Methane and Hydrogen Storage with Porous Cage-Based Composite Materials

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Project ID ST212

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Project Overview

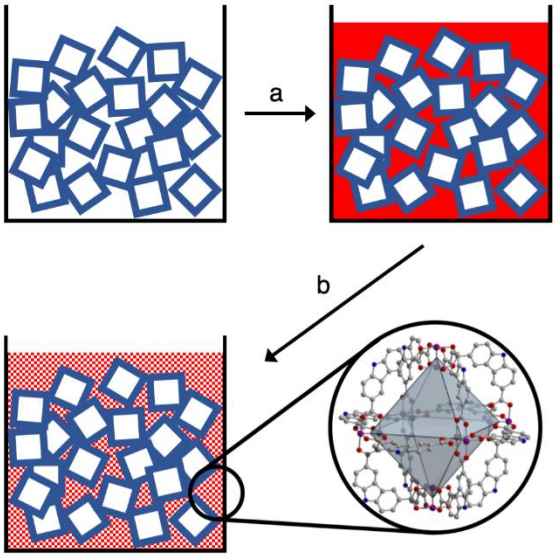
Award #	EE0008813
Start/End Date	11/15/2019 – 11/30/2022
Total Project Value Cost Share %	$1.148M 20%

Project Partners

Eric D. Bloch, University of Delaware

Project Vision

We are addressing the shortcomings of metal-organic frameworks (MOFs) as methane and hydrogen storage materials in terms of their prohibitively low bulk densities by preparing porous cage/MOF composites. Here, rather than minimizing or eliminating the void spaces that are detrimental to MOF capacities we are filling them with dense molecular adsorbents.



Project Impact

This project will further improve upon the record methane and hydrogen storage capacities of MOFs by addressing their bulk density shortcomings.

Approach: Summary

Project Motivation

We observed that porous molecular materials can easily display bulk densities that are greater than their crystallographic density. A porous-organic cage/metal-organic framework (POC/MOF) composite displays 65 bar CH_4 capacity 25% higher than the pure MOF.

Barriers

COVID-19. This has been the largest barrier to our project as we have been out of labs for 2+ months. Access will be granted in early June. Project-wise, the actual technical/scientific barriers have been small.

Key Impact

Metric	State of the Art	Expected Advance
Volumetric CH_4 capacity	*HKUST-1 263 cm^3/cm^3*	-
Real capacity	*104 cm^3/cm^3*	*30+% increase in actual capacity*
Cryst:Bulk Density	0.25 – 0.66	Have achieved >2-fold increase in dens.

Partnerships

- Jeffrey Long-UCB/LBNL: HyMARC point of contact. General adsorbent expertise
- Craig Brown-NIST: Structural Studies
- Phil Parilla-NREL: Adsorption expertise, helping to ensure accurate isotherms are measured

Approach: Innovation

- **<u>Budget Period 1 Scope of Work:</u> Initial MOF and Cage Screening and Structure/Function Elucidation.** Work during Budget Period 1 will focus on elucidation of the baseline MOF performance characteristics, preliminary screening of cage hydrogen and methane adsorption properties, and evaluation of Period 1 composite materials. Down-selection of MOFs to the most promising materials will occur during this period. In this regard, HyMARC resources were leveraged for gas adsorption analyzer validation (NREL) and advanced structural characterization (NIST).

Relevance and Impact

- As the current state-of-the art MOFs fall short of CH_4 and H_2 storage targets when real densities are considered, our project will target DOE storage and deliverable capacities for these gases.
- Our project fits well within HyMARC as we are taking a complete view of adsorbent properties and how they will be impacted by real system-level considerations. Our collaborations with NREL, NIST, and LBNL are perfectly aligned with the HyMARC approach.
- The broadly assembled expertise in adsorbents and adsorption on the overall HyMARC team has been invaluable for this project.

Accomplishments

- Q1 Milestone: Down-select 10 MOFs for incorporation into composite materials. MOFs with high total volumetric capacities at 298 K (200+ cm^3/cm^3 at 65 bar or 9+ g/L H_2 at 100 bar), and large discrepancies between bulk and crystallographic densities will be chosen. Percent Complete: 100%.

