Project ID #
st145

HyMARC Seedling
Super Metallated Frameworks as Hydrogen Sponges

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Project Overview

Timeline

- Project Start Date: 09/1/2017
- Project End Date: 08/31/2018
- Percent Complete: 50%

Budget

- FY17 DOE Funding: $250,000
- FY18 Planned DOE Funding: $370,000 (assumes Go decision)
- Total DOE Funds Received to Date: $250,000

Partners

- Lawrence Berkeley National Lab
- National Renewable Energy Lab

Technical Barriers

A metal-organic framework provides an ideal platform for H_2 storage *via* physisorption due to the following characteristics:

- High porosity and interaction strength lend to material **efficiency**
- Stability at ambient temperature and low pressure indicate **durability/operability**
- Facile kinetics ensure practical **charging/discharging rates**

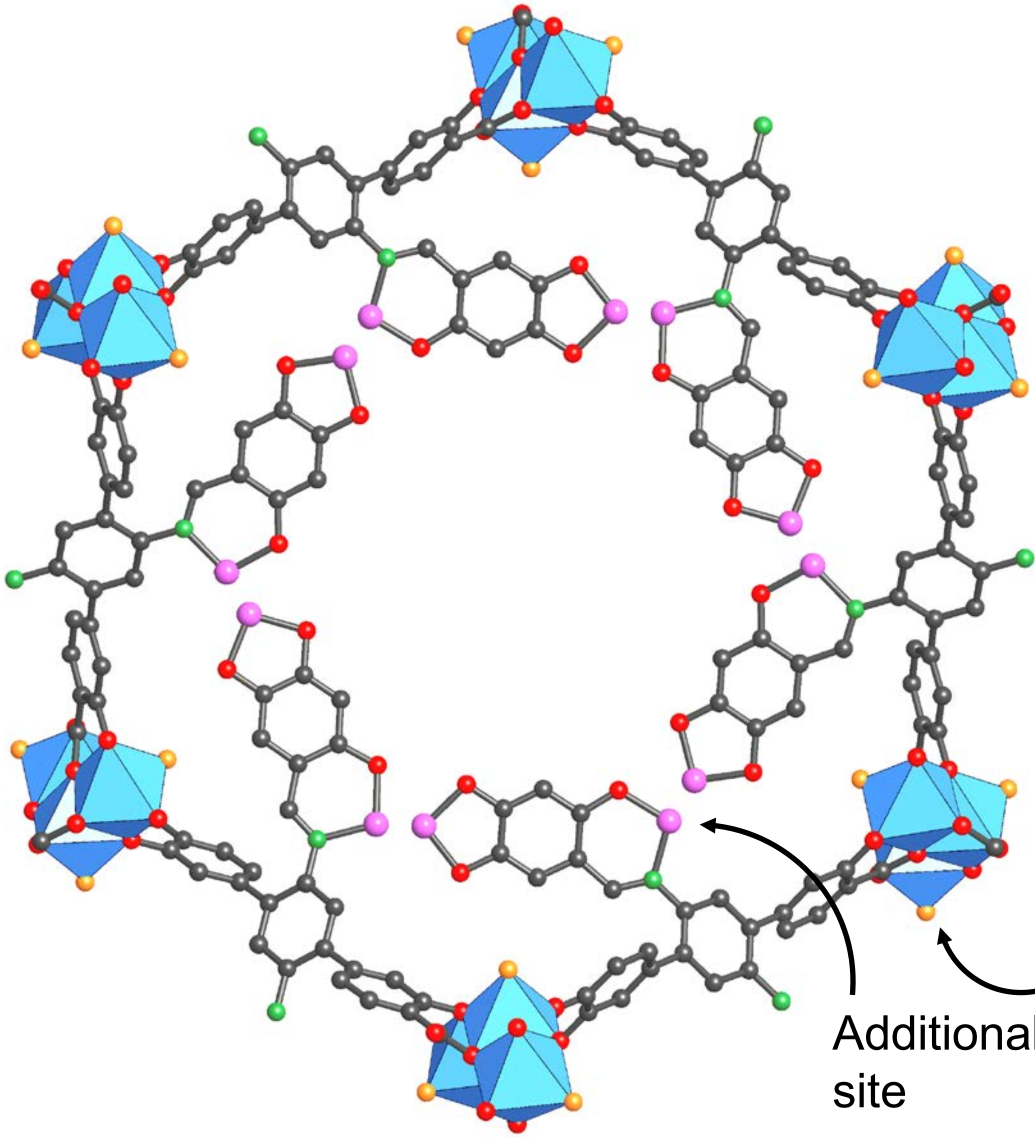
Relevance to DOE Objectives

Project Objective: We aim to produce a H_2 adsorbent capable of exceeding the 2025 DOE system targets of 40 g/L and 5.5 wt% under ambient conditions.

