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

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 the most promising compounds to the system level by parameterizing models developed by the Hydrogen Storage Engineering Center of Excellence (HSECoE).

Fiscal Year (FY) 2018 Objectives

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

- Computationally screen approximately 500,000 MOFs from the principal investigator's MOF meta-database for their usable capacities under pressure swing and temperature + pressure swing conditions; synthesize the most promising materials predicted by computation and characterize their hydrogen uptake.

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[1]:

(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 toward the development of materials that attempt to meet the DOE 2020 hydrogen storage targets, which are summarized in Table 1. The ultimate success of this project rests upon developing MOFs that outperform 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 and demonstrated by this project to-date: IRMOF-20, SNU-70, UMCM-9, and PCN-610/NU-100.

FY 2018 Accomplishments

- Identified and experimentally demonstrated several MOFs whose usable capacities exceed that of MOF-5. Nearly 500,000 MOFs were assessed computationally under pressure swing and temperature + pressure swing conditions.

- Determined that PCN-610/NU-100 exhibits the best combination of usable (pressure swing) volumetric and gravimetric hydrogen capacity

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[1] https://www.energy.gov/eere/fuelcells/downloads/fuel-cell-technologies-office-multi-year-research-development-and-22

of any MOF reported to date. These capacities set a new high-water mark for physisorptive hydrogen storage.

- Provided system-level projections for several of the highest-performing MOFs; these projections quantify how materials-level improvements translate to the system level.

Table 1. System-Level Technical Targets Compared to Materials-Level Performance of the Baseline MOF-5 Adsorbent and That Measured for Several MOFs Identified and Demonstrated by This Project

Storage Parameter	Units	DOE 2020 Target (System Level)	MOF-5 Baseline	Project Status: IRMOF-20	Project Status: SNU-70	Project Status: UMCM-9	Project Status: PCN-610/NU-100
Gravimetric Capacity	wt%	4.5	7.8/4.5	9.1/5.7	10.6/7.3	11.3/7.8	13.9/10.1
Volumetric Capacity	g H_2/L	30	51.9/31.1	51/33.4	47.9/34.3	47.4/34.1	47.6/35.5

Capacities are reported for two usable conditions: the first number refers to a temperature + pressure swing from 77 K, 100 bar to 160 K, 5 bar; the second value refers to an isothermal pressure swing at 77 K between 100 bar and 5 bar. All reported MOF capacities are reported at the materials level and are based on single-crystal densities.

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. In the case of operating temperatures, the relatively weak enthalpy of hydrogen 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 hydrogen-adsorbent interaction. Therefore, distinct approaches are needed to address these independent issues. While some effort has previously been devoted to increasing ΔH (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, the focus of this effort is to demonstrate MOFs with a hydrogen density that surpasses that of MOF-5 in its optimal or "pristine" form (i.e., MOF-5 that has not been exposed to air and from which all solvent/reactants have been removed). Toward this goal, in FY 2016 we demonstrated IRMOF-20, a MOF whose capacities slightly surpassed that of MOF-5 (see Table 1). Subsequently, in FY 2017 we aimed to improve performance further by identifying and demonstrating MOFs that surpass the usable capacity of MOF-5 by 15%. This was accomplished by screening 469,741 MOFs (5,109 known and 464,600 hypothetical) from seven databases [1-7] for their usable capacities, assuming pressure swing operation between 5 and 100 bar. These calculations and experimental measurements demonstrated that SNU-70 can outperform both MOF-5 and IRMOF-20, as also shown in Table 1.

In FY 2018 we expanded our catalogue of screened compounds to include 10,126 known MOFs and 8,482 hypothetical compounds from four additional databases: Cambridge Structural Database curated MOFs, in-silico surface MOFs, MOF-74 analogs, and the ToBaCCo database [8-11]. A summary of the resulting meta-database of MOFs is shown in Table 2. In addition, our screening protocol was extended to temperature + pressure swing conditions: (T_{min}= 77 K, P_{max}= 100 bar) to (T_{max}= 160 K, P_{min}= 5 bar). In total, usable capacities of 43,227 MOFs under both operating conditions were calculated using Grand Canonical Monte Carlo (GCMC) analysis. Under pressure swing conditions, 12,986 and 6,059 MOFs were identified whose capacities can theoretically surpass those of MOF-5 and IRMOF-20, respectively. For temperature + pressure

swing conditions, only 186 MOFs were identified whose capacities can theoretically surpass that of MOF-5, the best-performing MOF reported to date under these conditions.