- A large library of methane and/or hydrogen storage materials were initially targeted. Given the near complete dearth of reported bulk densities and the range under which adsorption uptakes are reported, the Bloch group independently synthesized 35+ MOFs for high-pressure methane storage and bulk density measurements.

- Of these samples, ~20 could be synthesized reproducibly with appropriate surface areas. The measured adsorption capacities and densities are on the following slide.

Accomplishments

- Q1 Milestone: Material Synthesis, adsorption validation, and bulk density measurement. Scale up syntheses of 10 down-selected materials and measure their bulk densities and real total volumetric adsorption capabilities for benchmarking purposes. Percent Complete: 100%.

MOF	Total CH_4 uptake (cm^3/cm^3)[a]	Total H_2 uptake (g/L)[b]	Conditions for H_2	Crystallographic density (g/cm^3)[c]	Bulk density (g/cm^3)[d]
Al-MIL-53	194.3	37	77 K, 1 bar	0.978	0.281
Co_2(m-dobdc)	232.0	11.4	298 K, 100 bar	1.118	0.256
$Co_2(bdc)_2$(dabco)	223.2	18.9	77 K, 1 bar	0.815	0.209
Co_2(dobdc)	248.0	9.5	298 K, 100 bar	1.173	0.777
Cr-MIL-100	177.5	23.7	77 K, 26.5 bar	0.700	0.187
Cu_2(adip)/PCN-14	257.6	36.6	298 K, 50 bar	0.829	0.234
DUT-4	184.6	16.6	77 K, 30 bar	0.773	0.209
DUT-8-Zn	49.6	7.7	77 K, 60 bar	0.680	0.449
HKUST-1	263.0	22.4	77 K, 1 bar	0.881	0.350
Mg_2(dobdc) N.P.	145.0	–		0.909	0.220
MOF-177	203.8	32	77 K, 70 bar	0.427	0.250
Ni(ndc)$(ted)_{0.5}$	225.3	41	77 K, 65 bar	0.789	0.221
Ni_2(m-dobdc)	243.2	11.9	298 K, 100 bar	1.200	0.343
Ni_2(dobdc)	253.2	10.7	298 K, 100 bar	1.195	0.539
Ni_2(dobdc) N.P.	204.7	–		1.195	0.538
Ti-MIL-125	165.0	–		0.810	0.276
UiO-66 (defect free)	176.5	32.5	77 K, 30 bar	1.320	0.268
UiO-66 (defective)	245.6	–		1.320	0.249
UiO-67	197.0	34.1	77 K, 38 bar	0.708	0.155
Zn(bdc)$(ted)_{0.5}$	215.1	38.2	77 K, 20 bar	0.893	0.378
$Zn_2(bdc)_2$(dabco)	213.2	16.1	77 K, 1 bar	0.822	0.490

