

High-Capacity and Low-Cost Hydrogen-Storage Sorbents for Automotive Applications

PI: Hong-Cai Zhou

Texas A&M University

Co-PI: D.J. Liu

Argonne National Laboratory

ID# ST121

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Overview

Timeline

- Project Start: June 2015
- Project Length: 3 years

Budget

- Total Project Budget: \$1,115,617
 - Total Recipient Share: \$0
 - Total Federal Share: \$1,115,617
- Percent Complete:0%

Barriers

- A. Inadequate hydrogen uptake
- J. Inadequate thermal conductivity
- O. Inadequate understanding of adsorption processes

Partners

- DOE: Sponsor and Funding
- Argonne National Lab
- Texas A&M University

Relevance

- Design and synthesize new materials which meet DOE gravimetric and volumetric targets while being cost-effective
- Thoroughly study the effect of open metal sites on hydrogen adsorption
- Analyze the possibility of using highly porous engineered carbons as a binder to improve packing density and thermal conductivity

Milestone/ Decision Point	Quarter	Description
D1	12	Demonstrate one material with $0.075 \text{ kg}_{\text{H}_2} / \text{Kg}_{\text{sorbent}}$
M5	18	Demonstrate >30% increase in packing density or 2x increase in thermal conductivity
D2	24	Demonstrate one Material with $0.10 \text{ kg}_{\text{H}_2} / \text{Kg}_{\text{sorbent}}$ and $0.05 \text{ kg}_{\text{H}_2} / \text{L}_{\text{sorbent}}$
M10	36	Demonstrate material with suitable uptake to allow for a system capacity of $0.055 \text{ kg}_{\text{H}_2} / \text{Kg}_{\text{system}}$ and $0.040 \text{ kg}_{\text{H}_2} / \text{L}_{\text{system}}$

Approach

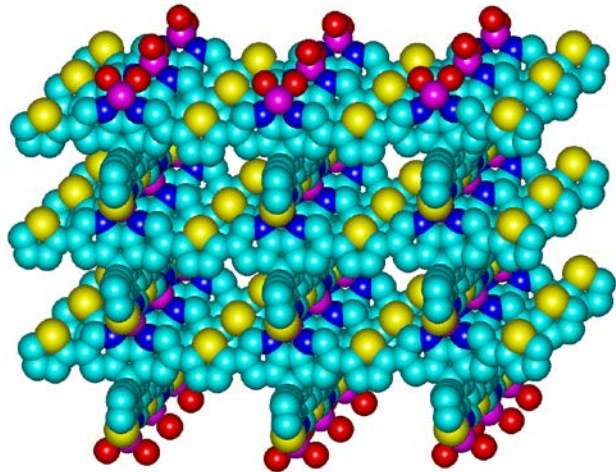
Year 1 consists of new materials discovery and characterization of proven materials.

Demonstrate at least one of the MOF/POP sorbents with gravimetric hydrogen storage capacity reaching $0.075 \text{ kg/kg}_{\text{sorbent}}$

