Title:

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

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Overview of Phase One SBIR

- Timeline and Budget
  - Project start date: 4/9/18
  - Project end date: 10/8/18
  - Total Budget $149,500
- Partners

  No partners currently
- Barriers[1]
  - 3.3.5 A. System Weight and Volume
  - 3.3.5 B. System Cost

1) http://energy.gov/eere/fuelcells/downloads/fuel-cell-technologies-office-multi-year-research-development-and-22

Project Abstract

Techniques to increase the density of porous materials including metal-organic frameworks (MOFs) are needed if porous materials are to realize their potential in volumetric hydrogen storage. Improvements in volumetric storage will bring porous materials closer to adoption in fuel cell electric vehicles (FCEVs). Considerable research effort has been deployed in the discovery of porous materials for hydrogen storage in FCEVs. In contrast, a relatively small amount of time has been invested in improving the volumetric storage of these porous materials. As a result, this is now seen as one of the key weaknesses in bringing this technology to market. Under this grant, NuMat Technologies (NuMat) will address this problem by developing formation techniques to significantly enhance the volumetric hydrogen storage capacity of MOFs. A range of generalizable techniques that can be applied to a wide range of MOFs will be developed under this SBIR at NuMat. This will be achieved utilizing the preexisting foundation in formation techniques that has already been established at NuMat. Most importantly, increases in density of packed hydrogen storage MOFs will be accomplished without adversely altering performance.

NuMat is a company dedicated to the commercialization of adsorbent-based systems that utilize MOFs. To achieve this goal a multidisplinary has been assembled that includes chemists, engineers, adsorption specialist and commercial product managers. This team has successfully developed ION-X®, a platform for low-pressure gas densification and the first MOF-enabled product in the world. While the promise of MOFs has been well documented in academia, commercialization complexities exist in the ability to form, package, and activate MOFs into fully integrated systems. As an application developer with MOF expertise, NuMat has extensive experience in designing engineered adsorption systems and is uniquely positioned to successfully achieve project deliverables. For example, through optimizing formation techniques in ION-X® product, generated significant know-how and intellectual property in densification techniques. This work has continued through our development of next generation separation systems which require tight controls of particle size and packing densities in a sieve bed. Critically, NuMat is the only company in the world with a ISO 9001 certified assembly line dedicated to integrating MOFs into gas storage and separation systems. This work will develop further under this SBIR with a focus on volumetric hydrogen storage for FCEVs.

This SBIR will serve as a stepping stone to transition MOFs to large scale volumetric storage applications, primarily hydrogen storage in FCEVs. NuMat's commercial team develop an integrated go-to-market strategy in coordination with key partners, including hydrogen producers, tank and car manufacturers. Phase two of this SBIR will focus on the scaling of the densified MOF systems identified for use in FCEV, in collaboration with commercial partners. Results of this SBIR have the potential to be utilized in other commercial sectors where volumetric gas storage is required, including oxygen and methane storage applications in the medical sector and transportation sector, respectively.

Relevance: Hydrogen Storage

- Primary Goals:
  1. Maximize volumetric packing density of MOFs through densification techniques.
  2. Improve volumetric packing density without altering underlying properties of the MOF (Surface area and hydrogen storage).
  3. Evaluate if the techniques developed can be transferred to other MOFs.

- Key DOE Target
  - 2020 targets: volumetric capacity of 40g/L (1.3 kWh/l)
  - Ultimate target: 50 g/l (1.7 kWh/l)
- Relevance
  1. MOFs are potential adsorbent material that could be used to achieve DOE targets.
  2. To realize the potential of these materials their volumetric density must be enhanced.
  3. The techniques developed here will be transferable to other MOFs.