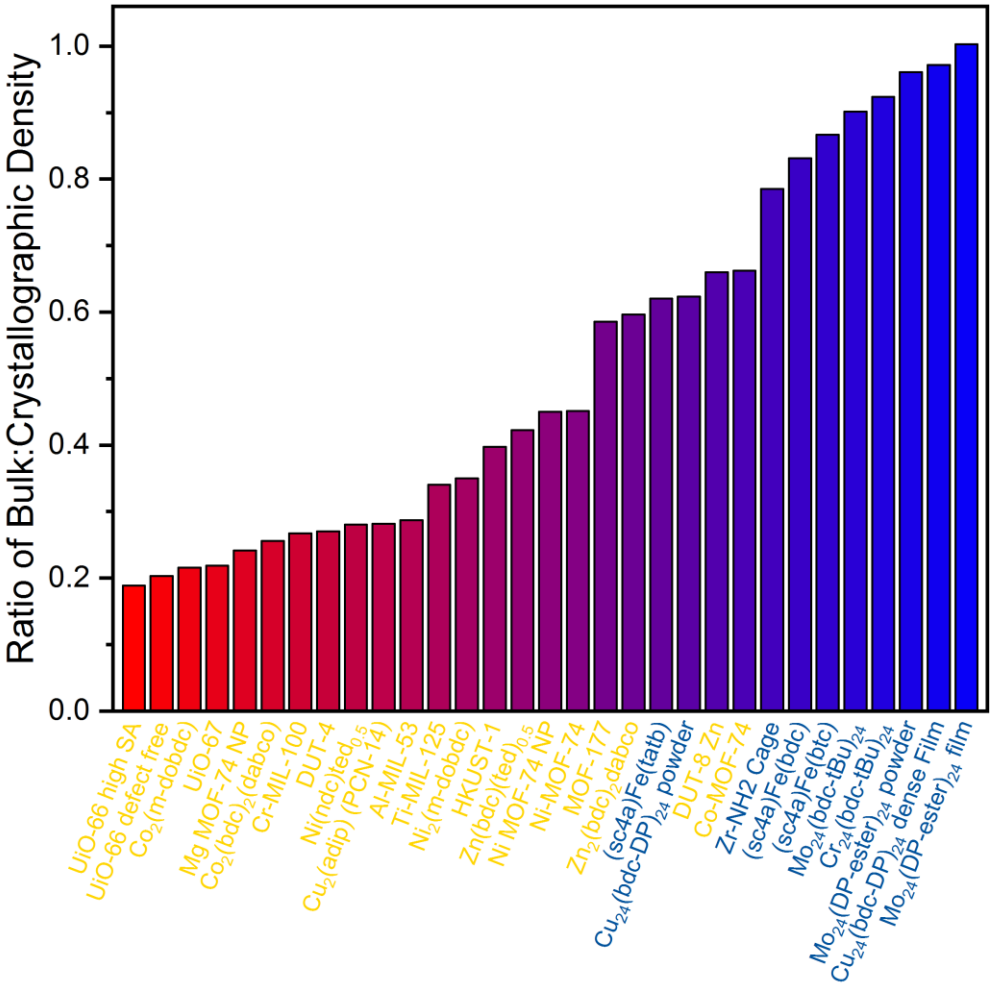
measured by the Bloch group at 298 K, 65 bar, [b]reported, [c]reported,[d]tap density measured by the Bloch Group

Accomplishments

- In addition to the ~20 MOF uptakes, high-pressure CH_4 isotherms and tap densities were measured for 10+ coordination cages.

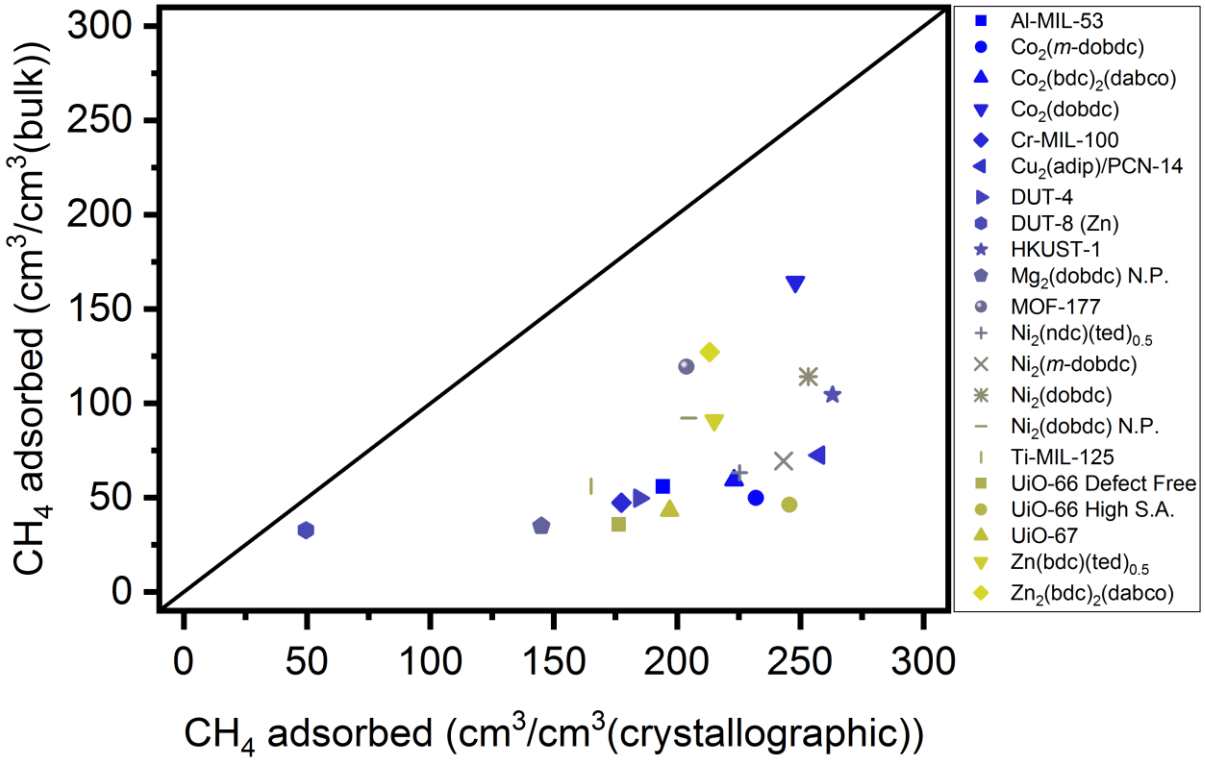
- This analysis illustrates the compelling discrepancy between bulk and crystallographic density of these materials.

