Project ID: ST220

AMR 2020

SBIR: General Techniques for Increasing Packing Density of Metal-Organic Frameworks for Enhanced Volumetric Storage of Hydrogen

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Timeline and Budget

- Project Start Date: 5/29/2019
- Project End Date: 5/28/2021
- Total Budget: 1,000,000

Collaboration and Coordination:

No Partners

- Barriers Addressed:
  - 3.3.5A System Weight and Volume
  - 3.3.5B System Cost
  - 3.3.5 D Durability/Operability
  - 3.3.5 E Charging Discharging Rates
  - 3.3.5 J Thermal Management

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

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Project Abstract

Abstract: Current hydrogen fuel cell electric vehicles (FCEVs) on the market rely on high-pressure hydrogen, 700 bar, storage systems to store and deliver hydrogen for use in the fuel cell. Bringing hydrogen to high pressures and storing hydrogen at high-pressure requires sophisticated compressors and specialized carbon wrapped tanks, respectively. This high-pressure constraint makes FCEVs vehicles challenging and expensive to implement at scale, with costs passed onto the end user. This cost is coupled with safety concerns, with equipment failure in the supply chain leading to the release of high-pressure flammable gas that would present significant hazards. Therefore, alternative technologies that could facilitate the storage of hydrogen at lower pressure are required if hydrogen cars are going to be widely adopted by the public.

Porous materials, in particular, metal-organic frameworks (MOFs), have been highlighted as materials that could be used to store and deliver hydrogen at lower pressures in FCEVs. One of the key drawbacks of these materials that is often overlooked in the academic literature is their poor volumetric packing. Low volumetric packing of these systems results in smaller amounts of adsorption per unit volume. Volumetric packing is of critical importance for fuel tank applications where storage space is limited. Therefore, to realize the potential of MOFs, the packing density of MOFs must be optimized before these materials can be used in FCEVs. For this reason, the purpose of this SBIR proposed by NuMat Technologies (NuMat) is to develop generalizable techniques for increasing the volumetric packing density of MOFs. The methods developed are transferable to other MOFs, are scalable, and will occur with no loss of performance.

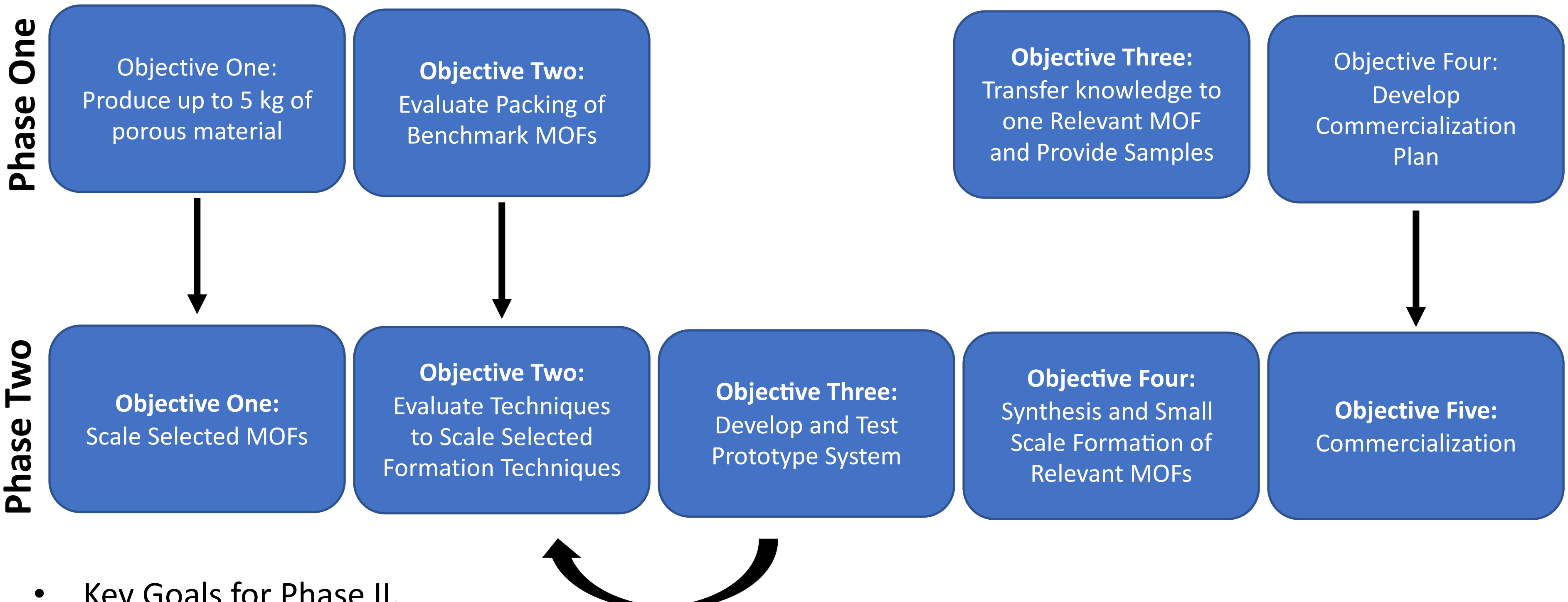
Towards achieving this goal through Phase I work, NuMat successfully evaluated several packing techniques on a small scale optimizing the volumetric packing density of several MOFs. The goal of eighty percent packing density outlined in Phase I, without altering the performance of the material, was achieved and results were shown to be transferable across a group of MOFs. Under Phase II, NuMat proposes to transition these formation techniques to commercial scales, identifying and validating the required equipment. Furthermore, high-density prototypes will be developed, and the tradeoff between high-packing density and other important parameters including the rates of adsorption and desorption will be understood.