Motivation	Metric	Ultimate DOE Target
Improve material **efficiency** by increasing physisorptive capacity.	Gravimetric capacity Volumetric capacity	0.065 kg H_2/kg system 0.050 kg H_2/L system
Meet **durability/operability** standards for H_2 storage under ambient conditions.	Temperature Operational Life Cycle Onboard efficiency	-40 to 60ºC 1500 cycles 90%
Quantify kinetics to validate practical **charging/discharging rates**.	System fill time (5 kg) Minimum full flow rate	3-5 min 0.02 (g/s)/kW

Approach

➢ *Use of a super metallated framework as a high capacity H_2 adsorbent*



1. Design a MOF to achieve high H_2 adsorption properties.

2. Synthesize and post-synthetically modify material to install open metal sites.

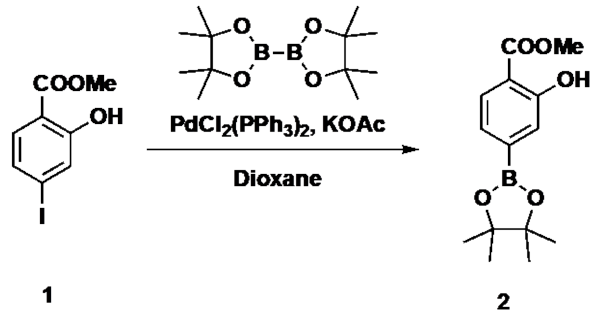
3. Use advanced characterization to quantify H_2 adsorptive capacity and provide feedback on material design.

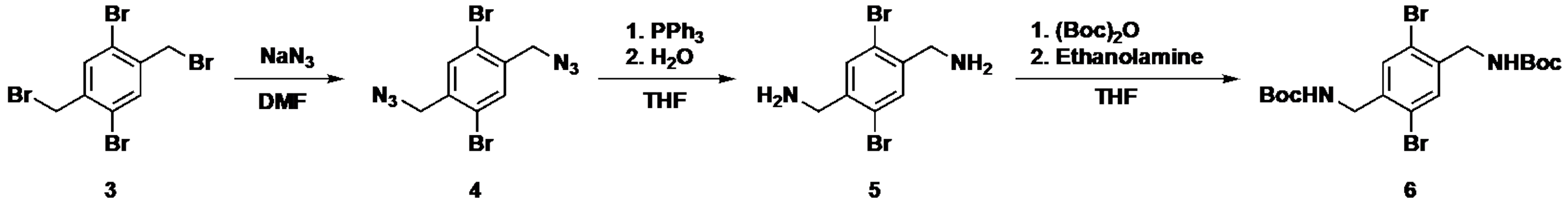
Open metal site

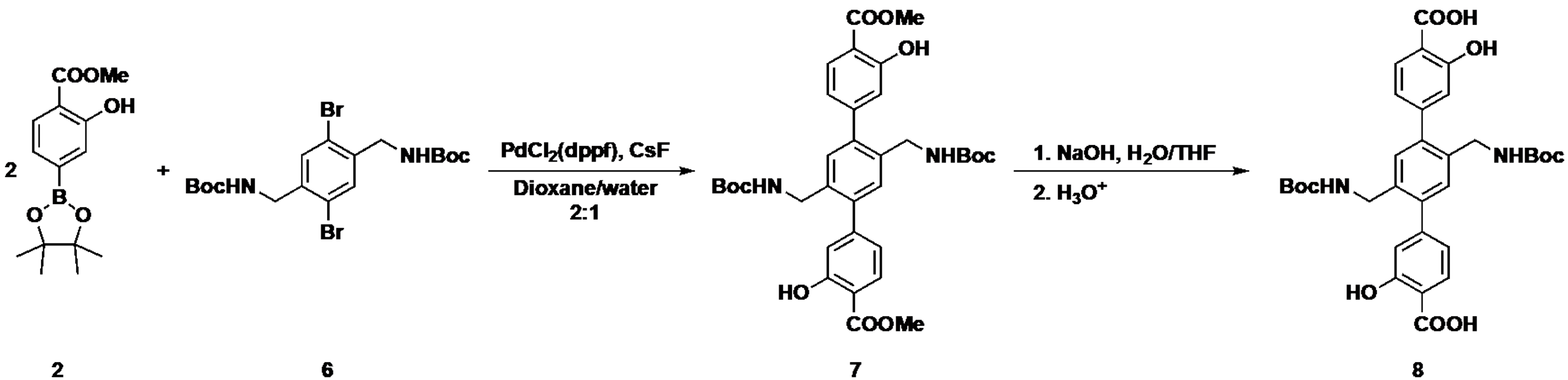
Additional open metal site

Accomplishments & Progress

- *Synthesis of an organic linker for introduction of open metal sites* via *post synthetic modification (Milestone 1.2.1)*