- Of the materials investigated, cages show the highest ration of bulk:crystallographic density.



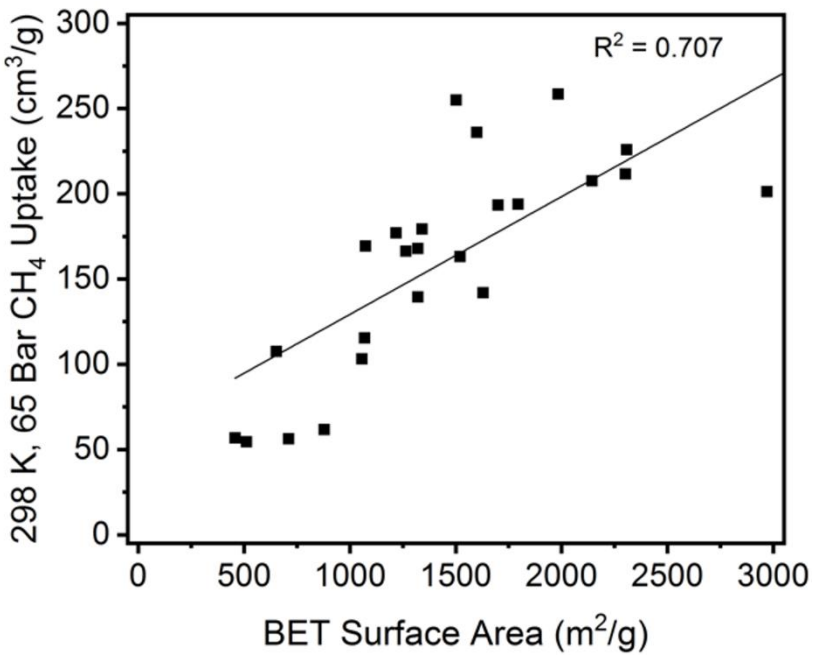
Accomplishments

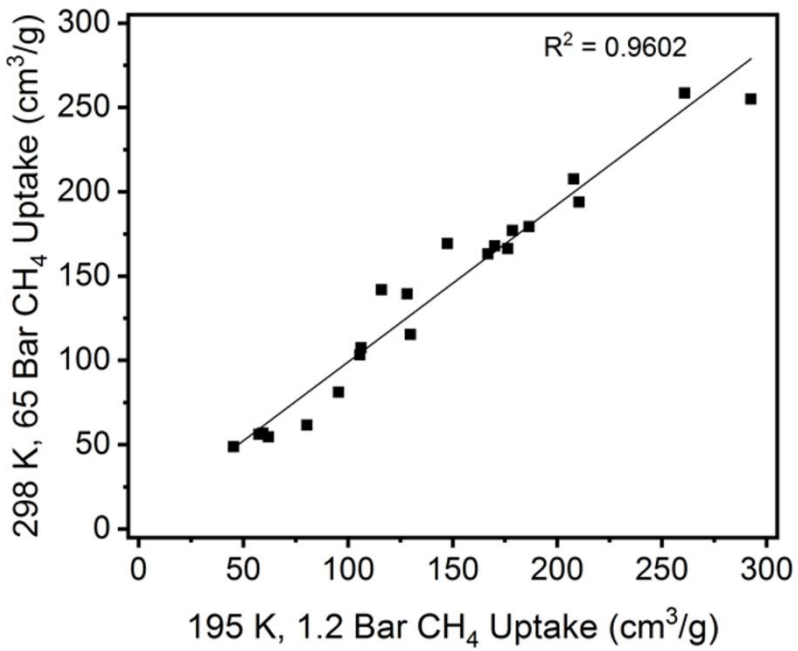
- We have identified ~20 promising MOFs to proceed with for preparation of composite materials. A subset of these have been prepared with varying particle size to further study density. Although compaction/palletization will likely be used for actual adsorbents, MOFs perform significantly worse when realistic densities are used.



Accomplishments

- During this study, a useful relationship between 195 K, 1.2 bar CH_4 adsorption and 298 K, 65 bar CH_4 adsorption was discovered.





- Although gravimetric surface area scales with gravimetric methane uptake, our trend shows much better agreement. This has allowed us to significantly increase the throughput of CH_4 screening measurements.