Table 2. Details of the MOF Databases and Their Subsequent Screening Based on Surface Area, Chahine Rule, and GCMC Calculated Usable Capacities of MOF-5 and IRMOF-20 at 77 K

Database	No. of MOFs	No. with Zero Surface Area	Capacity Evaluated Empirically	Capacity Evaluated with GCMC	Capacity Exceeds MOF-5 (PS/TPS)	Capacity Exceeds IRMOF-20 (PS only)
Real MOFs [1,2,11]: UM+CoRE+CSD	15,235	2,950	12,285	12,285	405/27	102
Mail-order [3]	112	4	108	112	30/0	19
In-silico deliverable [5]	2,816	154	2,662	466	27/0	6
In-silico surface [8]	8, 885	283	8,602	1,058	236/0	77
MOF-74 analogs [9]	61	0	61	61	0/0	0
ToBaCCo [10]	13,512	214	13,298	290	135/2	72
Zr-MOFs [6]	204	0	204	204	126/0	35
Northwestern [4]	137,000	30,160	106,840	12,374	4,397/153	2,154
Univ. of Ottawa [7]	324,500	32,993	291,507	16,372	7,612/4	3,581
In-house	18	0	18	5	18/0	13
Total	493,458	66,758	435,585	43,227	12,986/186	6,059

Assuming a pressure swing (PS) between 5 and 100 bar or temperature + pressure swing (TPS) from (T_{min}= 77 K, P_{max}= 100 bar) to (T_{max}= 160 K, P_{min}= 5 bar). To date, MOF-5 is the highest capacity MOF under TPS conditions, thus TPS performance was compared only to MOF-5.

Figure 1 shows the calculated usable volumetric capacities of 43,227 real and hypothetical MOFs as a function of their usable gravimetric capacities. Large dots indicate the measured capacities for some of the most promising MOFs identified; these MOFs were synthesized and characterized based on the computational predictions. For comparison, MOFs demonstrated as part of prior work in this or other projects (MOF-5, IRMOF-20) are also shown. In the case of the pressure swing data, Figure 1 shows this project has successfully identified and demonstrated a series of MOFs that outperform MOF-5 both gravimetrically and volumetrically. In the case of temperature + pressure swing operation, MOF-5 remains the MOF with the greatest usable volumetric capacity; nevertheless, IRMOF-20, SNU-70, and NU-100 all exceed the performance of MOF-5 on a gravimetric basis.
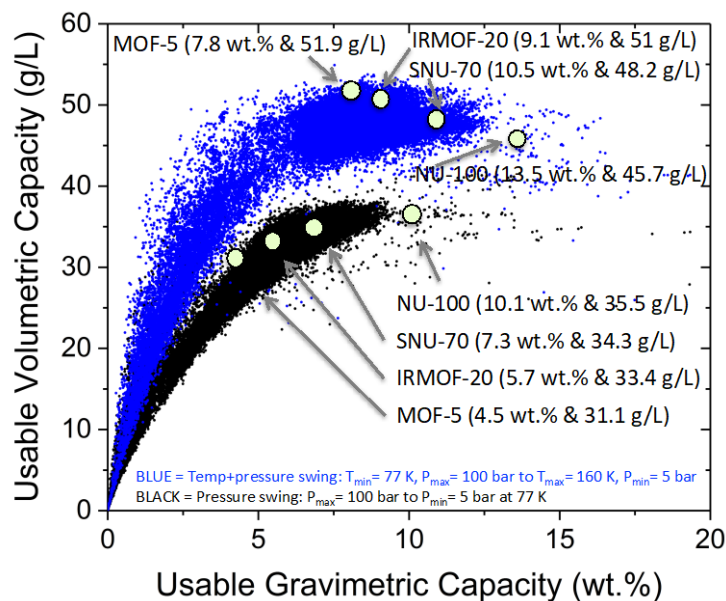
Figure 1. Calculated usable hydrogen storage capacities of 43,227 real and hypothetical MOFs assuming both pressure swing (black data points) and temperature + pressure swing operation (blue data points). Filled circles indicate measured hydrogen storage capacities of MOFs that were identified as promising compounds from computational screening.