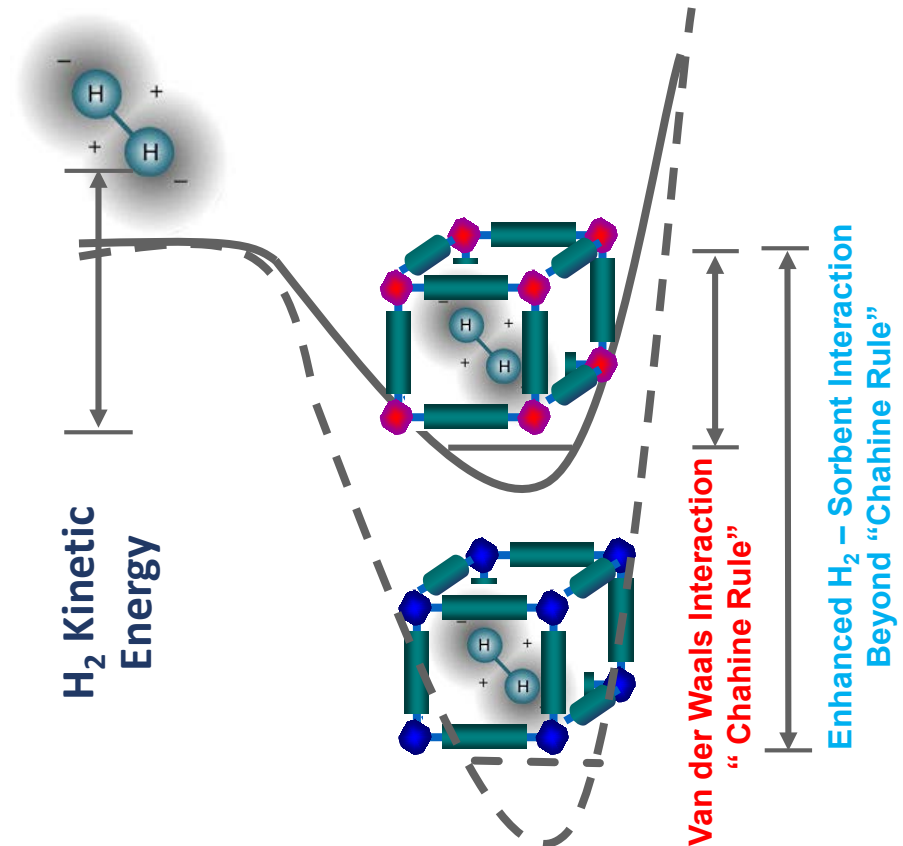
Tasks	Task Title	Milestone Type (Milestone or Go/No-Go Decision Point)	Milestone Number (Go/No-Go Decision Point Number)	Quarters from Start of the Project
3.2.1 & 3.2.2.	Development of the first batch ligand library for MOF sorbents	Milestone	M1	2
3.2.5	Advanced characterization on H ₂ -sorbent interaction using synchrotron X-ray based techniques	Milestone	M2	3
3.2.1. & 3.2.2.	Development of 1st generation of MOF sorbents for H ₂ storage	Milestone	M3	4
		Go/No-Go Decision point	D1	4

New Approach - H₂ Storage Beyond “Chahine Rule”

- Improve hydrogen – sorbent interaction through high valance metal center
- Improve hydrogen – sorbent interaction through unsaturated metal site
- Improve volumetric capacity and heat-transfer through ZIF-derived, metal doped carbons