The results achieved here will allow for MOFs to be implemented in FCEVs storage systems, which could bring reductions in the cost of these systems and improvements in safety. Removing high-pressure constraints currently in place would simplify storage systems, allowing for complex infrastructure to be simplified. These improvements will reduce the cost of FCEVs and alleviate safety concerns about the storage of hydrogen at high-pressure, making these vehicles competitive with gasoline vehicles. The work carried out by NuMat under this SBIR is broadly applicable to a wide range of volumetric storage challenges that are commercially relevant including the storage of light hydrocarbons for transportation, oxygen storage for medical applications, and safe transportation and delivery of toxic gases.

Gantt Chart For Phase II

			Month								
Objective	**Task**		**0-**	**3-**	**6-**	**9-**	**12-**	**15-**	**18-**	**21-**	**24**
1		**Scale Selected MOFs**									
	1.1	Optimize the synthesis of each MOF	X								
	1.2	Material Washing and Activation	X								
	1.3	Crystal Size	X								
	1.4	Pilot Plant Production		X	X						
	1.5	Material on Demand	X	X	X	X	X	X	X		
2		**Evaluate Techniques to Scale Selected Formation Techniques**									
	2.1	Multiphase Packing			X	X	X				
	2.2	Pelletization			X	X	X				
	2.3	Slurry-Based Packing			X	X	X				
	2.4	Determine Techniques For Prototyping					X				
3		**Develop and Test Protoype Storage System**									
	3.1	Build Prototype Testing System			X	X	X				
	3.2	Heat of Adsorption and Mass Transfer Data				X	X				
	3.2	Fill Prototype System with Different Volumetric Densities of MOF					X	X			
	3.3	Prototype Testing						X	X	X	
	3.4	Optimize Prototype							X	X	X
4		**Synthesis and small scale formation of relevant MOFs**									
	4.1	Idenify MOFs	X	X	X	X	X	X	X	X	X
	4.2	Optimize Synthesis	X	X	X	X	X	X	X	X	X
	4.3	Optimize Formation	X	X	X	X	X	X	X	X	X
6		**Commercialization**									
	5.1	Cost Analysis of Volumetric Hydrogen Storage Systems that Utilize MOFs								X	X
	5.2	Identify Other Opportunities For This Work					X	X	X	X	X
	5.3	Legal Strategy				X	X	X	X	X	X

Approach to Phase II Research



- Key Goals for Phase II,
    - **Objective One:** Produce enough material for later objectives
    - **Objective Two:** Evaluate which packing technique/s can be scaled without loss of performance
    - **Objective Three:** Understand how improvements in packing affect the performance of prototype system
    - **Objective Four:** Scale to new relevant MOFs
    - **Objective Five:** Evaluate commercialization of technology

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Relevance

- Current Fuel Cell Electric vehicles (FCEVs) require storage pressures of > 700 bar.
- Storage at high pressure increases the cost associated with storage, dispensing, compression, and supply chain management. These costs are passed directly to the consumer, increasing vehicle cost and reducing adoption.
- Therefore, storage at lower pressure is an attractive option for decreasing the cost of FCEV ownership.
- Several techniques have been proposed for decreasing the pressure of hydrogen storage including adsorbents and metal hydrides.
- One of the critical drawbacks of adsorbent based technoloy is the volumetric packing of the material.
- This proposal seeks to maximize the volumetric packing of MOFs through scalable techniques.
- Furthermore, the consequences of improved adsorbent packing are being investigated. Parameters, including hydrogen purity and fill-rates, are being evaluated at higher packing density.
- Metal-organic frameworks (MOFs) are the focus of this work.

