Non-dominated solutions were identified and ranked using a multi-criteria decision-making approach, where objectives such as cost, environmental impact, and technical feasibility were considered. Each MOF was evaluated based on its performance in terms of volumetric and gravimetric capacity, selectivity, and thermal stability. The results showed that the optimized MOFs demonstrated superior performance compared to the initial prototypes, with notable improvements in both volumetric and gravimetric capacities.

Technical 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 storage systems. This work will guide future research and development efforts in hydrogen storage technology.
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 ∆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 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 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 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 m²/g, with temperature + pressure swing capacities of 8.0 wt % and 61.1 g H₂/L. For TMOF-2 these values were 3038 m²/g and 7.5 wt % and 54.9 g H₂/L. Unfortunately, multiple efforts to synthesize these materials did not achieve high surface areas: for MOF-31 flowing supercritical CO₂ activation yielded a negligible surface area of 13 m²/g, while for TMOF-2 a slightly higher surface area of 631 m²/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 CH₂Cl₂ for 3 days, during which time the CH₂Cl₂ was replaced three times. Once solvent exchange was complete, the crystals were isolated by decanting the CH₂Cl₂ and evacuated under dynamic vacuum (0.05 torr) for 24 hours at room temperature.

![Figure 2](image)

**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 m²/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 m²/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>
<thead>
<tr>
<th>Property</th>
<th>Baseline MOF-5</th>
<th>UM MOF-5</th>
<th>Baseline MOF-5</th>
<th>UM MOF-5</th>
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<tr>
<td></td>
<td></td>
<td>Batch KS-3</td>
<td>Batch KS-4</td>
<td>Batch KS-1</td>
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<tr>
<td>Mean particle size (µM)</td>
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<td>Improvement over baseline MOF-5 (%)</td>
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<td>83%</td>
<td>81%</td>
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</table>
FY 2019 PUBLICATIONS/PRESENTATIONS

REFERENCES