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

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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 g H₂/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) 2018 Objectives

- Identify ranges for four MOF crystallographic properties (surface area, density, pore volume, and porosity) consistent with usable volumetric capacity of at least 40 g H₂/L and usable gravimetric capacity of at least 7 wt% (assuming an isothermal pressure swing

between 100 and 5 bar at 77 K) based on single-crystal density.

- Demonstrate that the identified ranges are within the realm of possibility for the development of new MOFs, and thus provide a pathway for meeting the DOE storage targets.
- Demonstrate the ability to predict usable capacity of an arbitrary MOF to within 85% of grand canonical Monte Carlo (GCMC) capacity using only crystal structure as input.
- Identify at least two additives to be employed during MOF synthesis that are capable of altering crystallite morphology from cubes to octahedra.

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 Plan¹:

- (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 following DOE 2020 hydrogen storage targets:

- Cost: \$333/kg H₂
- Gravimetric capacity: 4.5 wt%
- Volumetric capacity: 30 g H₂/L

The outcomes of this project contribute to the optimization and assessment of hydrogen storage materials by identifying higher-capacity hydrogen adsorbents, in particular adsorbents that maximize volumetric hydrogen density. This project also provides input to models that project the

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

performance of these materials at the system level by quantifying and optimizing the hydrogen storage media packing density.

FY 2018 Accomplishments

- Demonstrated the ability to predict four crystallographic properties of an arbitrary MOF that correspond to specified usable gravimetric and volumetric hydrogen capacities.
- Demonstrated that the ranges of predicted crystallographic properties are within the realm of possibility for the development of new MOFs.
- Identified three additives capable of controlling morphology of MOF-5 from cubes to octahedra.
- Demonstrated control over MOF particle size from a few microns to 2 mm by varying the metal:ligand ratio. The effect of temperature and time on MOF particle size distributions was also quantified.

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 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 metal-organic frameworks (MOFs), a class of hydrogen adsorbents with highly tunable properties.

At the materials level, machine learning (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 H₂/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 machine learning. 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

Table 1 summarizes the inputs and outputs used in developing ML models for predicting the range of crystallographic properties that correlate with specified usable hydrogen capacities. Usable gravimetric and volumetric capacities (at 77 K assuming a pressure swing between 5 and 100 bar) determined from grand canonical Monte Carlo (GCMC) calculations were used as ML input descriptors, while the crystallographic properties were the target outputs.

In total, data from 96,402 MOFs were used for training and testing the ML models. The extremely randomized trees (ERT) [2] supervised ML algorithm was trained and tested on GCMC-calculated capacities using the Scikit-learn [3] python package. The ERT model was identified as being the most accurate ML algorithm. ERT

models were trained using data from 72,300 randomly selected MOFs from the GCMC data set. The remaining GCMC data for 24,102 MOFs were used to assess the performance of the ML model. The tunable parameters of the ERT model were optimized via a randomized grid search over plausible parameter values with 10-fold cross validation using the RandomizedSearchCV and GridSearchCV functions as implemented in Scikit-learn [3]. Table 2 summarizes the accuracy of ML predictions of crystallographic properties of MOFs using four different metrics: R^2 (correlation coefficient), AUE (average unsigned error), RMSE (root-mean-square error), and Kendall τ .

Table 1. ML Input Descriptors and Target Output Properties

ML Input Descriptor: Hydrogen storage capacity calculated via GCMC	ML Target Output: Crystallographic properties calculated via the zeo++ code [1]
Usable gravimetric (in wt%) and volumetric (in g H ₂ /L) capacities at 77 K for a pressure swing between 5 and 100 bar	(1) Single crystal density (in g/cm ³) (2) Pore volume (in cm ³ /g) (3) Void fraction (unit free) (4) Gravimetric surface area (in m ² /g) (5) Volumetric surface area (in m ² /cm ³) (6) Largest cavity diameter (in Å) (7) Pore limiting diameter (in Å)

ML models are trained using inputs to reproduce outputs.