Approach: Four Key Objectives

Objective One: Synthesis

Produce up to five kilograms of porous material

- Synthesis optimization
- Production of three selected MOFs
- Evaluation of materials

Objective Two: Formation

Evaluate packing of selected MOFs

- Pressurization techniques including pelletization and extrusion
- Pressure free techniques including multiphase packing and slurry based packing
- Combination of multiple techniques

Objective Three: Validate

Transfer knowledge to one relevant MOF

- Identify a MOF to evaluate transferable nature of packing techniques
- Evaluate established packing techniques on selected MOF

Objective Four: Plan

Develop a commercialization plan

- Develop a cost model for scaling formation techniques
- Establish Phase two plan

Keys to Approach Success: Team, Facilities, and Collaboration

- **Knowledge**
  - NuMat’s team is comprised of over twenty individuals with experience in engineering, chemistry, and, business development.
  - NuMat’s team has developed extensive knowledge in the areas of MOF synthesis, formation, and commercialization over the past five years.
- **Facilities**
  - NuMat technologies has over 10,000 square feet of laboratory space
  - This space has dedicated areas for the synthesis, scale-up, and Formation of MOFs
- **Collaboration**
  - NuMat is working to establish collaborations with NREL and HyMARC to validate materials synthesized

THE LINDE GROUP

VERSUM MATERIALS

Keys to Approach Success: ION-X

First MOF based commercial product developed by NuMat, ION-X

- A MOF based gas delivery product used in the semiconductor industry
- Used to deliver AsH_3, PH_3, and BF_3 sub-atmospherically.
- key gases used in the doping of semiconductors
- Offers advantages over incumbent product
- Signed key distribution agreement with commercial partner for distribution,
  Versum materials

How

- MOF Discovery: Materials for adsorption were discovered
- Scale-up: Selected materials have been scaled
- Application Development: How do you package the material, activate it, and test it.
- Commercialization: Getting the product in the hand of customers.