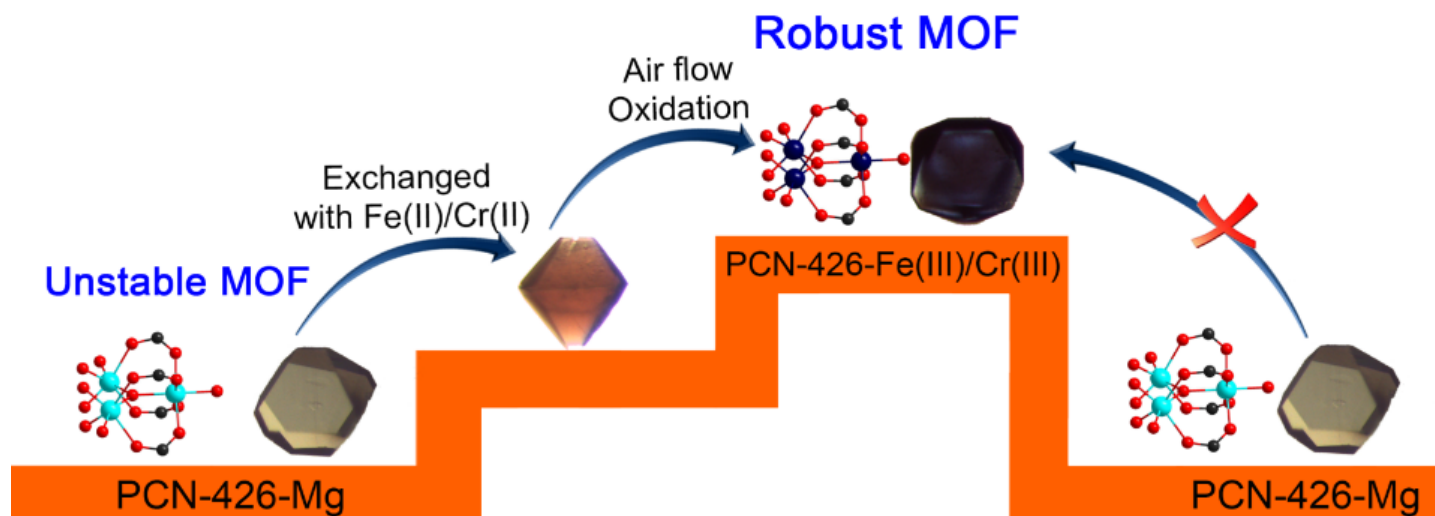


Enhancing H₂ adsorption enthalpy could improve storage uptake capacity beyond the limit by simple van der Waals interaction



Preliminary Accomplishments- MOF Synthetic Pathways

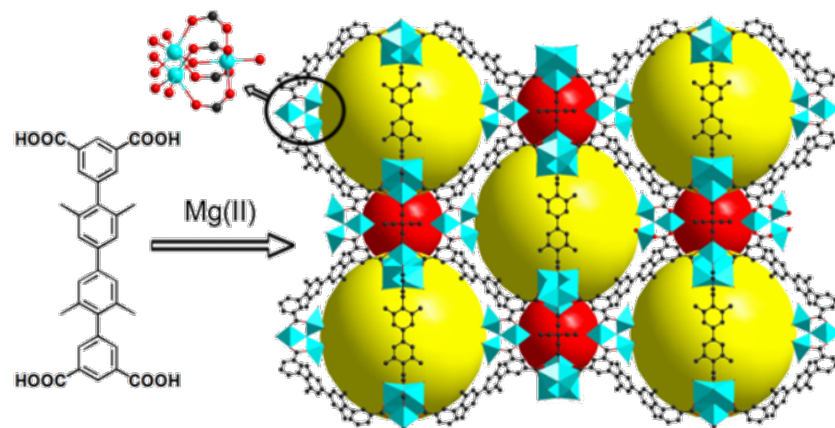
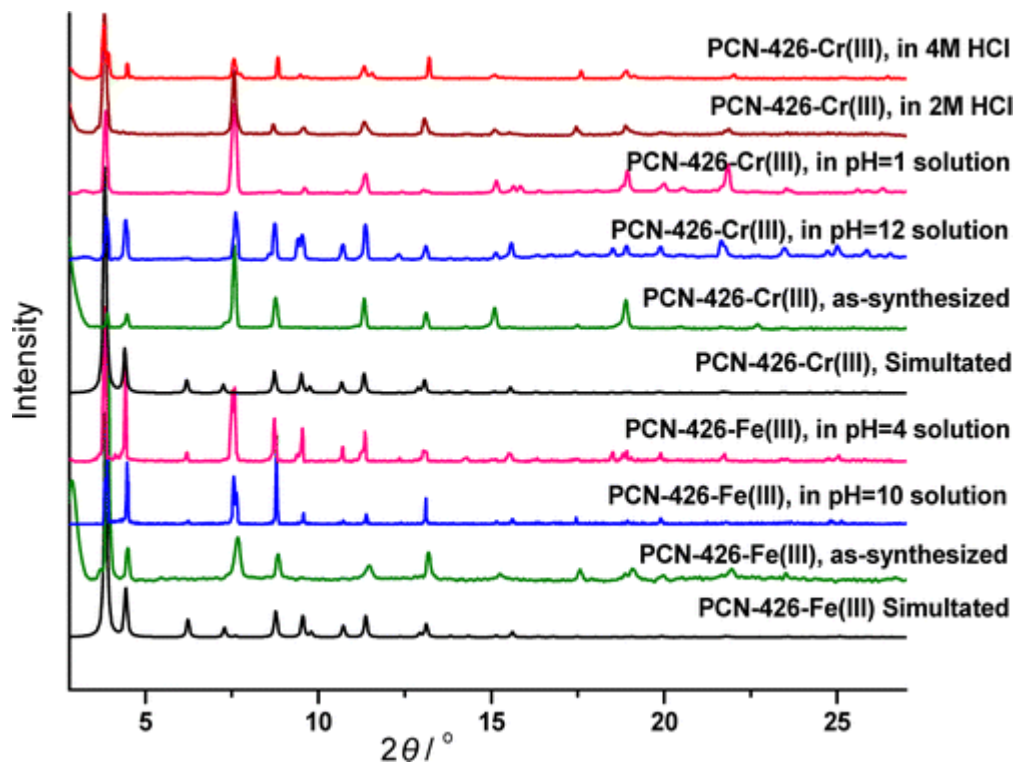
- Post-Synthetic Metathesis and Oxidation (PSMO)