Accomplishments

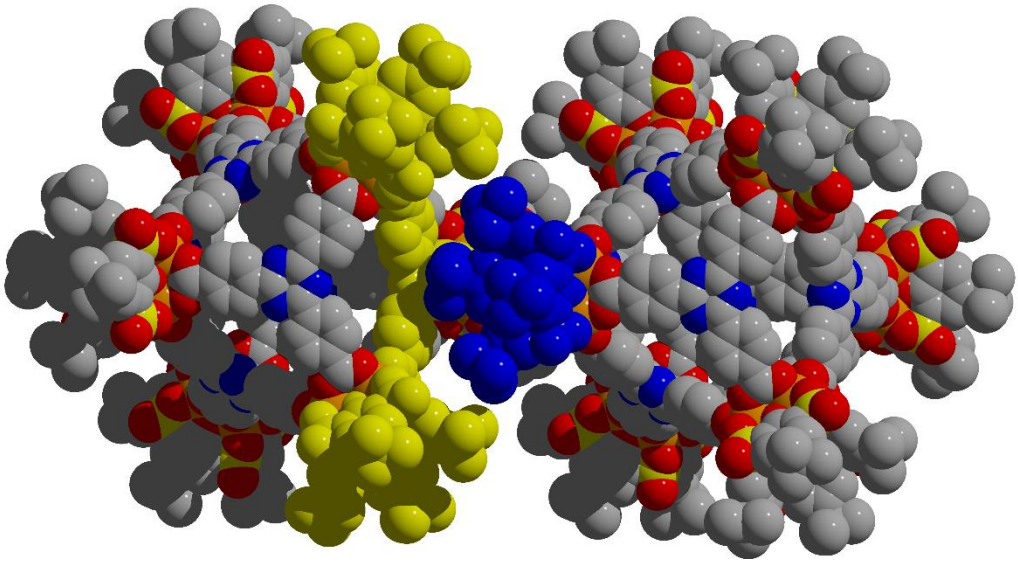
- Q1 Milestone: Determine particle size effects on bulk density for composite compatibility. Prepare a subset of MOFs (5-7 of 10 down-selected materials) via divergent reported syntheses to afford materials with varying particle size and morphology. Percent Complete: 50%.
- Prior to the COVID-19 shut down, 4 MOFs have been prepared by at least two different routes. Here UiO-66, Ni_2(dobdc), Mg_2(dobdc), and HKUST-1 were initially targeted.
- Given the lack of access to labs for the past two months, work on this front has stalled and will continue in the near future. As a result, there is no collected data to present for this milestone.