NuMat's Product Launch Highlighted in Chemistry World

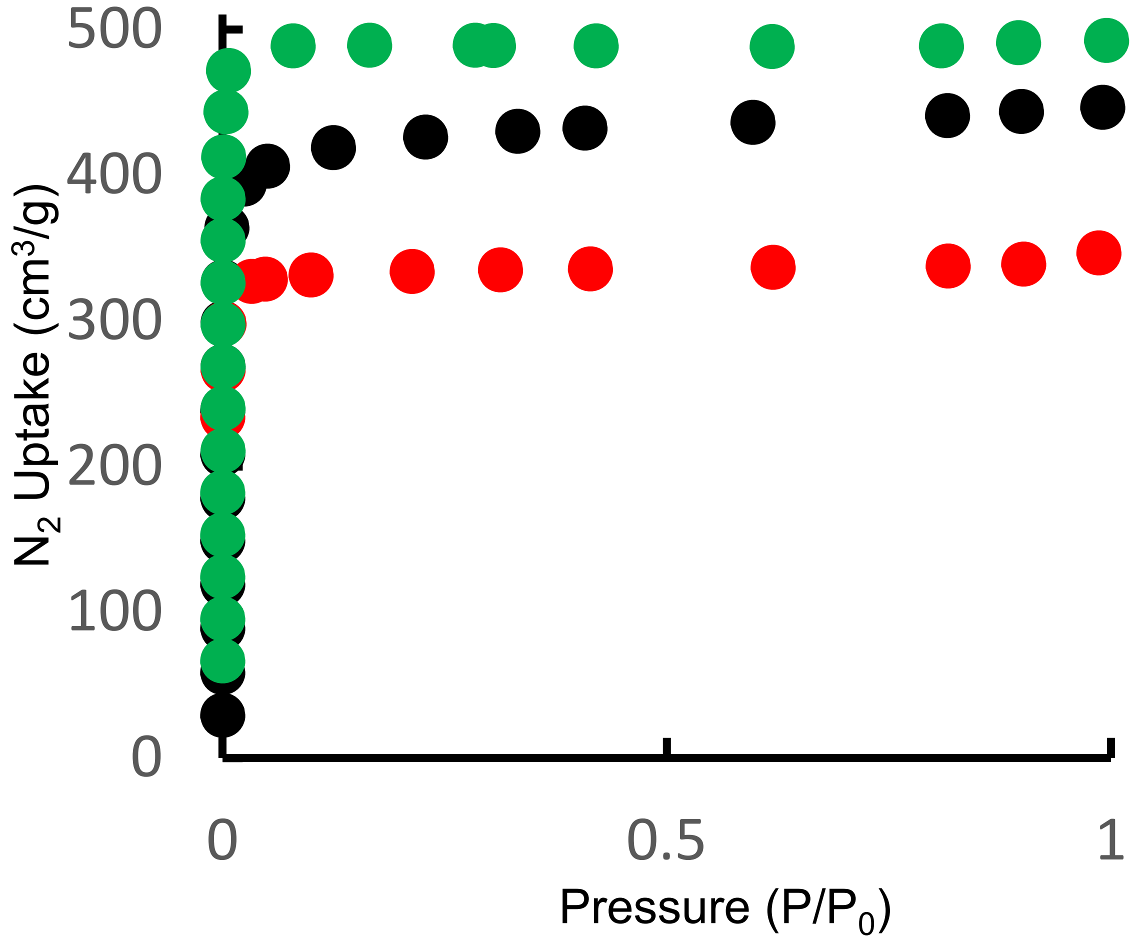
OCTOBER 2016

Feature on NuMat's innovative sub-atmospheric storage system for hazardous gases.

Approach: Timeline

Objective	Task	Title	Start	Finish	Month 1	2	3	4	5	6
1		**Produce up to 5 kg of porous materials**								
	1.1	Synthesis Optimization of three MOFs	0	1						
	1.2	Production of targeted MOFs	0	4						
	1.3	Characterization of Materials	1	4						
2		**Evaluate packing of benchmark MOFs**								
	2.1	Evaluate the role of pressure in achieving higher packing density	1	3						
	2.2	Tamping	1	3						
	2.3	Evaluate multiphase packing experiments	1	3						
	2.4	Evaluate slurry packing	1	3						
	2.5	Evaluate complimentary packing techniques	2	4						
	2.6	Crystal size	2	4						
	2.7	Evaluate the role of additives in the compaction of MOFs	3	4						
3		**Transfer knowledge to one relevant MOF and provide samples**								
	3.1	Identify High performing MOF in collaboration with HyMARC and validate developedformation protocols	0	2						
	3.2	Synthesize and densify high performing MOF	2	5						
	3.3	Provide samples of formed MOFs	5	6						
4		**Develop commercialization plan**								
	4.1	Develop cost model for scaled formation processes	4	6						
	4.2	Develop agreements with commercial partners	3	6						
	4.3	Develop key goals for future success	5	6						

Accomplishments and Progress: MOF Synthesis



NuMat-14
Expected N_2 uptake =500 cm^3/g

NuMat-18
Expected N_2 uptake =440 cm^3/g

NuMat-4
Expected N_2 uptake =340 cm^3/g

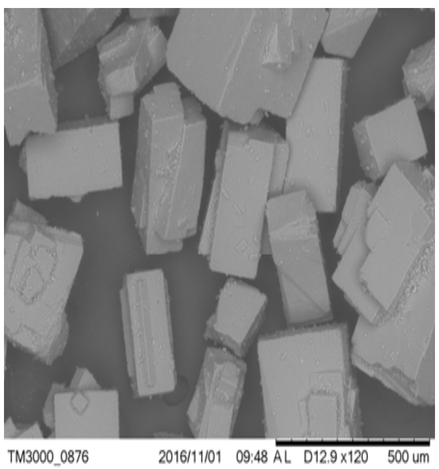
- Selected MOFs have been synthesized.
- Benchmark MOFs have been synthesized and characterized at the small-scale.

Accomplishments and Progress: MOF Size Characterization

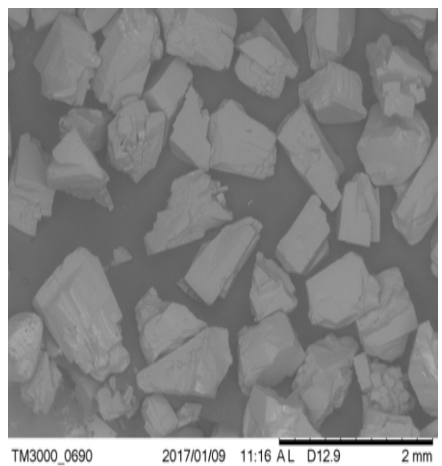
NuMat-14 – Sieve analysis

Reaction #	0-150 µm	150-500 µm	500-1000 µm	1000-2000 µm	2000-2360 µm	2360 µm+
Size analysis	8	13	30	28	9	12

