HyMARC Seedling: Optimized Hydrogen Adsorbents via Machine Learning and Crystal Engineering

Donald J. Siegel (Primary Contact, UM), Alauddin Ahmed (UM), Suresh Kuthuru (UM) Adam Matzger (UM), Justin Purewal (Ford), and Mike Veenstra (Ford)
University of Michigan (UM)
Ann Arbor, MI 48109
Phone: 734-764-4808
Email: djsiege@umich.edu

DOE Manager: Jesse Adams
Phone: 720-356-1421
Email: Jesse.Adams@ee.doe.gov

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Overall Objectives

- Apply machine learning (ML) techniques to design and experimentally demonstrate new metal organic frameworks (MOFs) having usable volumetric capacities exceeding 50 H_2 g/L (single-crystal/pressure swing) without compromising gravimetric capacity, kinetic performance, or reversibility.

- Control MOF crystal morphology and crystallite size distribution to increase packing density of target high-capacity MOF by at least 30% (compared to its powder tap density) with less than 15% decrease in gravimetric performance.

Fiscal Year (FY) 2019 Objectives

- Determine whether particle size influences packing efficiency by more than 10% for particles whose size varies by more than an order of magnitude.

- Make a list of MOF structures and associated properties available to the HyMARC team and to the general public via web download.

- Use grand canonical Monte Carlo (GCMC) to validate ML predictions of highest capacity MOFs on a pressure swing and temperature + pressure swing basis. Attempt to synthesize 1–2 of the most promising MOF candidates. Assess surface areas; if within 85% of theoretical value perform pressure, composition, temperature (PCT) capacity measurements.

- Demonstrate an improvement in either (a) a MOF with a single crystal volumetric capacity greater than 39 g/L usable capacity measured at 77 K and 5–100 bar pressure (i.e., a 10% increase over the current state-of-the-art NU-100) through ML-directed material development, or (b) a 15% increase in tap density through crystal engineering methods for a specific MOF compared to its non-optimized powder, with a minimal loss in surface area.

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

Insights gained from this study can be applied toward the development of materials that aim to meet the DOE 2020 hydrogen storage system targets:

- Cost: $333/kg H_2

- Gravimetric capacity: 4.5 wt %

- Volumetric capacity: 30 g H_2/L.

The outcomes of this project contribute to the optimization and assessment of hydrogen storage materials by identifying higher-capacity hydrogen

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

adsorbents, in particular adsorbents that maximize volumetric hydrogen density. This project also provides input to models that project the performance of these materials at the system level by quantifying and optimizing the hydrogen storage media packing density.

FY 2019 Accomplishments

- MOF-5 powders with mean particle sizes ranging from 279 microns to 2349 microns were synthesized. The volumeter-determined tap densities for these samples ranged from 0.31 to 0.35 g/cc.

- Three datasets describing MOF properties of relevance for hydrogen storage were deposited on the Hydrogen Materials Advanced Research Consortium (HyMARC) data hub (https://datahub.hymarc.org): (1) a set of computed crystallographic properties for

495,305 MOFs, (2) calculated pressure swing capacities for 98,695 MOFs, and (3) calculated temperature + pressure swing capacities for 98,695 MOFs.

- GCMC calculations were used to validate ML predictions of MOFs having the highest capacities on a temperature + pressure swing basis. Based on these predictions, two MOFs were synthesized (TMOF-2 and MOF-31), but the measured surface areas were low (i.e., less than 20% of the computationally predicted values).

- By controlling particle size, an 81% improvement in the tap density of powder MOF-5 (relative to its non-optimized form) was demonstrated with negligible loss in surface area.

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 Hydrogen Storage Engineering Center of Excellence 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 overcome volumetric limitations associated with physisorptive hydrogen storage at both the materials and system level. This goal will be achieved using a combination of computational techniques and experimental synthesis and testing. Our efforts will target storage media based on MOFs, a class of hydrogen adsorbents with highly tunable properties.

At the materials level, ML methods will be applied to our database of 476,007 real and hypothetical MOFs. This analysis will guide the discovery of new compounds that can break through the so-called *volumetric ceiling*. This performance ceiling was identified in our prior screening studies; it reveals that no known MOFs

can surpass a usable volumetric capacity of 40 g H_2/L (assuming an isothermal pressure swing between 100 and 5 bar at 77 K). In contrast to the conventional approach to MOF discovery, where capacity is predicted from a known crystal structure, this project aims to invert this process and "reverse engineer" optimal MOFs with the aid of ML. The most promising compounds will be synthesized and assessed experimentally with respect to their usable hydrogen capacities.

At the system level, we will develop crystal growth and processing techniques that result in MOF-based adsorbent beds with low void fractions. Packing inefficiencies have the potential to *negate* improvements in volumetric performance achieved at the materials level. This project aims to close this performance gap by developing synthetic procedures that optimize particle morphology and size distribution.