Table 2. Accuracy of ML Predictions of MOF Crystallographic Properties

ML Predicted MOF Crystallographic Properties	R^2	AUE	RMSE	Kendall τ
Single crystal density (g/cm ³)	0.980	0.010 (g/cm ³)	0.056 (g/cm ³)	0.984
Pore volume (cm ³ /g)	0.998	0.026 (cm ³ /g)	0.035 (cm ³ /g)	0.966
Void fraction	0.947	0.017	0.029	0.904
Gravimetric surface area (m ² /g)	0.920	402 (m ² /g)	539 (m ² /g)	0.906

Correlations between ML predictions and zeo++ calculations for four crystallographic properties of MOFs are shown in Figure 1. These properties include single-crystal density, pore volume, void fraction, and gravimetric surface area. These data demonstrate the ability to predict these properties to within 92% to 99% accuracy.

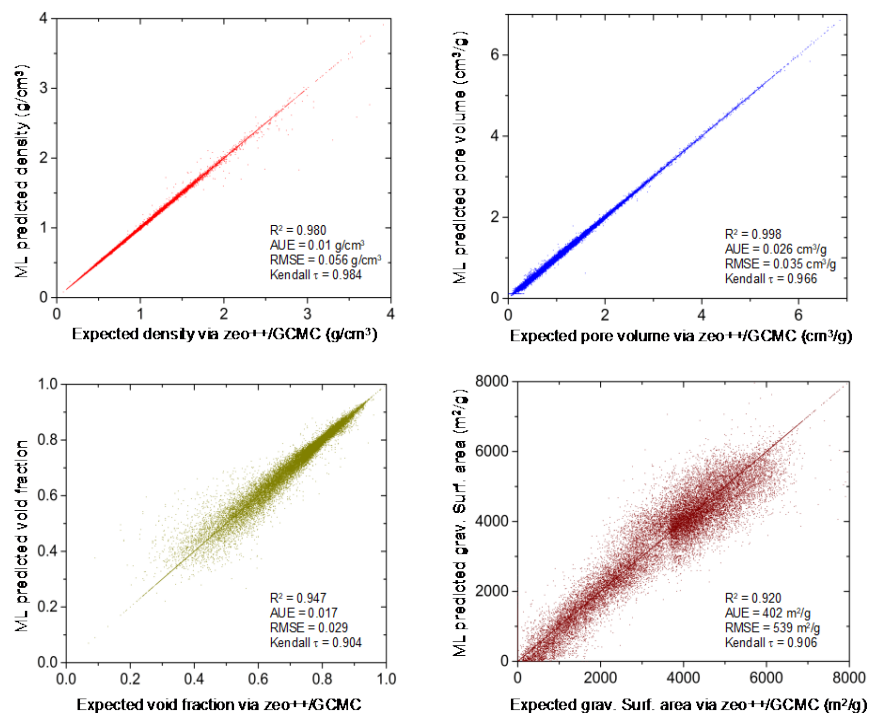


Figure 1. Comparison between ML predictions and zeo++/GCMC calculations of four crystallographic properties of 24,102 MOFs. ML models were trained using GCMC-calculated usable capacities of 72,300 MOFs as input descriptors.

Figure 2 illustrates ML predictions for four crystallographic descriptors as functions of usable gravimetric and volumetric capacities. The left y-axis represents input usable volumetric capacity while the right y-axis indicates values for a given crystallographic property. Input capacities (7 wt% and 40 g H₂/L) are indicated by white-filled black circles in each of the plots; their corresponding ML-predicted crystallographic properties are shown by filled red circles. Green dots represent the ML-predicted crystallographic properties of MOFs corresponding to the input capacities represented by the pink region. Table 3 summarizes the ML predictions of four MOF crystallographic properties corresponding to usable gravimetric and volumetric capacities of 7 wt% and 40 g H₂/L, respectively.