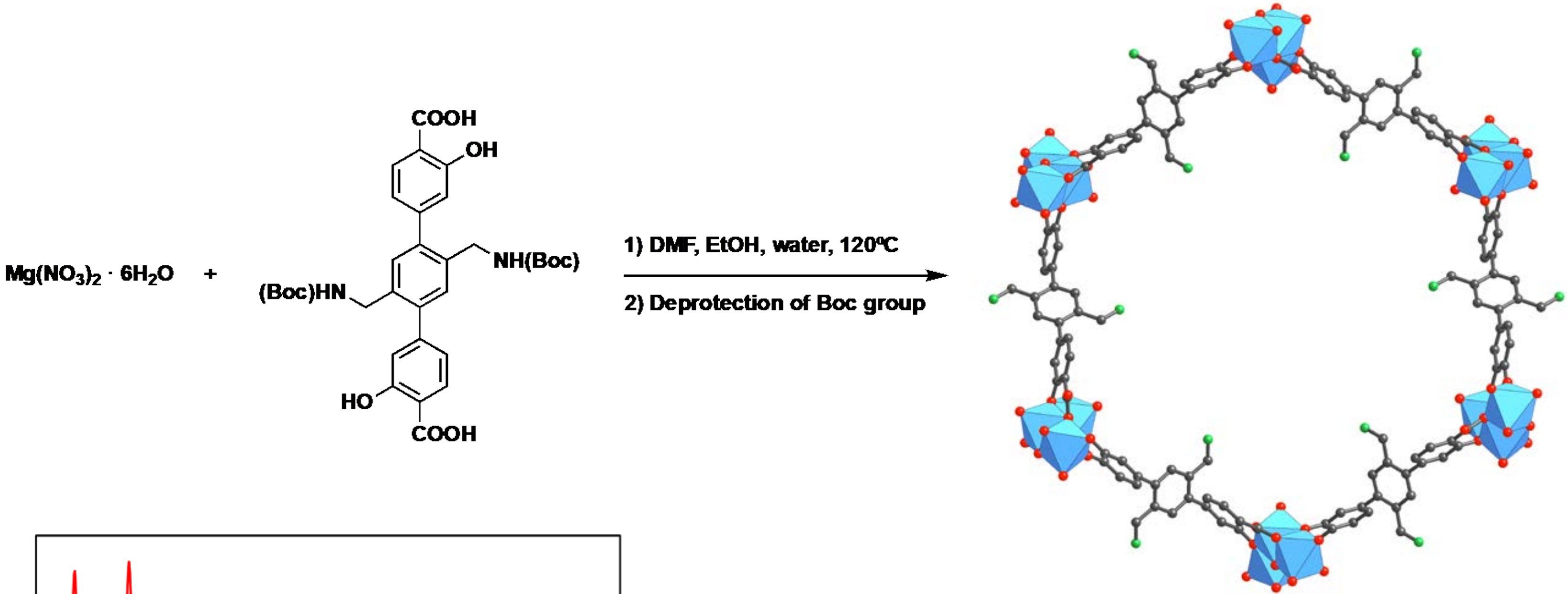




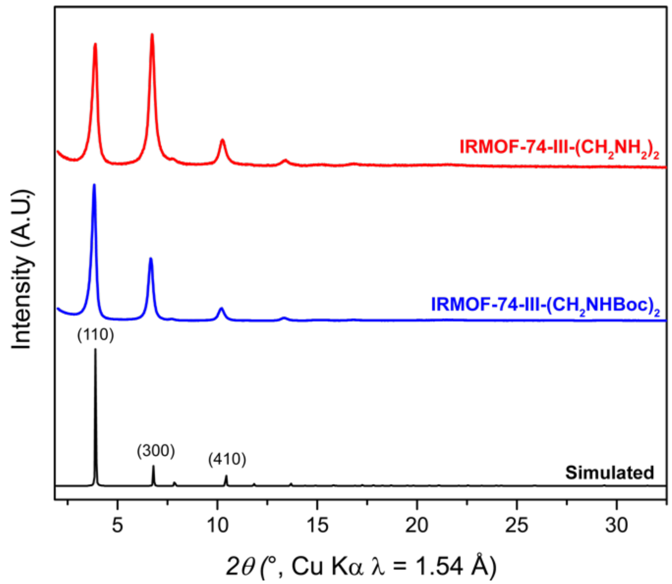


Accomplishments & Progress

- *Synthesis of isoreticular MOF-74, Mg-IRMOF-74-III-(CH_2NH_2)$_2$ (Milestone 1.2.1)*



