al., *Nat. Chem.*, 2012. **4**: 83–89.
6. Gomez-Gualdron, D.A., O.V. Gutov, V. Krungleviciute, et al., *Chem. Mater.*, 2014. **26**: p. 5632–5639.
7. Aghaji, M.Z., M. Fernandez, P.G. Boyd, T.D. Daff, and T.K. Woo, *Eur. J. In. Chem.*, 2016. **2016**: 4505–4511.
8. Cai, J. et al., *Chem. Commun.* **2014**, *50*, 1552.
9. Furukawa, H. et al., *Inorg. Chem.* **2011**, *50*, 9147.
10. Grüner, R. et al., *Eur. J. Inorg. Chem.* **2010**, 3835.
11. Dutta, A. et al., *Angew. Chem. Int. Ed.* **2015**, *54*, 3983.
12. Klein, N. et al., *Chem. Eur. J. Chem.* **2011**, *17*, 13007.
13. Rankine, D. et al., *Chem. Commun.* **2012**, *48*, 10328.
14. Eddaoudi, M. et al., *Science* **2002**, *295*, 469.
15. Yuan, D. et al., *Angew. Chem. Int. Ed.* **2010**, *49*, 5357.
16. Farha, O.K. *Nat. Chem.* **2010**, *2*, 944.