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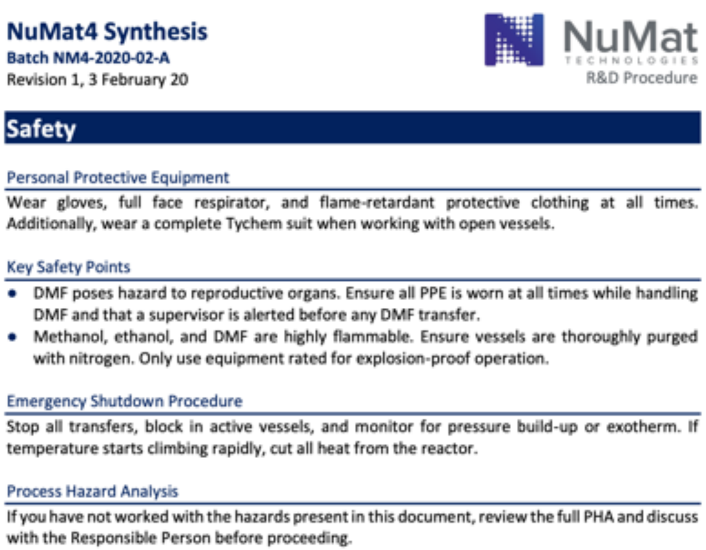
Objective One: Scale Selected MOFs

- Three MOFs were promoted for Scaling under Phase II efforts, NuMat-4, -14, -18.
- These materials have been successfully scaled in NuMat's pilot-plant facility
- Batch Sheets Generated and performance validated

A)



NuMat4 Synthesis
Batch NM4-2020-02-A
Revision 1, 3 February 20

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R&D Procedure

Safety

Personal Protective Equipment

Wear gloves, full face respirator, and flame-retardant protective clothing at all times. Additionally, wear a complete Tychem suit when working with open vessels.

Key Safety Points

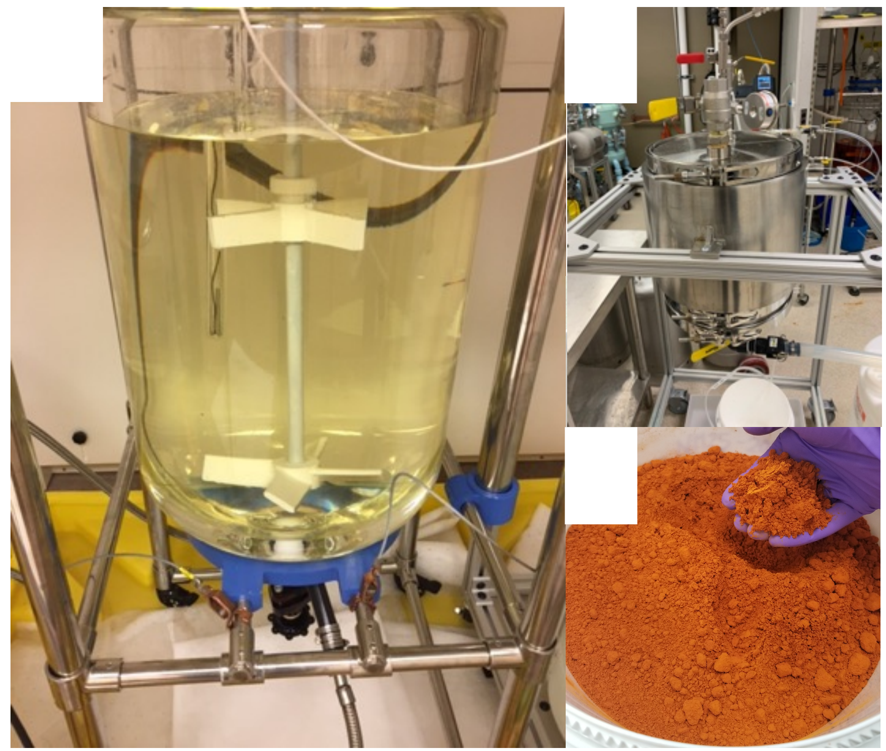
- DMF poses hazard to reproductive organs. Ensure all PPE is worn at all times while handling DMF and that a supervisor is alerted before any DMF transfer.
- Methanol, ethanol, and DMF are highly flammable. Ensure vessels are thoroughly purged with nitrogen. Only use equipment rated for explosion-proof operation.

Emergency Shutdown Procedure

Stop all transfers, block in active vessels, and monitor for pressure build-up or exotherm. If temperature starts climbing rapidly, cut all heat from the reactor.

Process Hazard Analysis

If you have not worked with the hazards present in this document, review the full PHA and discuss with the Responsible Person before proceeding.



A) Batch Sheet, B) Reaction in 50-l reactor, C) Filter apparatus, and D) Washed MOF