Accomplishments

- We have significantly increased the number of *soluble* porous coordination cages in our library. Methane adsorption isotherms of many of these materials have been measured with the remaining to be completed upon returning to labs.

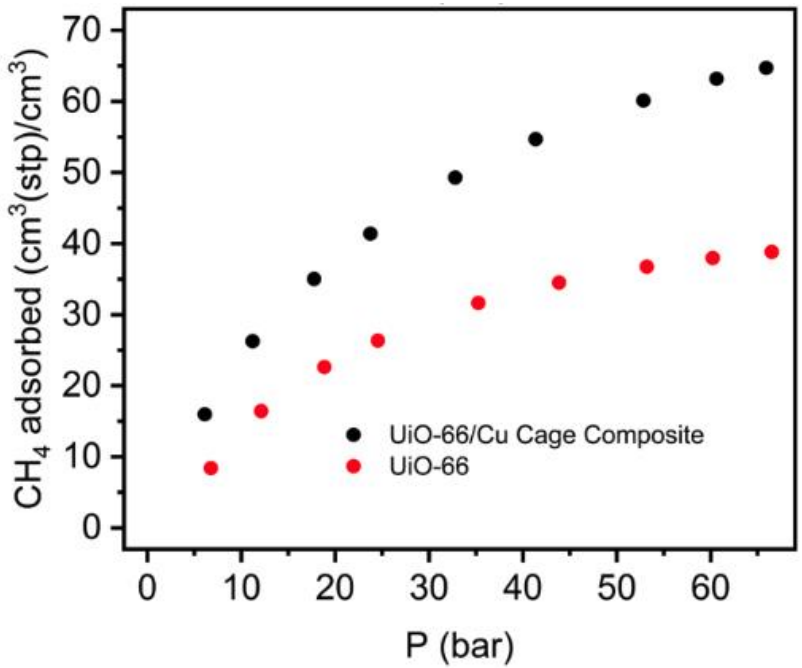
- This work has resulted in 4 recently published manuscripts with two more on the synthesis of novel cages currently submitted.

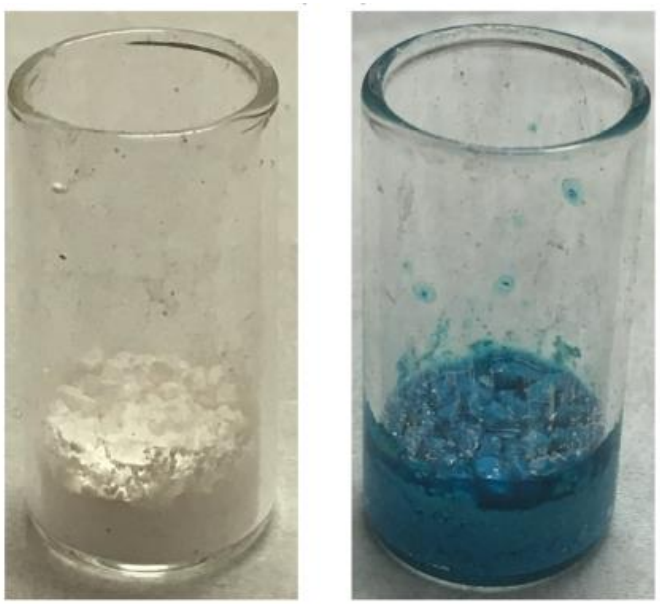
- The expanded iron-based cage displays a BET surface area within ~10% of the record value for coordination cages. Methane adsorption isotherms will be collected upon return to lab.



Accomplishments

- **Current Budget Period Go/No-Go:** Synthesis of a porous cage-MOF composite material with at least a 25% increase in total CH_4 (H_2) volumetric capacity based on bulk density at 298 K (65 bar for CH_4, 100 bar for H_2), compared to the corresponding pure MOFs value from benchmarking data collection. **<u>Percent Complete: 10%.</u>**





UiO-66 UiO-66/Cu cage

Collaboration: Effectiveness

- Have had positive interactions with Jeffrey Long and his research group in terms of sample preparation, isotherm measurement, and solgel syntheses. We will be sending samples for infrared spectroscopy measurements.
- We have continued to collaborate with NIST for the structural studies of materials prepared here, including neutron powder diffraction and inelastic neutron scattering.
- Have optimized our adsorption instrument and analysis of isotherms through interactions with NREL and Phil Parilla.