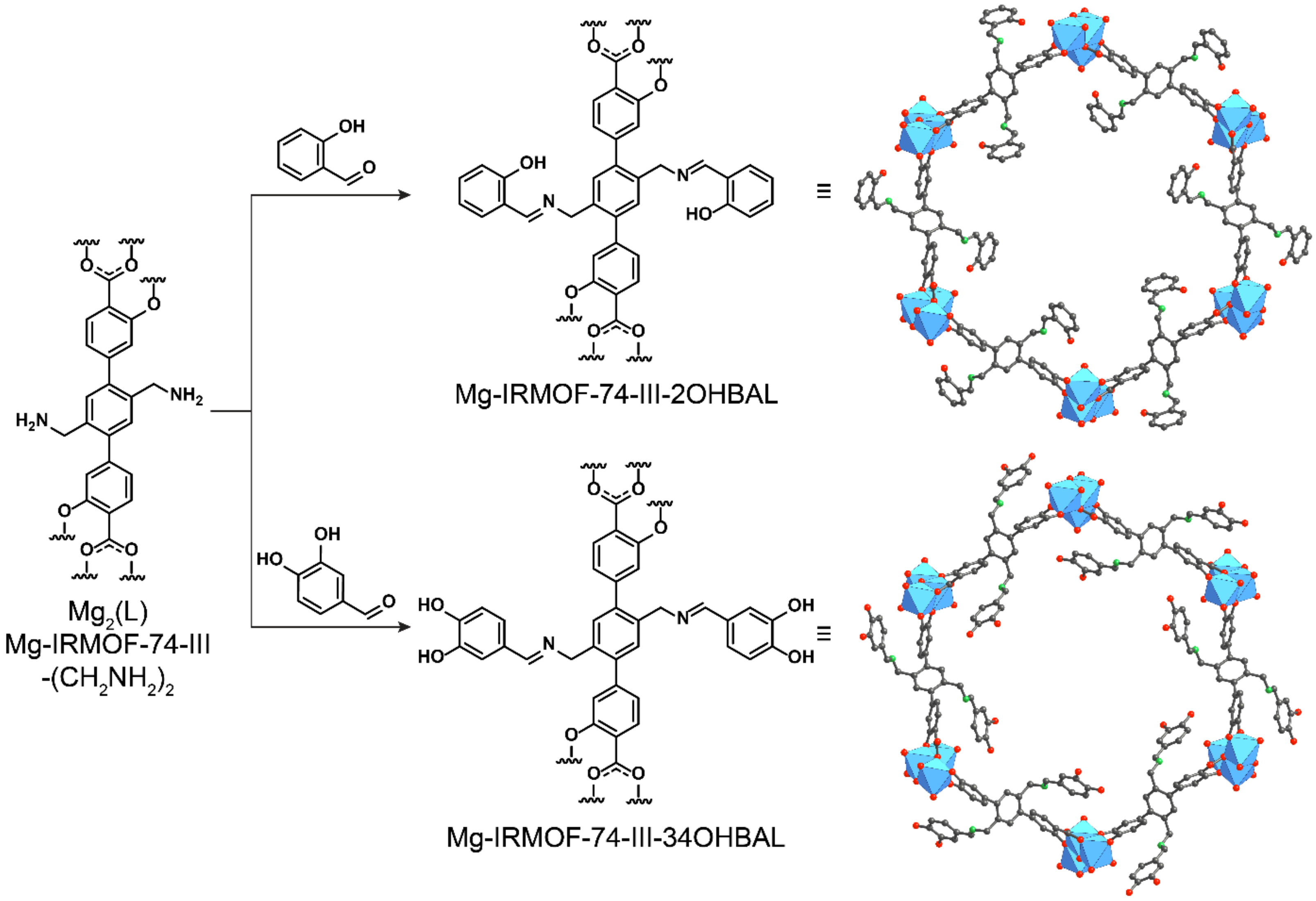
Mg-IRMOF-74-III-(CH_2NH_2)$_2$



Experimental PXRD patterns of IRMOF-74-III-(NHBoc)$_2$ and deprotected IRMOF-74-III-(CH_2NH_2)$_2$ in comparison with simulated pattern.