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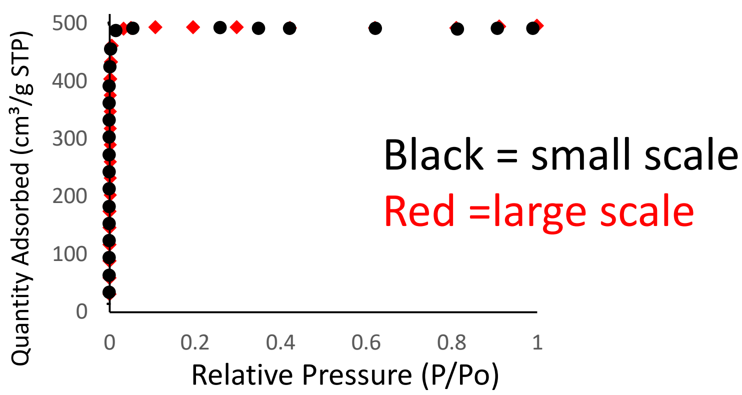
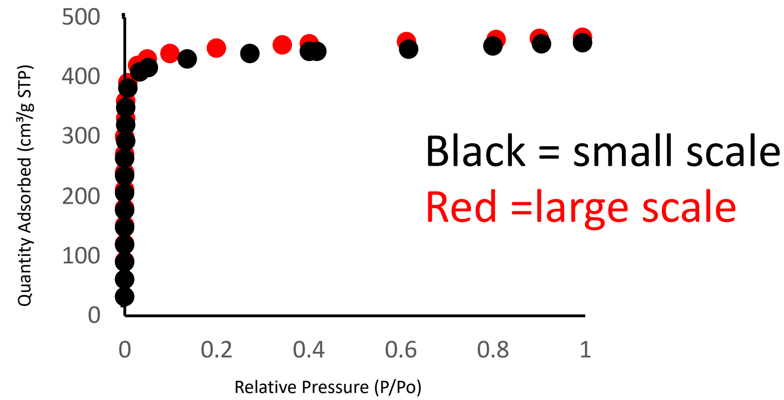
Objective One: Performance of Large-Scale Synthesis

NuMat-14



NuMat-18



MOF	NuMat4	NuMat14	NuMat18	HKUST-1	Ni-Meta MOF-74
Small scale (Vial)	✓	✓	✓	✓	✓
2-liter	✓	✓	✓	✓	
50-liter	✓	✓	✓		
Size range	Nano-micron	10 µm - 2mm	1-10 µm	Nano-mm	

- Targeted materials successfully produced
- Quality maintained at larger scales
- Material on demand

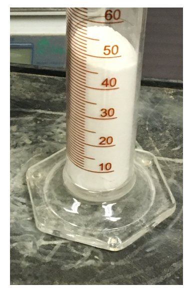
Objective Two: Evaluate Techniques to Scale Selected Formation Techniques

Goals,

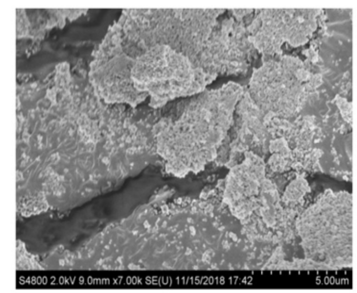
- Scale the most promising formation techniques from Phase One
- Achieve similar performance to small-scale results

Four packing techniques were identified from Phase One,

Pelletization/Puck formation



Multiphase Packing



Slurry Packing

The selected technique will need to be scalable to a prototype system (2.5 liters) and beyond ultimately.

Material Performance following packing

Throughput of formation technique

MOF Activation

Objective Two: Pelletization/Puck Formation

- Pellets and puck techniques have been scaled and material activation has been optimized.

Scaled Pellets

Scaled Pucks

- Performance comparable to small-scale samples
- Limited by pressure delivered – Evaluating larger equipment
- Material formation for prototype system being targeted both pucks and pellets

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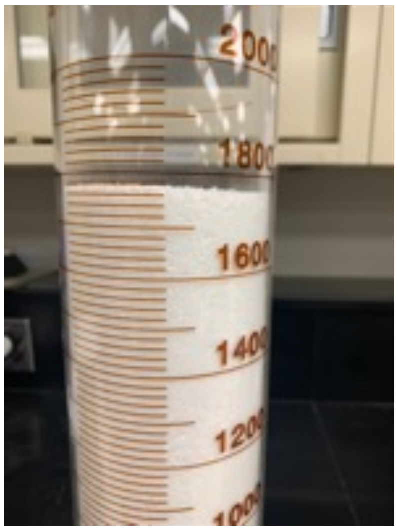
Objective Two: Multiphase Packing

- Experiments have been validated to the two-liter scales



Large crystal

+ small crystal

Vibrate

70% density achieved at large scale.

- No Performance loss
- 75% density achieved at the small-scale trying to understand difference between large and small-scale
- Will be scaled to prototype system
- Has been extended to HKUST-1

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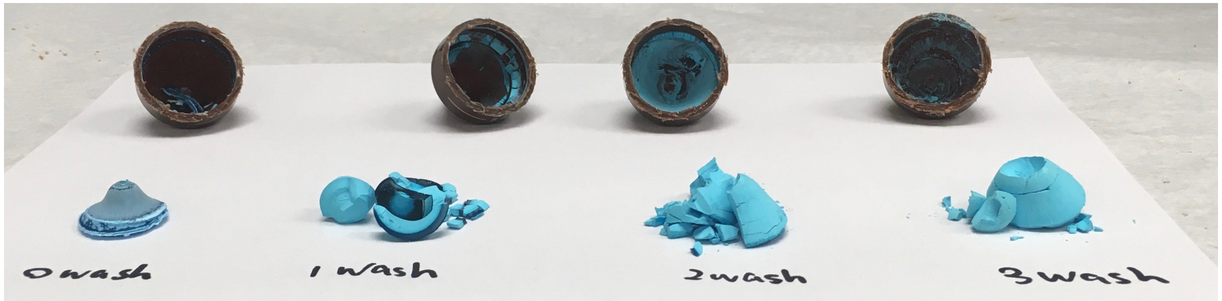
Objective Two: Slurry Packing

- Nanoscale HKUST-1 was synthesized and monoliths were formed by centrifugation.