- Through a sequential methathesis of labile metals and subsequent oxidation stable crystalline high valent MOFs have been obtained

Preliminary Accomplishments- Stable MOFs

- PCN-426(Fe/Cr) are synthesized through the PMSO method
- The MOFs maintain their structure across a wide PH range
- This allows for the synthesis of MOFs with rare or unreported nodes with high-valent metals

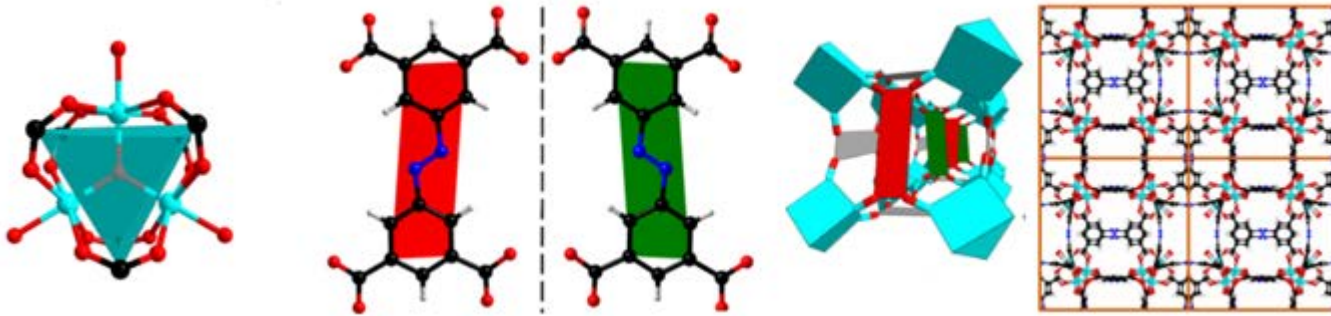


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Preliminary Accomplishments- MOF Synthetic Pathways

- Kinetically Tuned Dimension Augmentation (KDTA)

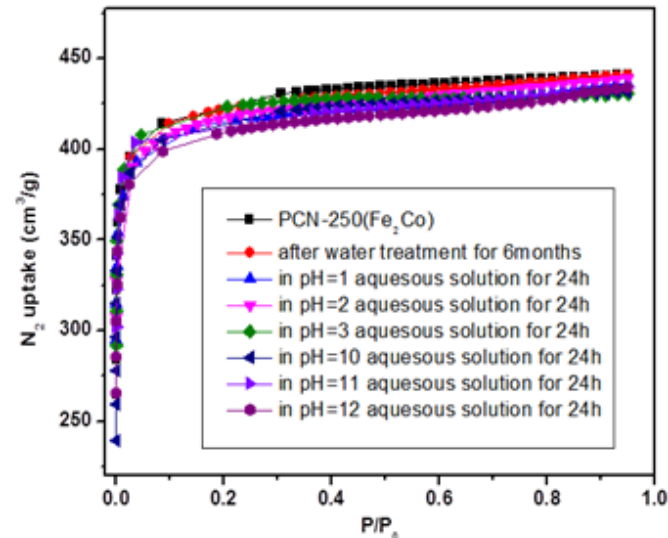
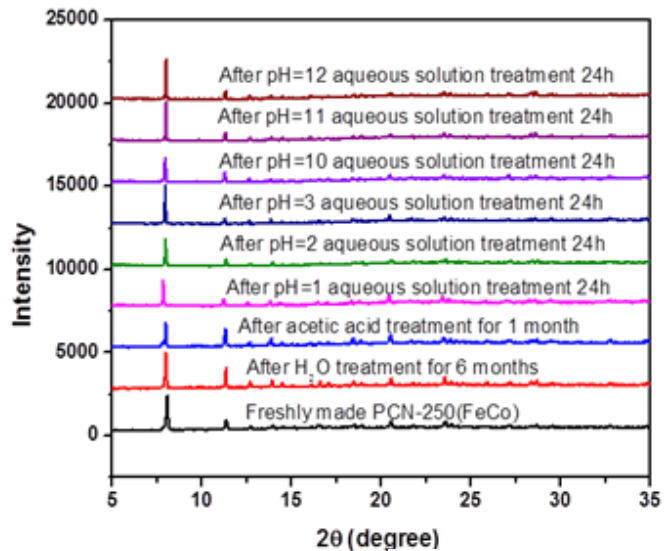
PCN-250