RESULTS

The usable hydrogen capacities of 4,847 MOFs predicted by ML to be high-capacity materials for temperature + pressure swing conditions were examined using GCMC simulations. These MOFs were predicted by ML to exhibit usable capacities ≥48 g/L and ≥7.5 wt %. These MOFs appear within the pink rectangular region in Figure 1a. A combination of previously benchmarked pseudo-Feynman [1, 2] interatomic potential and universal force field [3] simulations were carried out using the RASPA [4] package.
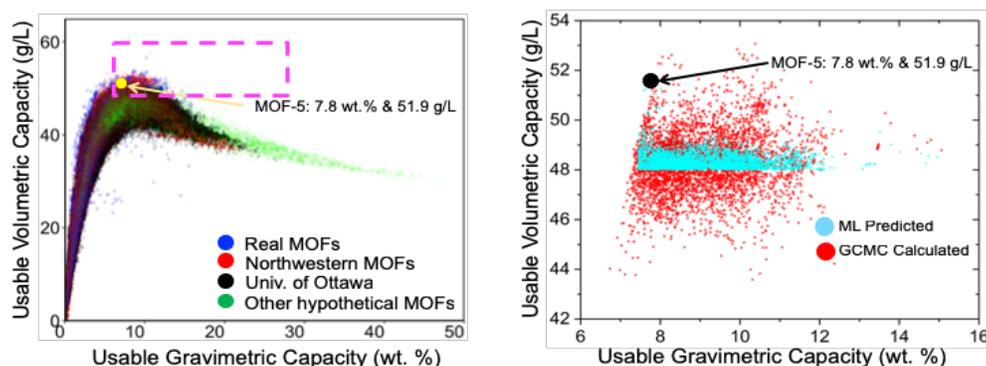

Figure 1. Verification calculations using GCMC on the top 4,847 MOFs predicted to be high-capacity materials by ML at temperature + pressure swing conditions between 100 bar at 77 K and 5 bar at 160 K. (a) Usable volumetric hydrogen storage capacity as a function of usable gravimetric capacity of 396,610 unseen MOFs (out of in total 495,305 MOFs excluding 98,695 compounds for which GCMC calculated capacities are available and used in training and testing ML models) predicted by ML. MOFs selected for further study by GCMC are shown by the pink dashed rectangular region; this includes MOFs with pressure swing capacities greater than or equal to 48 g/L and 7.5 wt %. (b) Usable volumetric hydrogen storage capacity as a function of usable gravimetric capacity for the 4,847 MOFs selected in panel a. For reference, the capacity of MOF-5 (7.8 wt % and 51.9 g/L), the highest capacity identified thus far, is also shown.

Figure 1b shows usable volumetric capacities as a function of usable gravimetric capacities for the 4,847 MOFs examined with GCMC. The ML-predicted capacities are also shown for comparison. Good agreement was obtained between the ML predictions and the GCMC validation calculations. The performance of MOF-5 (7.8 wt % and 51.9 g/L) under temperature + pressure swing conditions is depicted as the black filled circle. Only 20 MOFs were identified by GCMC with the potential to outperform MOF-5 under these conditions. This observation further confirms the notion that MOF-5 has excellent performance under temperature + pressure swing conditions.

Based on these ML calculations, and on earlier calculations on a training set of ~100,000 MOFs, a pair of MOFs were selected for synthesis: MOF-31 and TMOF-2. MOF-31 was projected to have a surface area of 3,072 m^2/g, with temperature + pressure swing capacities of 8.0 wt % and 61.1 g H_2/L. For TMOF-2 these values were 3038 m^2/g and 7.5 wt % and 54.9 g H_2/L. Unfortunately, multiple efforts to synthesize these materials did not achieve high surface areas: for MOF-31 flowing supercritical CO_2 activation yielded a negligible surface area of 13 m^2/g, while for TMOF-2 a slightly higher surface area of 631 m^2/g was achieved. Due to the low surface areas achieved, further characterization of hydrogen uptake was not performed.