Wash #	0	1	2	3
Density (g/ml)	0.93	0.74	0.61	0.53
Surface area (m^2/g)	470	1220	1580	1580

- Density Decreased as a function of washes performed but surface area uptake increased
- Performance at small-scale is promising
- Technique not scaled for several key reasons,
  - Requirement for nanoscale materials
  - Challenges in developing regular shapes with technique will decrease packing density

Objective Three: Develop and Test Prototype System

- **Key Goal:** Understand how improvements in packing affect the performance of prototype system

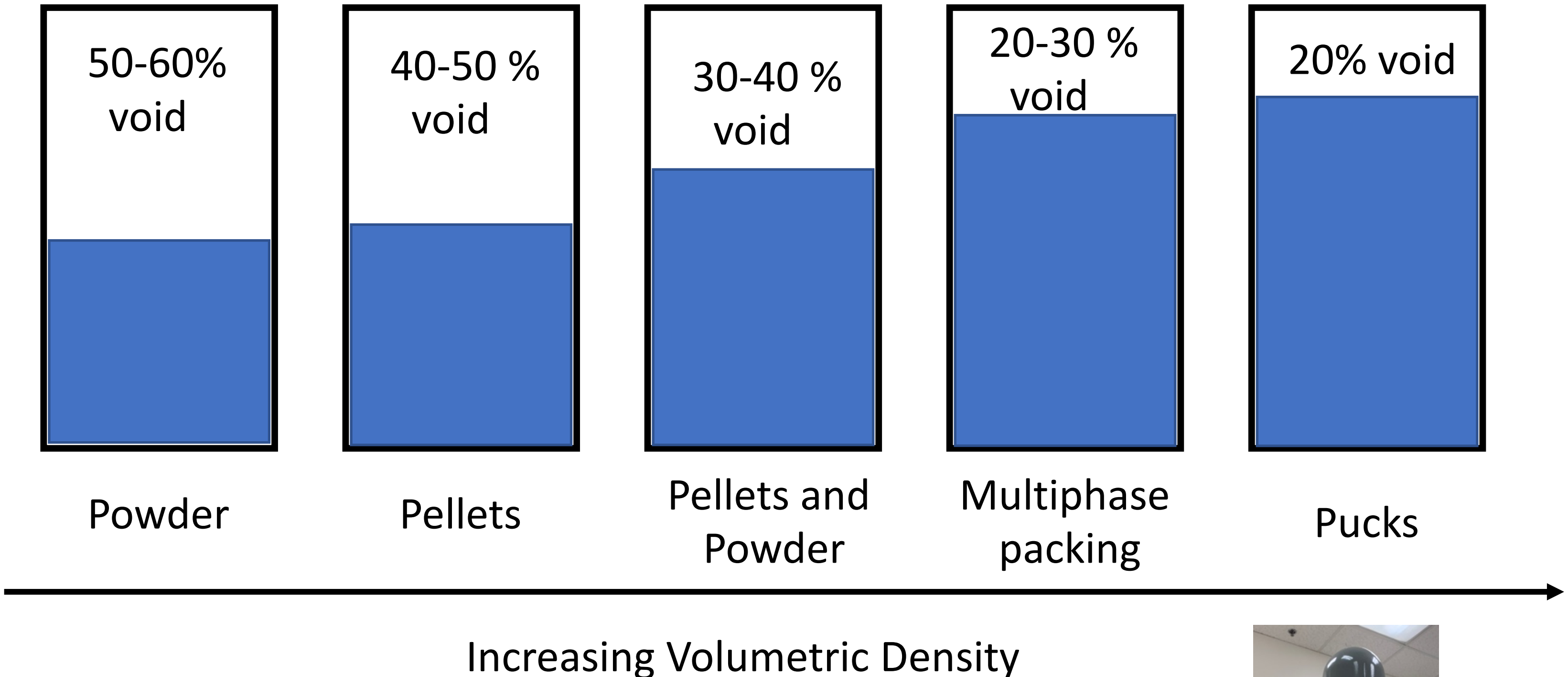
How,

- Prototype system to evaluate relevant parameters to hydrogen delivery.

