Project ID: ST122

Hydrogen Adsorbents with High Volumetric Density:

New Materials and System Projections

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Overview

Timeline and Budget

- Project Start Date: TBD
- Project End Date: TBD + 3 years
- Total Project Budget: $ TBD
  - Total Recipient Share: $ TBD
  - Total Federal Share: $ TBD
  - Total DOE Funds Spent: $0 – new project

Barriers

- Barriers addressed
  - Volumetric Density
  - Gravimetric Density

Partners

- **Interactions/collaborations:** Hydrogen Storage Engineering Center of Excellence (HSECoE)
- **Project lead:** D. Siegel, University of Michigan

Background

- A high-capacity, low-cost method for storing hydrogen remains one of the primary barriers to the widespread commercialization of fuel cell vehicles
- Storage via adsorption presents one of the more promising approaches due to its fast kinetics, facile reversibility, and high gravimetric densities
- An unfortunate characteristic of adsorptive hydrogen storage is that high gravimetric densities typically come at the expense of volumetric density.
- Development of adsorbents that *simultaneously* achieve high volumetric and gravimetric hydrogen densities – while maintaining reversibility and fast kinetics – would constitute a significant advance

Relevance: Importance of Volumetric Density

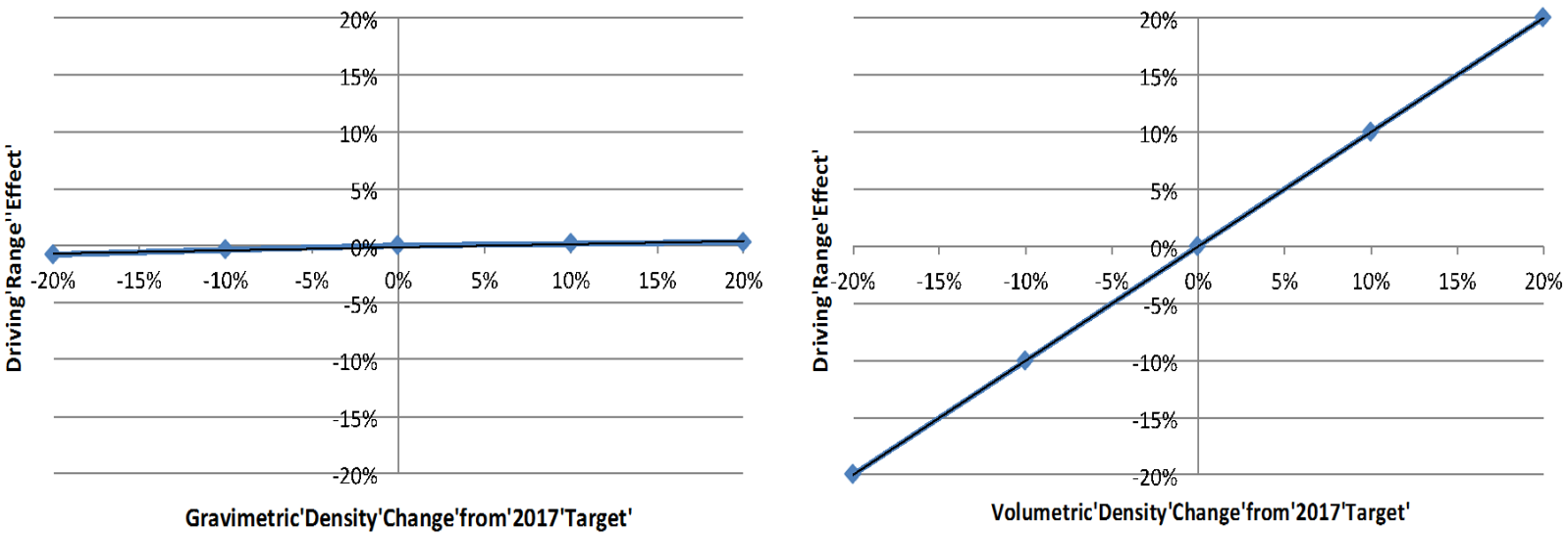
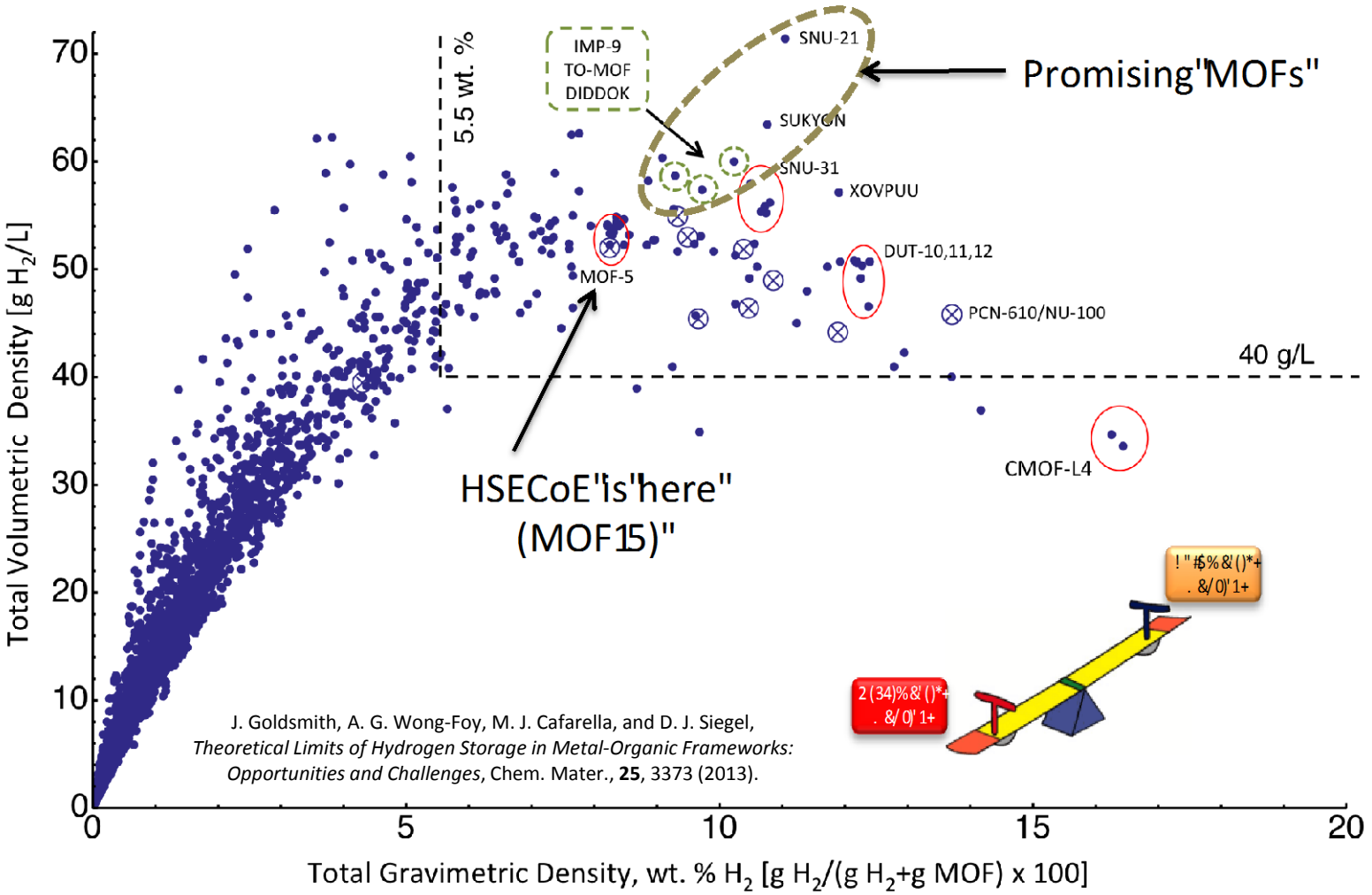