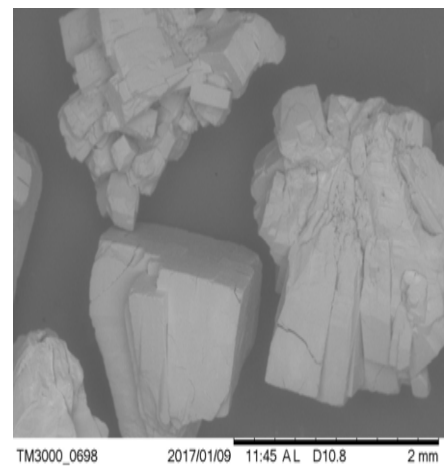
SEM



150 – 500 µm



500 – 1000 µm



1000 – 2000 µm

- Size control of select MOF can be achieved.
- Crucial to achieving formation goals.

Remaining Challenges and Barriers

Remaining challenges of phase one work

- MOFs scaling will be optimized
- The formation of benchmark MOFs will be evaluated by the techniques outlined
- The transferable nature of established formation techniques will be evaluated
- Collaborations will be established
- Phase two plan will be determined

Barriers to completion of phase one work

- No barriers to the completion of phase one work have been identified at this point

Future Work: Phase One

- Phase one: Complete outlined tasks on the schedule provided.

Objective	Task	Title	Start	Finish	Month					
					1	2	3	4	5	6
1		Produce up to 5 kg of porous materials	0	4						
2		Evaluate packing of benchmark MOFs	1	4						
3		Transfer knowledge to one relevant MOF and provide samples	0	6						
4		Develop commercialization plan	3	6						

Any proposed future work is subject to change based on funding levels

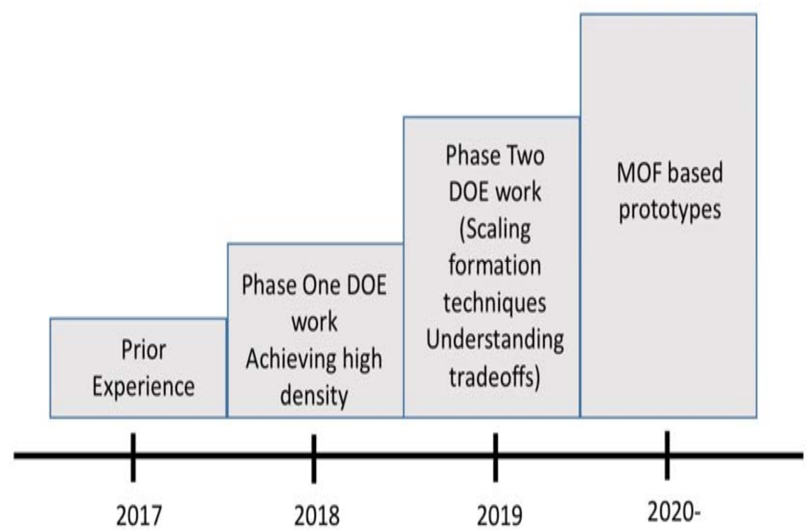
Future Work: Formation Efforts will be Key to Hydrogen Storage Products

- Phase One will serve as a stepping stone for future work in the area of formation for hydrogen storage solutions and a wide range of commercial applications being developed by NuMat.

Key Tasks

- Phase One
  - Evaluating a variety of packing techniques
  - Utilizing a set of three benchmark MOFs
  - Evaluate if packing techniques can be transferred
- Phase Two
  - Scaling selected formation techniques
  - Developing in-house equipment to carryout scaling of formation
  - Understand tradeoffs of high density solutions

Timeline



Any proposed future work is subject to change based on funding levels

Summary

- Under this Phase One SBIR NuMat Technologies is focusing on improving the packing density of metal-organic frameworks for volumetric hydrogen storage.
- Three benchmark MOFs will be used for this study, these MOFs have already been synthesized on the small scale in the initial weeks of the proposal.
- Formation techniques that will be evaluated include pelletization, extrusion, multiphase packing, and slurry based packing.
- NuMat Technologies has the personnel, experience, and equipment to carryout the goals of this SBIR.