- Initial focus was on improving system weight and volume (Barrier 3.3.5A) Other parameters will be evaluated under Phase II with prototype system,
  - Barrier 3.3.5 D Durability/Operability
  - Barrier 3.3.5 E Charging Discharging Rates
  - Barrier 3.3.5 J Thermal Management

- How does packing to different densities alter these outputs
- Both high density and low-density evaluation
- How does packing by different techniques affect these parameters
  - Multiphase packing vs pelletization
- Will investigate moving to higher enthalpy materials by using a surrogate gas, CO_2

Objective Three: Evaluate Filling of Different Packing Densities



Key Questions:
- What is the effect of moving to higher packing densities
- How can we mitigate against these effects

2.4 liter cylinder will be used

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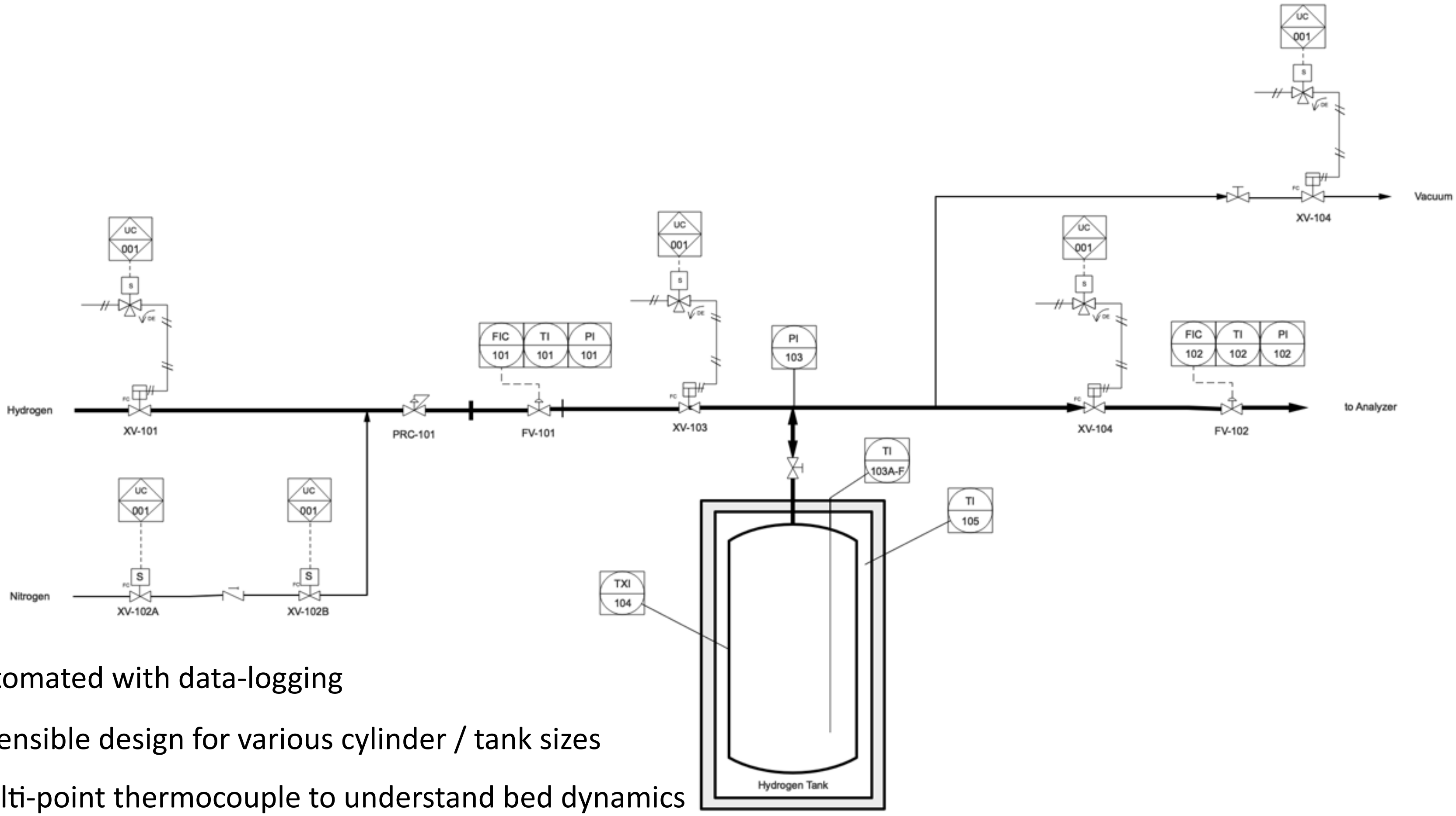
Objective Three: Manifold Design



- Automated with data-logging
- Extensible design for various cylinder / tank sizes
- Multi-point thermocouple to understand bed dynamics
- Full-Scale thermal property measurement (heat capacity, thermal conductivity, Q_{st})
- Full analysis unit

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Project	DOE H2 storage		
Description	DOE Phase II Hydrogen Storage		
Drafter	AMR	Reviewer	JS
Drw	Rev B	Date	11/22/19