Figure: Effect of gravimetric and volumetric hydrogen storage density on the driving range of a fuel cell vehicle. (Left) Percentage change in driving range as a function of gravimetric density. assuming the system achieves the 2017 volumetric target. (Right) Percentage change in driving range as a function of volumetric density, assuming the system achieves the 2017 gravimetric target. From Ref. 4.

High-throughput Screening of MOFs

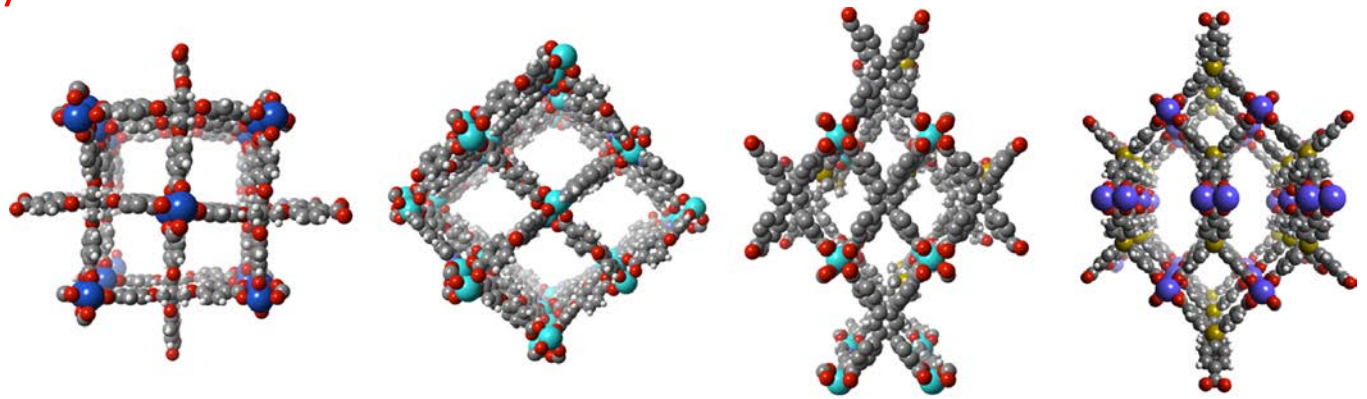
Our database of known MOFs is available for download:

http://esms-lab.engin.umich.edu/MOF_Search_Query.php



Top-Performing MOFs Identified by Screening

- Several MOF "Targets of Opportunity" were identified
- Combine high gravimetric and volumetric densities
- "Overlooked:" no/limited experimental evaluation
- Can these be synthesized in a robust form?



	EPOTAF (SNU-21)	DIDDOK	LURGEL (TO-MOF)	ENITAX (IMP-9)
Total Grav. (wt. %)	11	10.2	9.7	9.3
Total Volumetric (g/L)	71	60	57	59
Crystal Density (g/cm^3)	0.58	0.53	0.53	0.57
Calc'd/Meas. SA (m^2/g)	5208/700-900	4651	4386/680	4162
Notes	Best combination of grav. & vol. density. H_2 uptake measured previously: 5 wt %	No measurements	CO_2 uptake measured.	No measurements

Objectives

Develop MOFs with high volumetric and gravimetric hydrogen densities:

- Prior studies have largely focused on maximizing gravimetric density alone
- The proposed effort aims to maximize gravimetric and volumetric performance *simultaneously*, by synthesizing specific MOFs projected to embody both of these traits
- These targeted compounds have been largely overlooked by the community; realizing their performance experimentally would set a new high-water mark for hydrogen storage density in MOFs

System-level projections:

- We will project the performance of the most promising identified compounds to the system level by parameterizing system models developed by the Hydrogen Storage Engineering Center of Excellence (HSECoE)
- By leveraging these tools we will further clarify how materials properties impact system performance