Regarding packing density improvements, four MOF-5 samples with different particle size distributions were generated (sample names KS-1 to KS-4) using different metal/ligand and solvent (N,N-diethylformamide) concentrations, and via heating at 100°C for 24 hours (Figure 2). The resulting crystals were isolated by decanting the mother liquid and washed with N,N-dimethylformamide. Crystals were immersed in CH_2Cl_2 for 3 days, during which time the CH_2Cl_2 was replaced three times. Once solvent exchange was complete, the crystals were isolated by decanting the CH_2Cl_2 and evacuated under dynamic vacuum (0.05 torr) for 24 hours at room temperature.
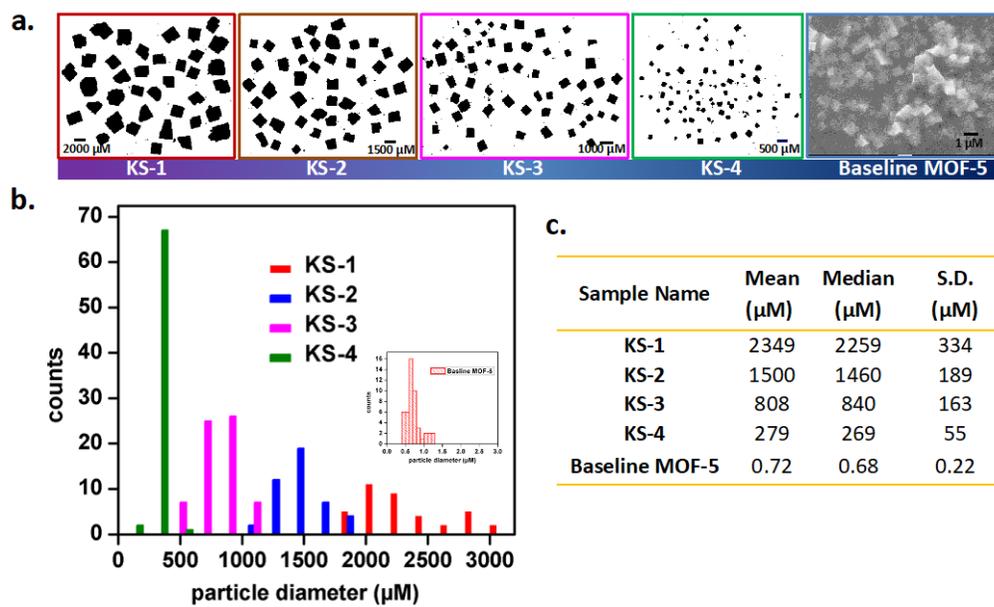

Figure 2. (a) Images and (b) plot of particle size distribution for five MOF-5 powders of varying particle sizes (KS-1 to KS-4, and baseline MOF-5). (c) Table of particle size range and median diameter for all samples.

The Brunauer-Emmett-Teller surface area was evaluated for all samples, as seen in Table 1. It was found that all samples exhibit high surface area, ~3,500 m^2/g, consistent with expectations for pure MOF-5. Tap density measurements were performed for all samples using a custom-built jolting volumeter. Tapping in the volumeter was carried out until the tap density of the sample being studied converged to a constant value. This typically required a minimum of 2,000 taps. It was observed (Table 1) that tapped samples exhibit a small reduction (at most ~100 m^2/g) in surface area. Furthermore, samples with particle diameters averaging 800–15,000 micron achieved packing densities up to 83% larger than the MOF-t baseline. This improvement exceeds the go/no-go milestone for improvement of 15%.

Table 1. Mean Particle Size, Tap Density, and Surface Area Values for Four MOF-5 Powders of Varying Particle Sizes (KS-1 to KS-4), as Compared to Baseline MOF-5 Supplied by BASF

Property	Baseline MOF-5	UM MOF-5			
		Batch KS-4	Batch KS-3	Batch KS-2	Batch KS-1
Mean particle size (μM)	<1	279	808	1500	2349
Standard deviation	<1	55	163	189	334
Volumeter tap density (g/cc)	0.189	0.31	0.35	0.34	0.32
Improvement over baseline MOF-5	N/A	63%	83%	81%	67%
Surface area as synthesized (m^2/g, UM)	N/A	3,550	3,539	3,457	3,497
Surface area after tap density measurement (m^2/g)	2,937	3,435	3,435	3,428	3,447
Degradation	–	none	none	none	none

FY 2019 PUBLICATIONS/PRESENTATIONS

1. D. Siegel, "Advancements in Porous Materials for Hydrogen Adsorption," presentation at Gordon Research Conference on Hydrogen-Metal Systems, Barcelona, Spain, June 30–July 5, 2019.

REFERENCES

1. M. Fischer, F. Hoffmann, and M. Fröba, "Preferred Hydrogen Adsorption Sites in Various MOFs-A Comparative Computational Study," *ChemPhysChem* 10, no. 15 (2009): 2647–2657.

2. A. Ahmed, Y. Liu, J. Purewal, L.D. Tran, M. Veenstra, A. Wong-Froy, A. Matzger, and D. Siegel, "Balancing Gravimetric and Volumetric Hydrogen Density in MOFs," *Energy Environ. Sci.* 10 (2017): 2459–2471.

3. A.K. Rappe, C.J. Casewit, K.S. Colwell, W.A. Goddard, and W.M. Skiff, "UFF, a Full Periodic Table Force Field for Molecular Mechanics and Molecular Dynamics Simulations," *J. Am. Chem. Soc.* 114, no. 25 (1992): 10024–10035.

4. D. Dubbeldam, S. Calero, D.E. Ellis, and R.Q. Snurr, "RASPA: Molecular Simulation Software for Adsorption and Diffusion in Flexible Nanoporous Materials," *Mol. Simul.* 42, vol. 2 (2016): 81–101.