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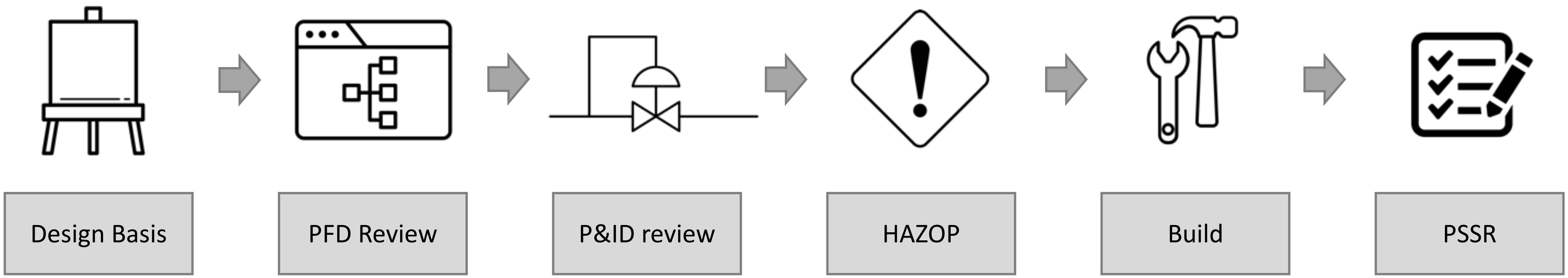
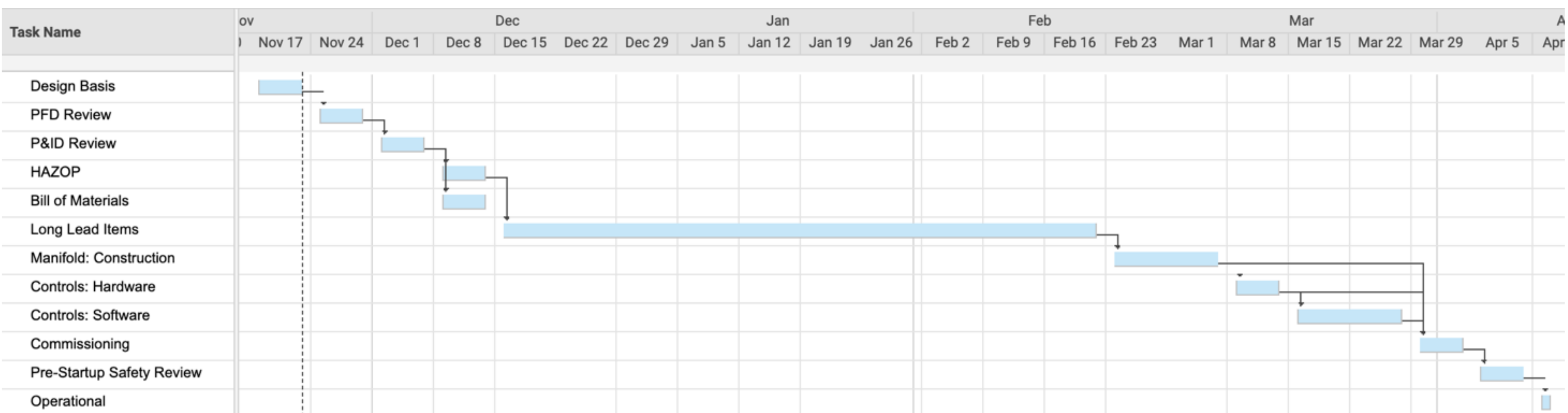
Objective Three: Initial Timeline





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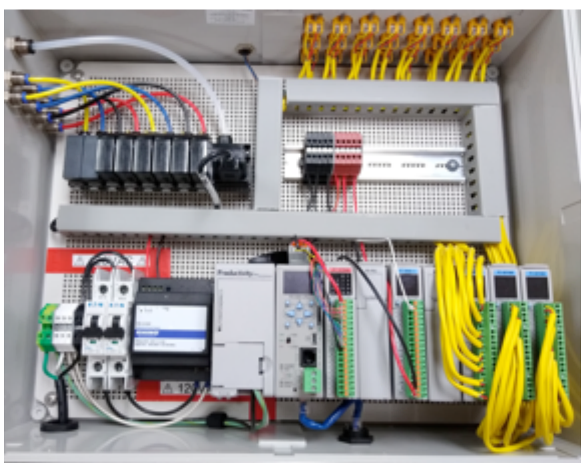
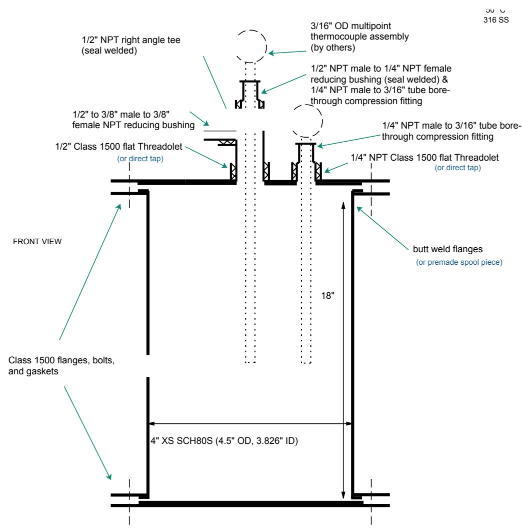
Objective Three: Current Progress