Proposed Future Work

- Should we progress past funding period 1, we will push the limits of the composite approach.

- Validation testing and composite preparation will be complete in period 1, therefore, we expect significant improvements in real methane and hydrogen adsorption capacities for MOF-based adsorbents during subsequent funding period.

Project Summary

- Prior to the COVID-19-related shutdown of labs, we were progressing ahead of schedule. MOF benchmarking and validation is complete.

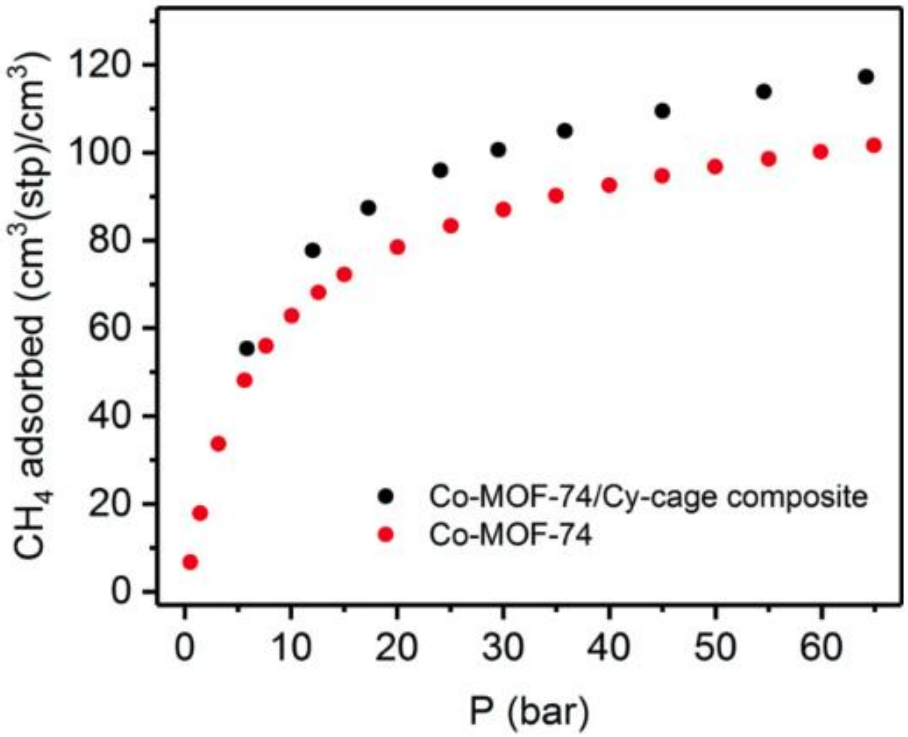
- A large body of work concerning porous coordination cages was compiled during the first ~4 months of this project and will continue for the foreseeable future.