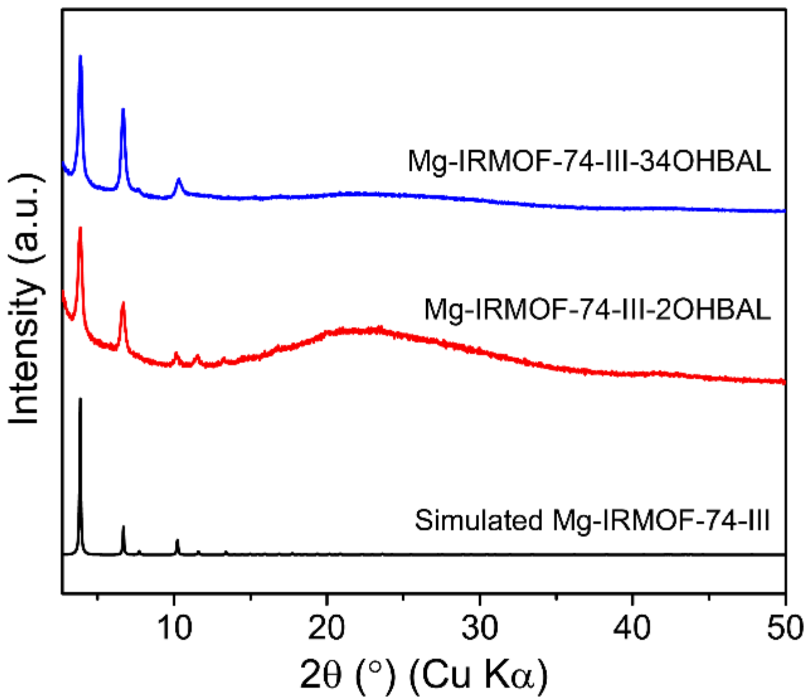
Accomplishments & Progress

- *Post-synthetic modification of Mg-IRMOF-74-III-$(CH_2NH_2)_2$ will enable installation of open metal sites (Milestone 2.2.1)*

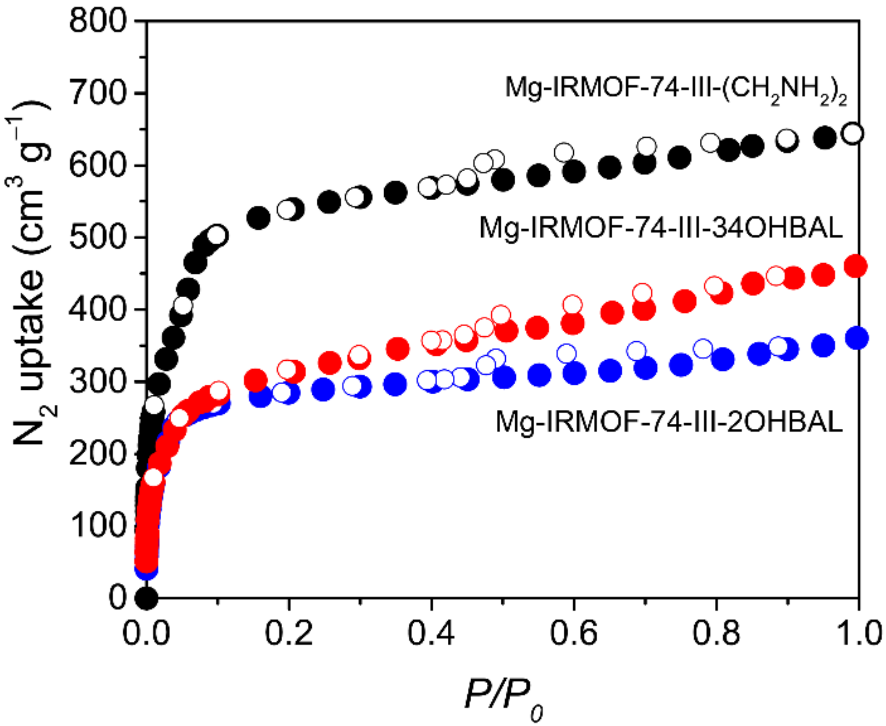


Accomplishments & Progress

- *Material characterization by powder x-ray diffraction (PXRD) and N_2 isotherms (Milestone 2.2.1)*



Experimental PXRD patterns of functionalized Mg-IRMOF-74-III-$(CH_2NH_2)_2$ in comparison with simulated patterns of Mg-IRMOF-74-III-$(CH_2NH_2)_2$.