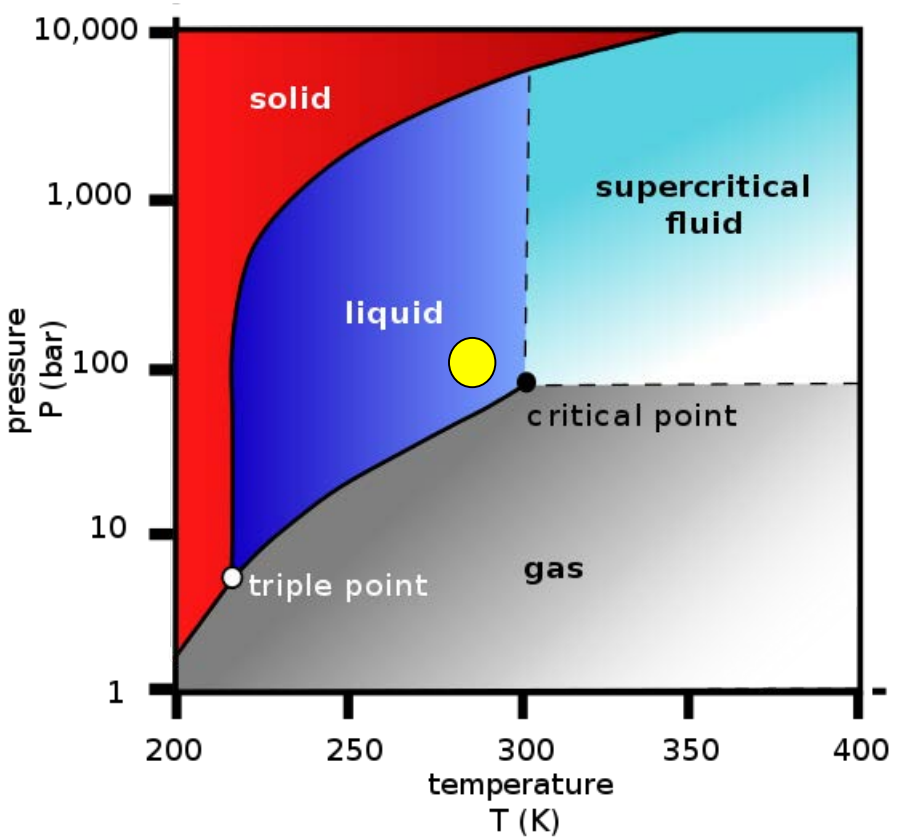
Approach

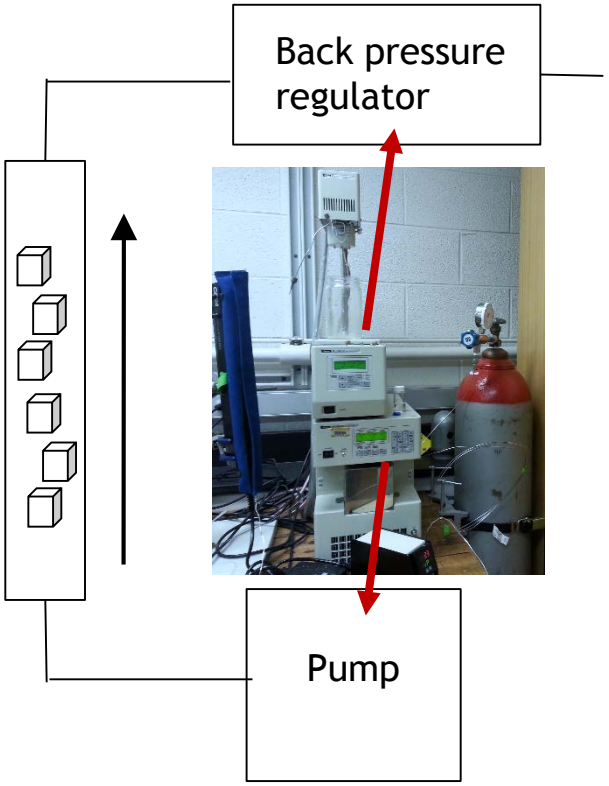
Our approach links atomic scale computation, experimental synthesis and characterization, and system level modeling

Task or Subtask #	Task Description
1	**Develop "overlooked" MOFs having potential for high gravimetric and volumetric density simultaneously**
1.1	Refine computational hydrogen uptake predictions using grand canonical Monte Carlo
1.2	Experimental synthesis of MOF targets suggested by screening
1.3	Materials characterization: Hydrogen uptake, kinetics, surface area, porosity, composition crystallinity, *etc.*
1.4	Project performance to system level by parameterizing HSECoE models

Supercritical CO_2 Activation

- Flowing supercritical CO_2 activation is milder than vacuum activation





Batch activation: Nelson, A. P.; Farha, O. K.; Mulfort, K; Hupp, J. T. *J. Am. Chem. Soc.* **2009**, *131*, 458.
Flow activation: Liu, B.; Wong-Foy, A. G.; Matzger, A. J. *Chem. Commun.* **2013**, *49*, 1419.

Vacuum or Batch Sc-CO_2 Activation vs Flow Sc-CO_2 Activation

Materials	SA from flow Sc-CO_2 activation	SA from vacuum/ batch Sc-CO_2 activation
UMCM-9	5357 m^2/g	1330 m^2/g (vac)
FJI	4813 m^2/g	4043 m^2/g (batch)
MOF-74 (Zn/DOBDC)	1108 m^2/g	750-950 m^2/g (vac)
UMCM-10	4001 m^2/g	Structure collapses under vac activation
UMCM-12	4849 m^2/g	Structure collapses under vac activation
IRMOF-8 (non-interpenetrated)	4461 m^2/g	Structure collapses under vac activation
A series of functionalized IRMOF-8 (non-interpenetrated)	~ 4000 m^2/g	-
HKUST-1	1710-1770 m^2/g (heating required)	682-1944 m^2/g (vac)

Liu, B.; Wong-Foy, A. G.; Matzger, A. J. *Chem. Commun.* **2013,** *49,* 1419.
Dutta, A.; Wong-Foy, A. G.; Matzger, A. J. *Chem. Sci.* **2014,** *5,* 3729.
Feldblyum, J. I.; Wong-Foy, A. G.; Matzger, A. J. *Chem. Commun.* **2012,** *48,* 9838.
Tran, L. D.; Feldblyum, J. I.; Wong-Foy, A. G.; Matzger, A. J. *Langmuir* **2015,** *31,* 2211.

Collaborations

University of Michigan, Mechanical Engineering

- Responsible for project management and atomistic simulation

University of Michigan, Department of Chemistry

- Responsible for synthesis and characterization of targeted MOFs

Ford Motor Company (sub-contractor)

- Responsible for materials augmentation, scale-up, and system modeling

Summary

- New project: slated for late summer/early fall kick-off

- Primary goal is to identify, synthesize, and characterize known MOFs that have the potential to exhibit high volumetric and gravimetric densities simultaneously
- Promising materials will be assessed with regard to their engineering properties
- Materials parameters will be used to parameterize HSECoE models and project performance at the system level

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