- Utilizing a piece by piece approach the kinetics of MOF growth can be tuned to ensure crystallinity.
- This led to 34 new Fe(III) MOFs and is highly scalable

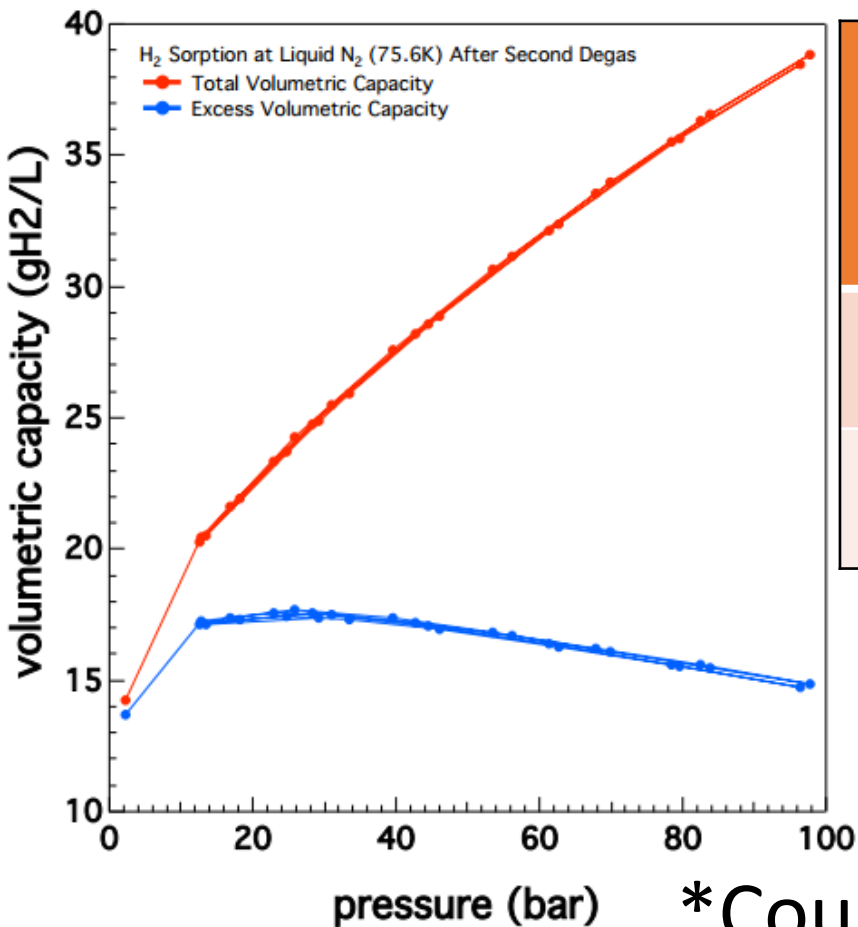
Preliminary Accomplishments- Stable MOFs

- PCN-250 is a promising example of a KDTA synthesized MOF
- Costs could be <\$50/kg to manufacture
- Extremely robust