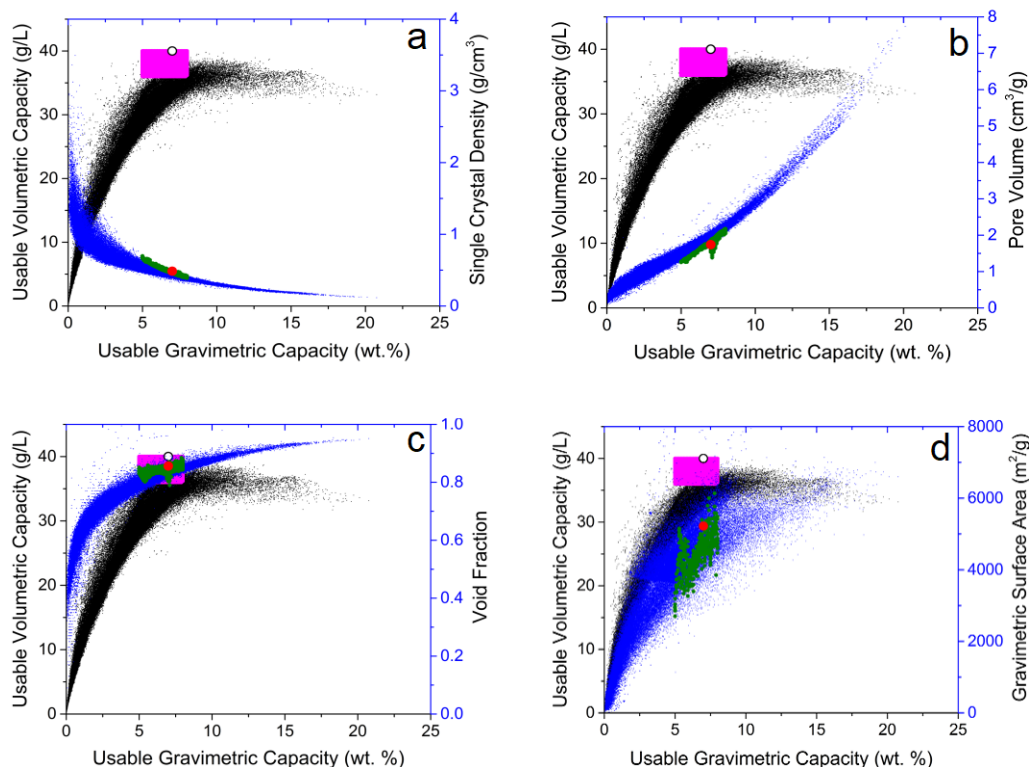


Figure 2. ML-predicted (a) single-crystal density, (b) pore volume, (c) void fraction, and (d) gravimetric surface area as a function of usable capacities. Each point in the pink rectangular region represents a usable gravimetric and volumetric capacity. Each point on the green region represents an ML-predicted crystallographic property corresponding to a specified usable gravimetric and volumetric capacity shown in the pink rectangular region. The filled red circles represent the predicted crystallographic properties corresponding to the input capacities of 7 wt% and 40 g H₂/L (indicated by white empty circles).

Table 3. MOF Crystallographic Properties Predicted by Machine Learning that Correspond to Usable Gravimetric and Volumetric Capacities of 7 wt% and 40 g H₂/L

Crystallographic Property	Range of Crystallographic Property
Single-crystal density (g/cm ³)	0.49 ± 0.01
Pore volume (cm ³ /g)	1.74 ± 0.03
Void fraction (dimensionless)	0.86 ± 0.02
Gravimetric surface area (m ² /g)	5,222 ± 402

An important aspect of MOF synthesis is the control of particle morphology, which allows properties to be tuned without changing the material composition. The morphology can be controlled via a proper choice of synthetic conditions. Usually, temperature, solvent, and the molar ratio of reagents allow for the shaping of crystal morphology. However, in the case of MOFs these effects are typically too subtle to cause gross morphological changes. In contrast, using additives in the reaction mixture strongly affects the crystal morphology, as illustrated here.