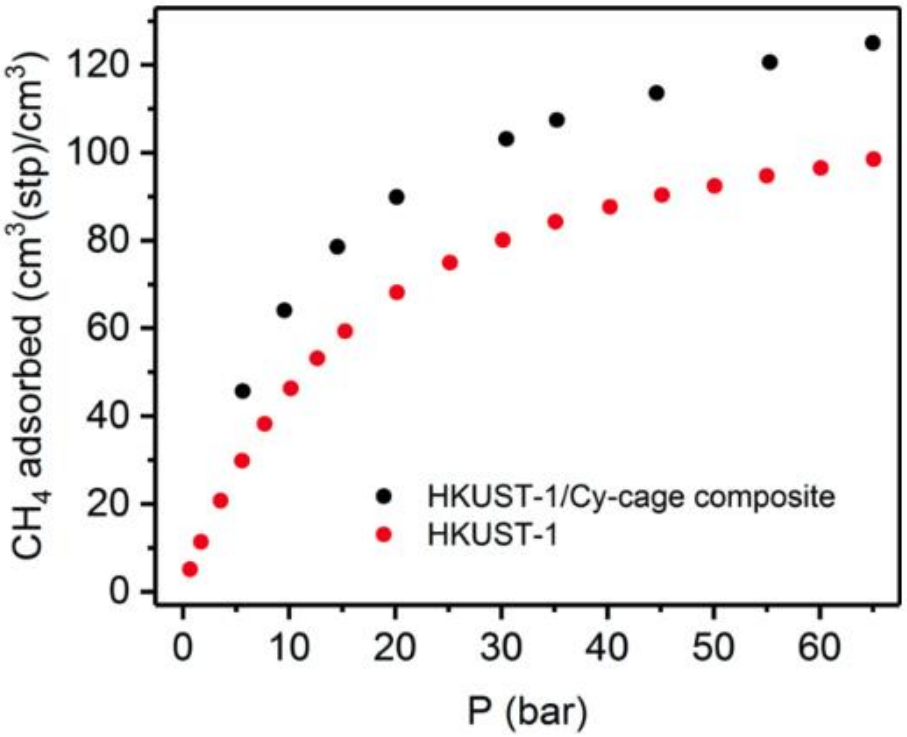
- It is expected that we will have no issues meeting our Period 1 Go Decision.

Publications and Presentations

- Publications this fiscal year:
  - 1. Deegan, M. M.; Ahmed, T. S.; Yap, G. P. A.; Bloch, E. D. Structure and Redox Tuning of Gas Adsorption Properties in Calixarene-Supported Fe(II)-Based Porous Cages. *Chem. Sci.* **2020**, *11*, 5273-5279.
  - 2. Gosselin, E. J.; Decker, G. E.; Antonio, A. M.; Lorzing, G. R.; Yap, G. P. A.; Bloch, E. D. A Charged Coordination Cage-Based Porous Salt. *J. Am. Chem. Soc.* **2020**, *142*, 9594-9598.
  - 3. Taggart, G. A.; Antonio, A. M.; Lorzing, G. R.; Yap, G. P. A.; Bloch, E. D. Tuning the Porosity, Solubility, and Gas-Storage Properties of Cuboctahedral Coordination Cages via Amide of Ester Functionalization. *ACS Appl. Mater. Interfaces* **2020**, Article ASAP. DOI:10.1021/acsami.0c06434.
  - 4. Rowland, C. A.; Yap, G. P. A.; Bloch, E. D. Novel Syntheses of Carbazole-3,6-Dicarboxylate Ligands and Their Utilization for Porous Coordination Cages. *Dalton Trans.* **2020**, Advance Article. DOI:10.1039/D0DT01149E
  - 5. Gosselin, E. J.; Rowland, C. A.; Bloch, E. D. Permanently Microporous Metal-Organic Polyhedra (MOPs). *Chem. Rev.* **2020**, Accepted. DOI:10.1021/acs.chemrev.9b00803.
  - 6. Gosselin, E. J.; Decker, G. E.; McNichols, B. W.; Baumann, J. E.; Yap, G. P. A.; Sellinger, A.; Bloch, E. D. Ligand-Based Phase Control in Porous Zirconium Coordination Cages. Submitted.
  - 7. Taggart, G. A.; Lorzing, G. R.; Yap, G. P. A.; Bloch, E. D. Synthesis and Characterization of Low-Nuclearity Lantern-Type Porous Coordination Cages. Submitted.
  - 8. Korman, K. J.; Decker, G. E.; Bloch, E. D. Using Low-Pressure Methane Adsorption Isotherms for Higher-Throughput Screening of Methane Storage Materials. Submitted.

Technical Backup Slides


CH4 adsorbed (cm3(stp)/cm3)
P (bar)
Co-MOF-74/Cy-cage composite
Co-MOF-74
0
20
40
60
80
100
120
0
10
20
30
40
50
60


CH4 adsorbed (cm3(stp)/cm3)
P (bar)
HKUST-1/Cy-cage composite
HKUST-1
0
20
40
60
80
100
120
0
10
20
30
40
50
60