Preliminary Accomplishments- Hydrogen Uptake

- PCN-250



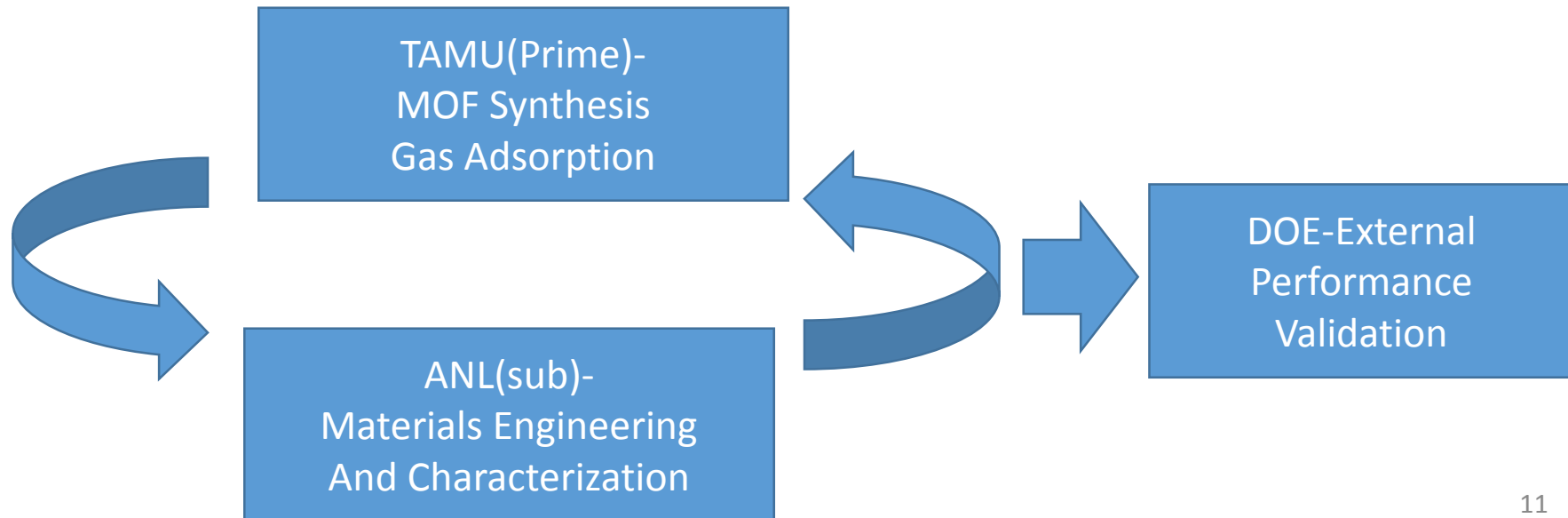
Capacity	Pressure / bar	Capacity, packing density/ g/L	Capacity, crystal density/ g/L
Volumetric capacity*	97.7	39	85
Deliverable capacity*	5– 97.7	23	50

PCN-250 exceeds the Chahine rule prediction by 50% but capacity is ~half of DOE target for packed MOF

*Courtesy of NREL

Collaboration

- TAMU will design synthesize, and characterize new materials
- ANL will perform x-ray characterization studies, develop ZDC based binding agents and perform ALD Studies
- All deliverables will be sent to DOE for external Validation