As shown in Figure 3, different morphologies of MOF-5 were synthesized by mixing a constant concentration of initial reagents (H₂BDC and Zn(NO₃)₂·6H₂O) and using different concentrations of polycarboxylates, including H₃L (a tricarboxylic linker) and H₄L (a tetracarboxylic linker). It was found that introducing ~3.7 mol% H₃L (H₃BTB, L1) to the reaction mixture generates octahedral-shaped crystals in 24 hours; introducing

the same polycarboxylate at ~ 1.9 mol% to the reaction mixture generates cuboctahedra-shaped crystals (24 h). Additionally, another H₃L (amine group functionalized H₃BTB, L2) polycarboxylate was identified for morphology control. Introducing ~ 2.8 mol% of this molecule to the reaction mixture generates cuboctahedra-shaped crystals (24 h). Finally, introducing H₄L (L3) polycarboxylate in concentrations of ~ 1.6 and ~ 6.6 mol% generates cuboctahedral- and spherical-shaped MOF-5 crystals, respectively, over the same 24-hour timeframe.

In total, the H₃L/ H₄L polycarboxylate concentration was found to be effective in controlling the crystal morphology. We succeeded in identifying three polycarboxylates that can control octahedra and cuboctahedra morphologies of MOF-5. The phase purity of obtained morphologies was confirmed through powder X-ray diffraction. The powder patterns of all morphologies were found to agree with the expected pattern of MOF-5.