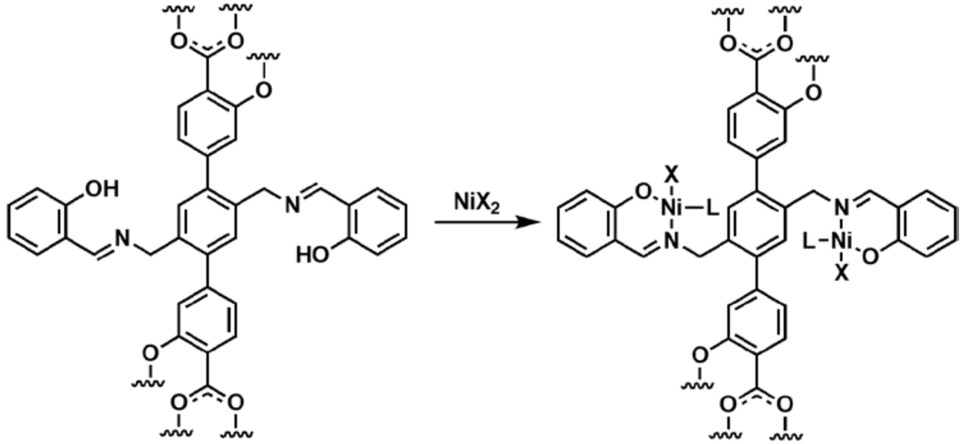


N_2 adsorption-desorption isotherms at 77 K with adsorption and desorption points represented by closed circles and open circles, respectively ($P/P_○$, relative pressure).

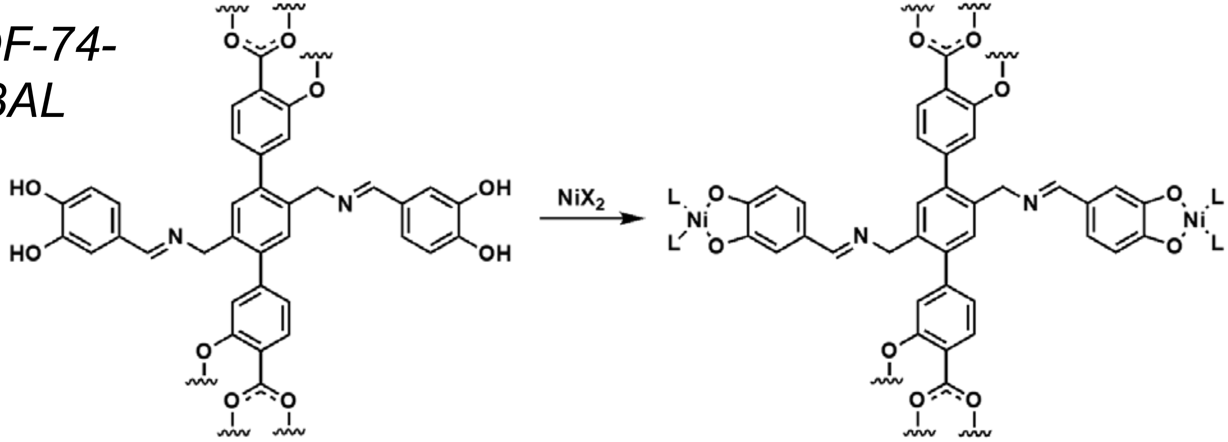
Accomplishments & Progress

- *Metallation with Ni(II) salts to achieve additional open metal sites (Milestone 3.2.1)*