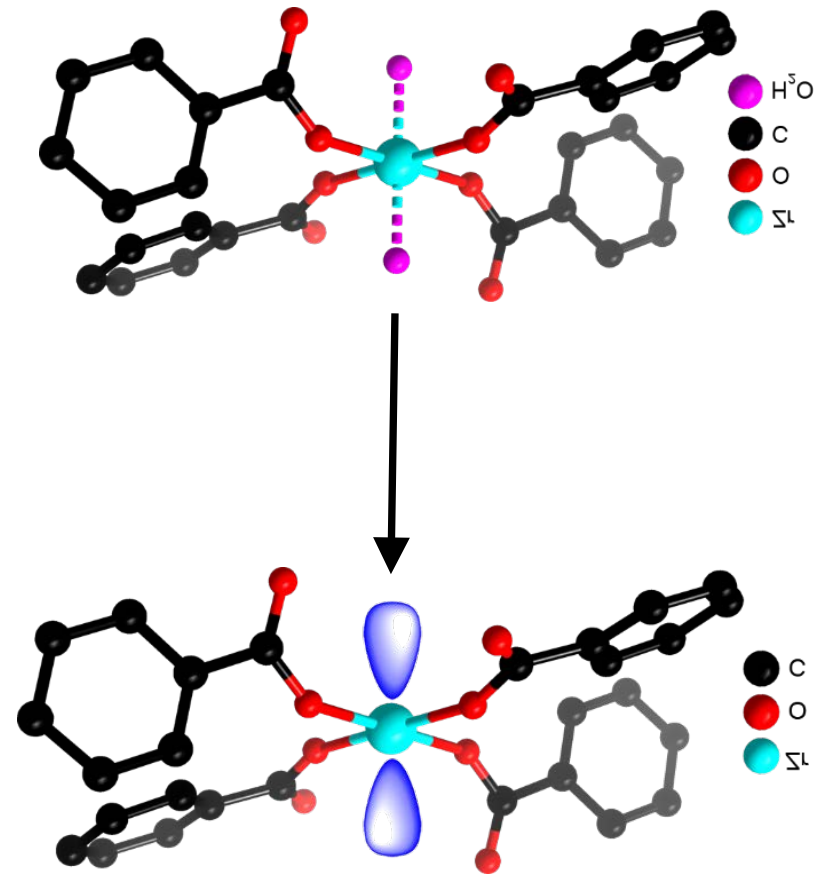


Challenges

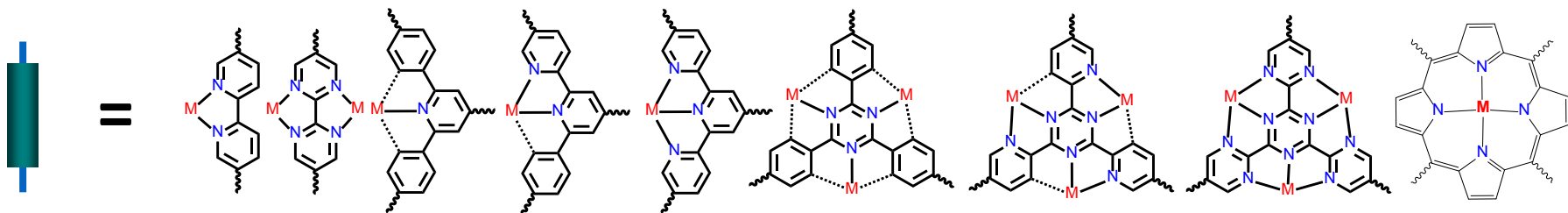
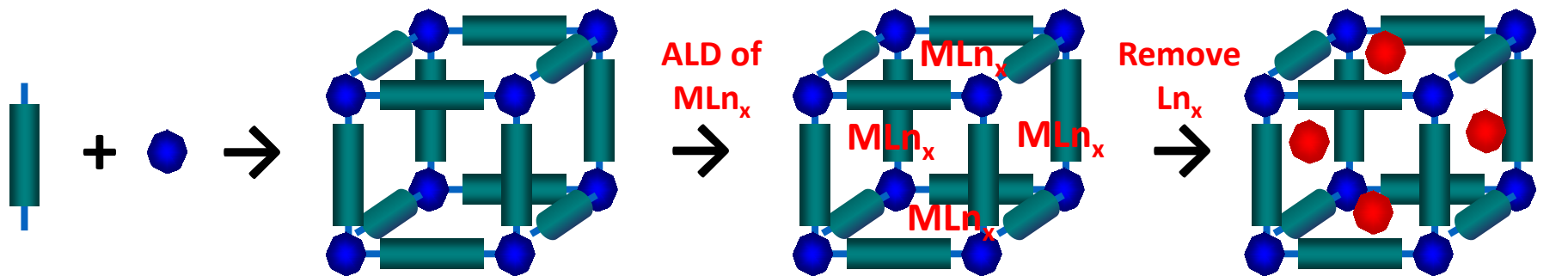
- While Chahine's Rule applies to many compounds it doesn't to others.
- Finding the determining factor other than pure surface area, such as open metal site density or pore geometry is key to overcoming current limitations
- The feasibility of scale-up and bulk physical properties must also be easily maintained from lab scale

Proposed Work-Stable MOFs with Open Metal Sites

- New MOFs with stable unsaturated nodes are under study
- Introducing a large number of open metal-sites is hypothesized to greatly increase hydrogen-framework interactions