- Manifold Online Targeting: July 1st
- Still needs:
  - Analytic setup (mass spec delivery June 1st)
  - Safety testing
  - Inert gas pressure testing

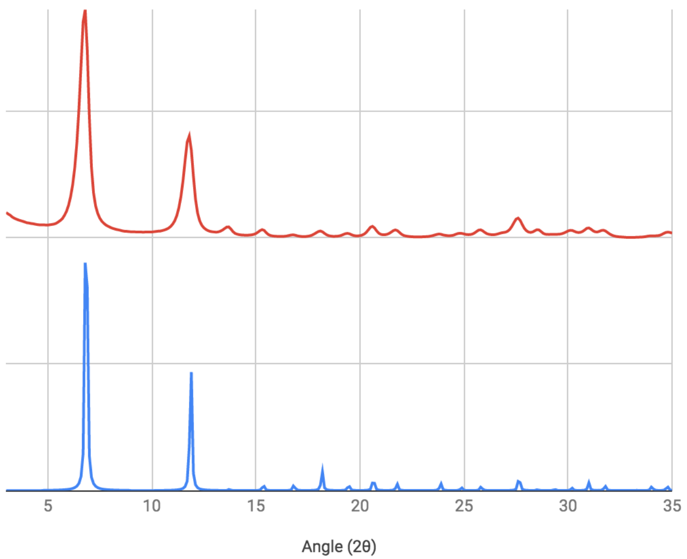




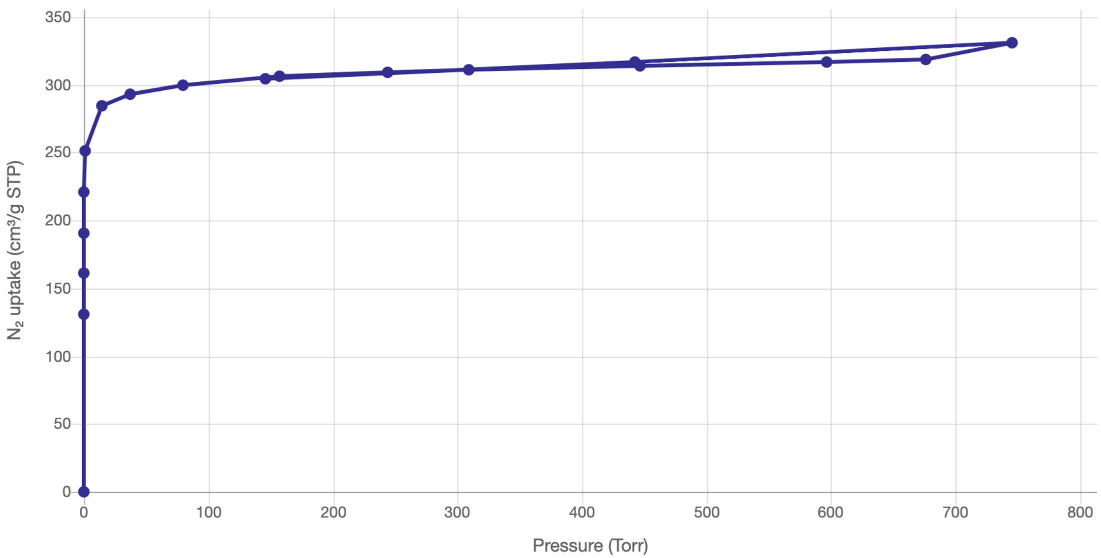
Objective Four: Synthesis and Small-Scale Formation of Relevant MOFs

- Ni_2-mdobdc has been synthesized
- Material synthesis validated by PXRD and measurements of surface area.

PXRD



N_2 isotherm



- Multigram synthesis at the 2-liter scale successful
- Pelletization studies ongoing

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Summary

- Objective One (100 % complete)
  - Relevant MOFs Scaled
  - Material Produced on demand
- Objective Two (80 % complete)
  - Three formation techniques developed for prototype system (pelletization, puck formation, multiphase packing)
- Objective Three (40 % Complete)
  - Manifold close to being complete
  - Techniques to achieve packing of prototype validated
- Objective Four (40 % complete)
  - One MOF produced
  - Formation tests targeted
- Objective Five (25 % complete)
  - IP and publication strategy solidified
  - Establishing how learnings can be applied to other volumetric solutions

Future Work: Phase II Year Two

- To date work has focused on techniques that improved system weight and volume of an adsorbent based hydrogen storage system (Barrier 3.3.5A).

- Under the second year of this project, the consequences of this optimization will be understood on other associated barriers. NuMat's prototype system will be used to evaluate several barriers.

The barriers that will be addressed include,

- System Cost (3.3.5B)
- Durability/Operability (3.3.5 D)
- Charging Discharging Rates (3.3.5 E)
- Thermal Management (3.3.5 J

- Further optimization will be carried out using the prototype system

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

Reviewers' Comments

- This project was not reviewed last year