Mg-IRMOF-74-III-2OHBAL



Mg-IRMOF-74-III-34OHBAL



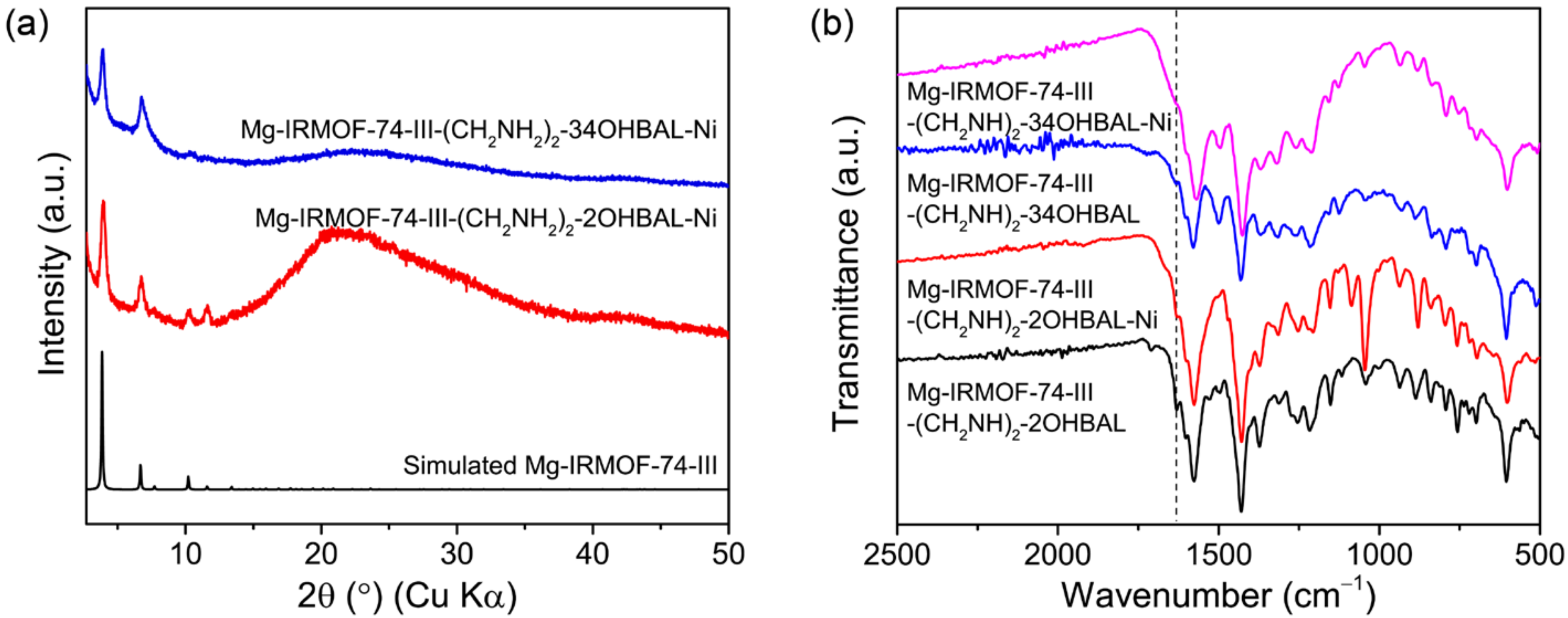
Accomplishments & Progress

➢ *Characterization of super metallated framework by inductively coupled plasma (ICP) analysis shows addition of open metal sites (Milestone 3.2.1)*

MOF	Ni salts	Ni/Mg molar ratio
Mg-IRMOF-74-III-2OHBAL	$Ni(OAc)_2{\cdot}4H_2O$	0.43
	$NiCl_2{\cdot}$glyme	0.09
	$Ni(NO_3)_2{\cdot}6H_2O$	0.06
Mg-IRMOF-74-III-34OHBAL	$Ni(OAc)_2{\cdot}4H_2O$	0.44
	$NiCl_2{\cdot}$glyme	0.22
	$Ni(NO_3)_2{\cdot}6H_2O$	0.33

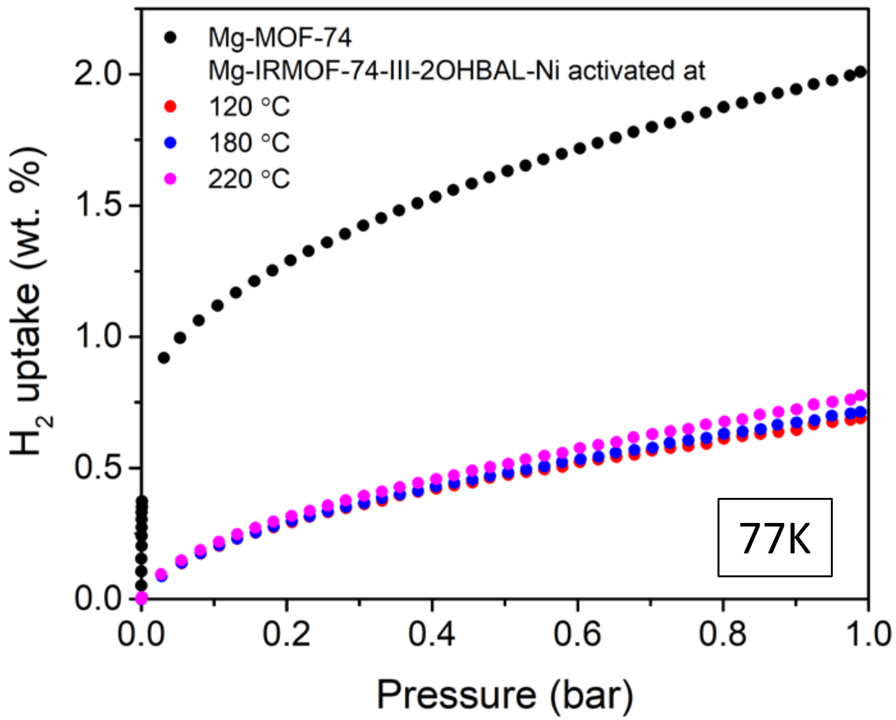
Accomplishments & Progress

- *Characterization of super metallated MOF by (a) PXRD and (b) FT-IR shows retained crystallinity and covalent linkages (Milestone 3.2.1)*