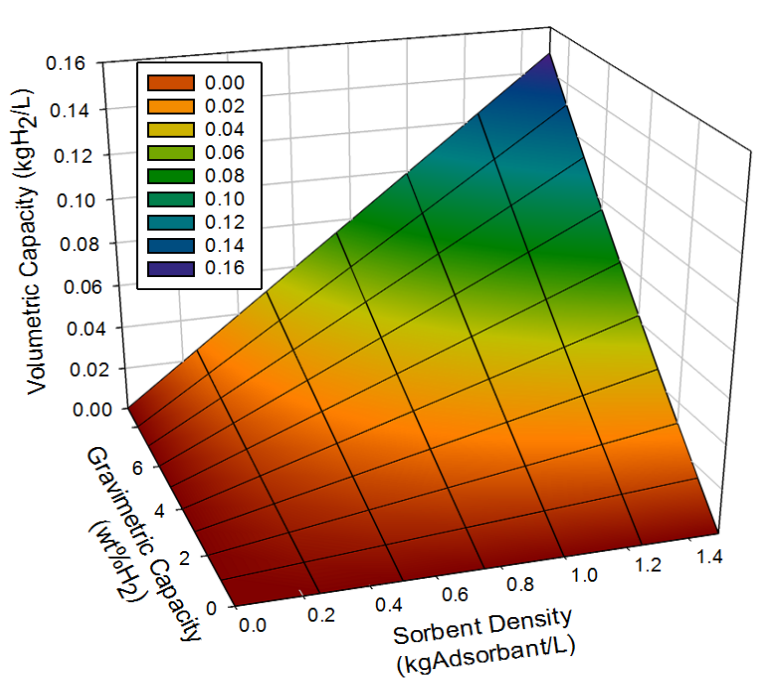
Proposed Work– Improving Adsorption Enthalpy through Unsaturated Metal Center (UMCs) in MOF by ALD



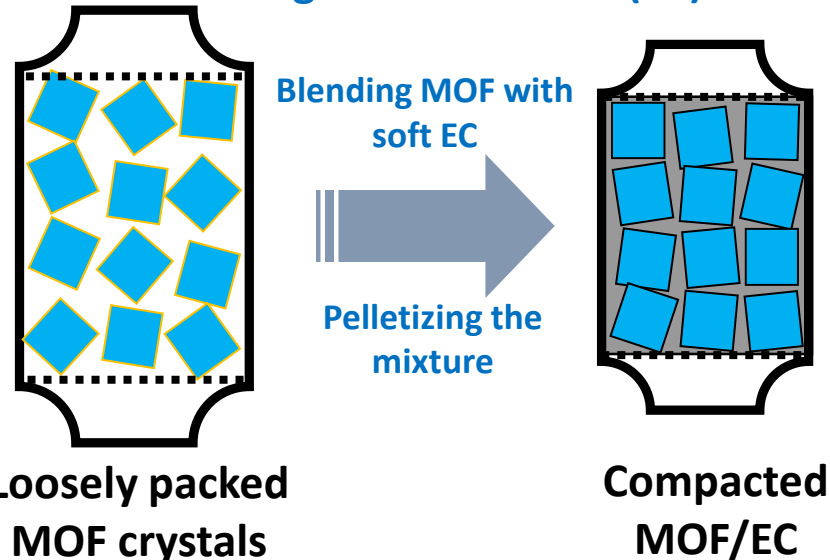
- Various N-containing ligand will be used to prepare MOF at TAMU with open chelation site to react with metal complexes
- Metal-ligand complexes can be introduced by atomic layer deposition at ANL
- UMCs can be formed after removing complex ligand to enhance H₂-adsorbent interaction

Proposed Work- Improving Volumetric Capacity & Thermal Conductivity through Engineered Carbon

Hydrogen storage volumetric capacity intertwines closely with gravimetric capacity and sorbent density



Volumetric capacity & thermal conductivity can be improved by compounding MOFs with engineered carbon (EC)



- High surface area, soft EC can be prepared from porous precursors
- EC surface can also be functionalized for H₂ adsorption

Summary

- New materials for the adsorption of hydrogen for onboard fuel use will be studied
- The effect of open metal sites will be probed through new materials discovery and ALD metal doping
- Implementation of engineered carbon based binders will be used to increase packing efficiency and thermal conductivity
- Through collaboration new composite materials will be created to meet the DOE targets