Figure 2 illustrates how improvements in volumetric capacity at the materials level (assuming single-crystal density) translate to the system level. These projections were made using the Hex-Cell version of the adsorption system model developed by the HSECoE and adopt a realistic powder packing density. The data show that improvements in capacity achieved at the materials level are carried over to the system: a 14% increase in materials-level capacity achieved by substituting NU-100 for MOF-5 results in a similar 12% increase at the system level. Nevertheless, the absolute value of the hydrogen density is approximately 40% smaller at the system level for all MOFs considered. This is due to the large volumes associated with the insulation of the storage tank and to the volumes of other balance-of-plant components. In a similar manner, the improvement between gravimetric density on a materials level to that on the system level also was evaluated. For NU-100, a gravimetric density improvement of 124% on the materials level equated to only a 7% improvement on a system level. On an absolute basis, system gravimetric values are 40% to 70% smaller than materials-level gravimetric capacities.
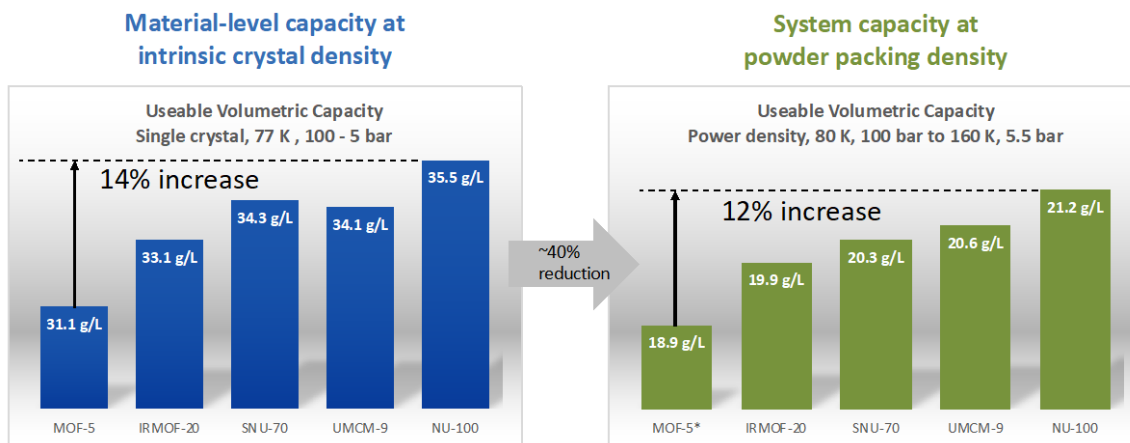

Figure 2. Demonstration of how improvements to materials-level volumetric capacity impact system-level volumetric capacity across a series of five MOFs examined in this project

CONCLUSIONS AND UPCOMING ACTIVITIES

This work has demonstrated that computational screening can successfully identify MOFs with enhanced volumetric and gravimetric hydrogen capacities. Several of the MOFs predicted by computation were synthesized, and their experimentally measured hydrogen uptake was shown to be in good agreement with the computational predictions. Based on these measurements, the HSECoE system model was used to extrapolate gains in capacity achieved at the materials level to performance at the system level.

Although this project ended in July 2018, several areas of R&D remain ripe for exploration. One obvious area is the experimental evaluation of the many other MOFs predicted by computation to have high hydrogen capacities (Table 2). The present project did not have the experimental throughput to explore more than a few dozen of these possibilities. A second area involves the efficient packing of MOF storage media. At present, gains in the single-crystal storage density predicted by the present project can be a challenge to realize at the system level due to low packing densities of the MOF powder. Strategies for increasing these densities should be explored.

FY 2018 PUBLICATIONS/PRESENTATIONS

1. M.D. Allendorf, Z. Hulvey, T. Gennett, A. Ahmed, T. Autrey, J. Camp, H. Furukawa, M. Haranczyk, M. Head-Gordon, A. Karkamkar, D.-J. Liu, J.R. Long, K.R. Meihaus, I.H. Nayyar, R. Nazarov, D.J. Siegel, V. Stavila, J.J. Urban, S.P. Veccham, and B. C. Wood, "An Assessment of Strategies for the Development of Solid-State Adsorbents for Vehicular Hydrogen Storage," *Energy & Environmental Science* 11 (2018): 2784–2812. DOI: 10.1039/c8ee01085d.

2. Alauddin Ahmed, Yiyang Liu, Justin Purewal, Ly D. Tran, Antek G. Wong-Foy, Mike Veenstra, Adam J. Matzger, and D. J. Siegel, "Balancing Gravimetric and Volumetric Hydrogen Density in MOFs," *Energy & Environmental Science* 10 (2017): 2459–2471. DOI: 10.1039/C7EE02477K.

3. D.J. Siegel (invited presentation), 2nd Bosch Energy Research Network (BERN) Symposium on Innovative Energy Research, Sunnyvale, CA, September 6–7, 2018.

4. D.J. Siegel (invited presentation), American Chemical Society's 256th National Meeting, symposium on Nanoscience of Energy Storage, Boston, MA, August 19–23, 2018.

5. D.J. Siegel (invited presentation), Indian Institute of Science Education and Research (IISER-BPR), Berhampur, India, September 4, 2017.

6. D.J. Siegel (invited presentation), Telluride Science Research Center, Computational Materials Chemistry Workshop, Telluride, CO, August 7–11, 2017.

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6. D.A. Gomez-Gualdron, O.V. Gutov, V. Krungleviciute, B. Borah, J.E. Mondloch, J.T. Hupp, T. Yildirim, O.K. Farha, and R.Q. Snurr. "Computational Design of Metal-Organic Frameworks Based on Stable Zirconium Building Units for Storage and Delivery of Methane." *Chem. Mater.* 26, no. 19 (2014): 5632–5639.

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