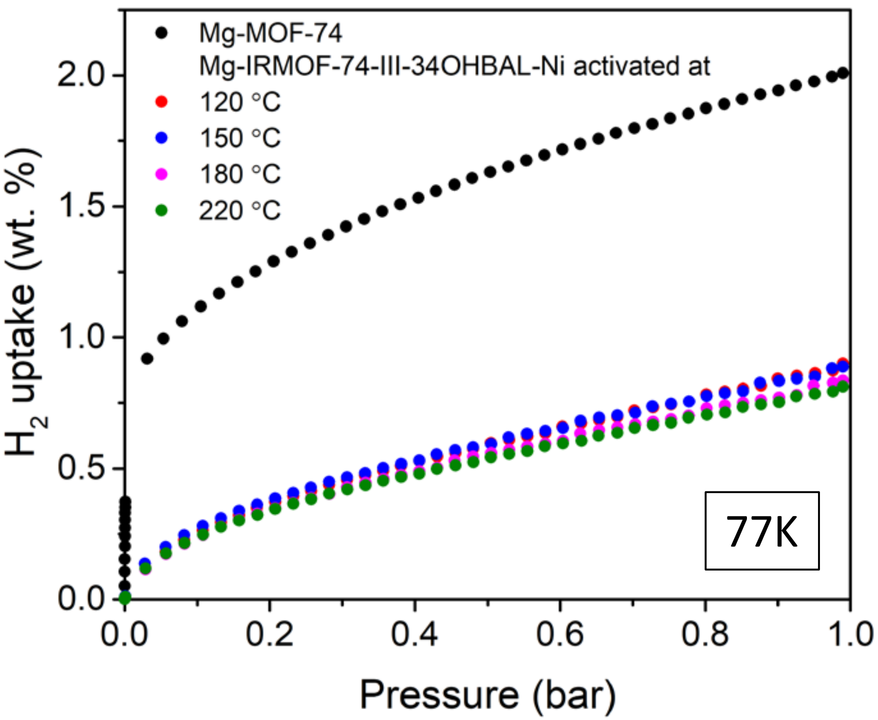


Accomplishments & Progress

- Initial results for H_2 sorption are lower than for Mg-MOF-74 and theoretical calculations indicating incomplete material activation— push for optimization (Milestone 3.2.1)



Mg-IRMOF-74-III-2OHBAL-Ni



Mg-IRMOF-74-III-34OHBAL-Ni

Response to Previous Year Reviewers' Comments

- *This project was not reviewed last year.*

Collaboration

Organization	Type	Support
Lawrence Berkeley National Laboratory	National	Material characterization
National Renewable Energy Lab	National	Discussion & material characterization

Remaining Barriers and Challenges

- Activation of metallated frameworks to generate open metal sites is an outstanding challenge in achieving maximum material **efficiency**.

- Scale-up and further advanced characterization of materials is necessary to determine **durability/operability**.

- Precise tuning of metal-adsorbate interaction strength requires molecular linker optimization. This will influence **charging/discharging rates**.

- The variability of our system endows us with options to address these issues.

Project Milestones & Proposed Future Work

Any proposed future work is subject to change depending on funding levels.

Milestone	Description	Completion Date	% Completed
1.2.1	Synthesize crystalline functionalized IRMOF-74 series (MOF-74 and its extended derivatives IRMOF-74 III, IV and V).	11/30/17	100
2.2.1	Characterization of IRMOF-74 backbones after PSM to quantify their pore volume and amount of metal binding sites.	2/28/18	100
3.2.1	Characterizing the as-synthesized super metallated frameworks to quantify metal incorporation.	5/31/18	30
Go/No-Go 1	Develop a MOF with (1) Double the amount of open metal sites compared to the unfunctionalized IRMOF-74 backbone before PSM and (2) total volumetric capacity of 18 g/L H_2 at 20°C and less than 100 bar (1.5 times of state-of-the-art) based on single crystal density.	8/31/18	n/a

Summary

- **Project Timeline:** September 2017-September 2018
- **Objective:** Produce a H_2 adsorbent capable of exceeding the 2025 DOE system targets of 40 g/L and 5.5 wt% under ambient conditions.
- **Relevant Barriers:** System efficiency, durability/operability, and charging/discharging rates for practical application in on-board H_2 fuel cells.
- **Approach:** Design and synthesis of a super metallated IRMOF-74 by post-synthetic installation of open metal sites to increase adsorptive capacity.
- **Accomplishments:** Crystalline Mg-IRMOF-74-III-$(CH_2NH_2)_2$ was synthesized. Installation of open metal sites was achieved by post-synthetic modification. Initial results show that material integrity is maintained after open metal site incorporation.
- **Future Work:** Optimize H_2 adsorptive capacity through improved activation procedures to reach system target and go/no-go milestone.