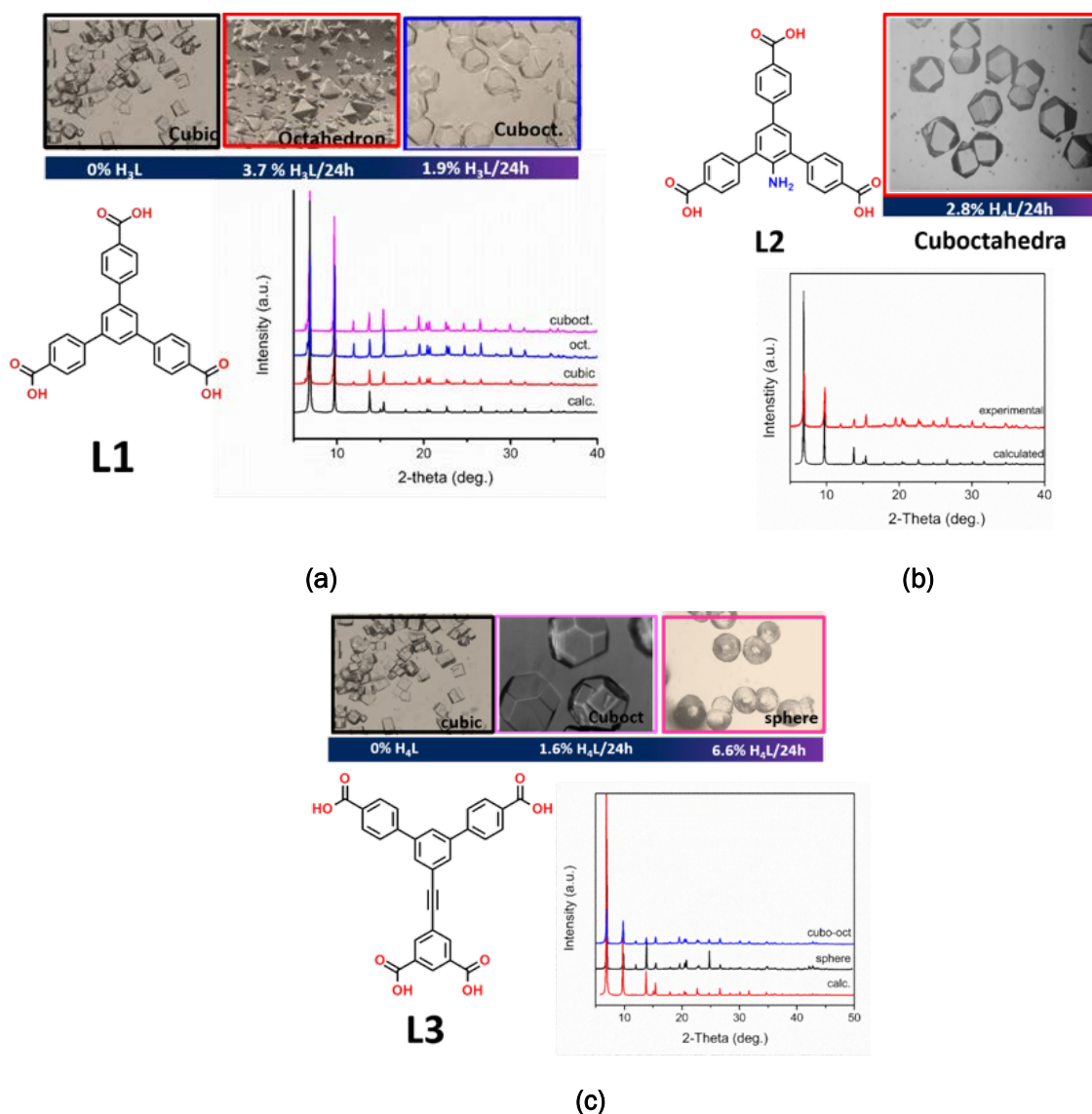


Figure 3. Optical images of different morphologies of MOF-5 crystals obtained by the addition of L1 (a), L2 (b), and L3 (c) polycarboxylates to the reaction mixture of H₂BDC and Zn(NO₃)₂·6H₂O. The respective powder X-ray diffraction patterns are also shown.

CONCLUSIONS AND UPCOMING ACTIVITIES

Using machine learning and a database of previously-calculated MOF properties, this project has demonstrated the ability to predict or “reverse-engineer” the crystallographic properties of an arbitrary MOF that correspond to a specified usable gravimetric and volumetric hydrogen capacity. Furthermore, it was demonstrated that the ranges of the predicted crystallographic properties are within the realm of possibility for the development of new MOFs. In addition to these computational accomplishments, experimental activities identified three additives capable of controlling the morphology of MOF-5 from cubes to octahedra. This development is a prerequisite for more efficient packing of MOF powders.

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. D.J. Siegel (invited presentation), 2nd Bosch Energy Research Network (BERN) Symposium on Innovative Energy Research, Sunnyvale, CA, September 6–7, 2018.
3. D.J. Siegel (invited presentation), American Chemical Society’s 256th National Meeting, symposium on Nanoscience of Energy Storage, Boston, MA, August 19–23, 2018.
4. D.J. Siegel (invited presentation), Indian Institute of Science Education and Research (IISER-BPR), Berhampur, India, September 4, 2017.
5. D.J. Siegel (invited presentation), Telluride Science Research Center, Computational Materials Chemistry Workshop, Telluride, CO, August 7–11, 2017.

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1. T.F. Willems, C.H. Rycroft, M. Kazi, J.C. Meza, and M. Haranczyk, “Algorithms and Tools for High-Throughput Geometry- Based Analysis of Crystalline Porous Materials,” *Microporous and Mesoporous Materials* 149 (2012): 134-141.
2. P. Geurts, D. Ernst and L. Wehenkel, “Extremely Randomized Trees,” *Mach. Learn.* 63 (2006): 3–42.
3. F. Pedregosa, G. Varoquaux, A. Gramfort, V. Michel, B. Thirion, O. Grisel, M. Blondel, P. Prettenhofer, R. Weiss, V. Dubourg, J. Vanderplas, A. Passos, D. Cournapeau, M. Brucher, M. Perrot and É. Duchesnay, “Scikit-learn: Machine Learning in Python,” *J. Mach. Learn. Res.* 12 (2011): 2825–2830.
4. Jonas Mockus, *Bayesian Approach to Global Optimization: Theory and Applications* (Kluwer Academic 2013).