High Capacity Step-Shaped Hydrogen Adsorption in Robust, Pore-Gating Zeolitic Imidazolate Frameworks

PI: C. Michael McGuirk

Colorado School of Mines

5/29/20

ST218

Overview

Timeline

- Project Start Date: 10/01/19
- Project End Date: 5/31/21

Barriers

- Barriers addressed
  - The cost of producing and delivering hydrogen from zero- or near-zero-carbon sources must be reduced
  - Compact, lightweight, and low-cost hydrogen storage systems must be developed.

Budget

- Total Project Budget: $476,279
  - Total Recipient Share: $95,256
  - Total Federal Share: $381,023
  - Total DOE Funds Spent*: $45,899

* As of 05/29/2020

Partners

- LBNL
- PNNL
- SNL
- NIST
- LLNL
- NREL

Relevance

- Objective: Increase hydrogen delivery working capacity, while simultaneously lowering energy consumption during on- and off-loading, through development of stimuli-responsive porous adsorbent materials with high capacity “step-shaped” adsorption–desorption profiles in relevant pressure and temperature regimes.
  - During this year, we have taken initial steps to achieve a step-shaped profile below 180 bar at 195 K.

- Addressing Identified Barriers
  - The cost of producing and delivering hydrogen from zero- or near-zero-carbon sources must be reduced
    - *By moving away from extreme pressurization or cryogenic conditions for high capacity hydrogen delivery, energy expenditure will be reduced, lowering the cost of delivery*
  - Compact, lightweight, and low-cost hydrogen storage systems must be developed.
    - *Porous materials can achieve high capacities of deliverable hydrogen with a reduced footprint under parallel temperature and pressure conditions, lowering requirements for storage tank footprint.*

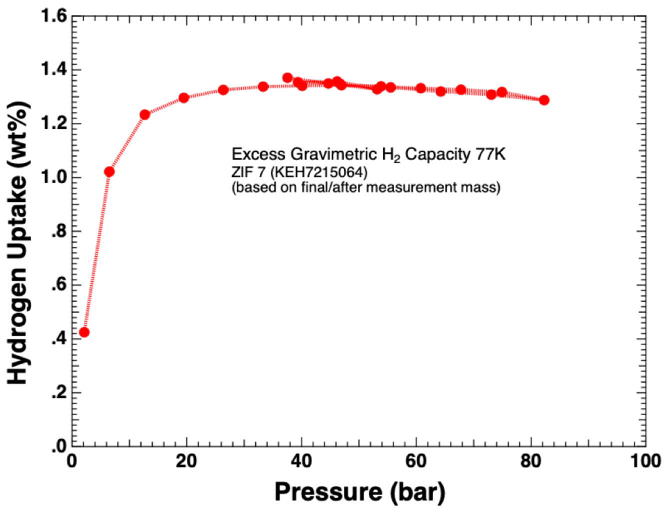
Approach

- Since the initiation of this project our technical approach has been focused on establishing step-shaped adsorption–desorption behavior for H_2 with known stimuli-responsive porous materials that display such behavior with more strongly adsorbing gases, such as CO_2.
- Observation of this unique adsorption–desorption behavior for H_2 in known materials will take a major step towards validating high efficiency on- and off-loading of H_2 during transport and delivery.
  - Improving energetic efficiency in this process will help lower net expense of H_2 fuel
- This work is being performed in conjunction with various HyMARC teams, towards characterizing adsorption and the responsive phenomena in these known porous materials.
- FY20 Milestone 1: Synthesis of fully modified and/or mixed linker CdIF-13 derivatives
  - We have established the ability to synthesize isostructural frameworks containing two different organic linkers
- FY20 Milestone 2: Characterization of structure and stimulus response
  - Diffraction experiments show that mixed-linker frameworks retain desired structural topology
- FY20 Milestone 3: Analysis of hydrogen adsorption performance
  - Hydrogen adsorption experiments are currently underway at NREL

Accomplishments and Progress

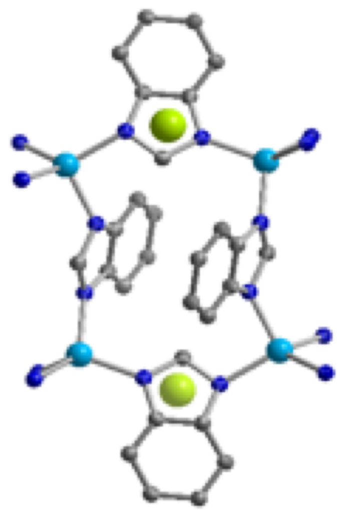
- Our primary accomplishment yet far has been initial characterization of H_2 adsorption in the known stimuli-responsive porous adsorbent ZIF-7 (sod-Zn(benzimidazolate)$_2$)
  - This has been achieved through H_2 adsorption measurements (NREL) and neutron diffraction (NIST)

H_2 Adsorption–Desorption via PCT @ NREL



- These initial measurements demonstrate the ability of H_2 to induce stimuli-responsive behavior in the porous adsorbent

H_2 Adsorption Sites via Neutron Diffraction @ NIST



- Diffraction experiments identify sites of H_2 adsorption, giving us insight in how to tune the structure to achieve high efficiency delivery

Collaboration and Coordination

- National Renewable Energy Laboratory
  - PCT measurements of H_2 adsorption–desorption led by Tom Gennett
- Pacific Northwest National Laboratory
  - *In situ* solid-state NMR spectroscopy measurements of stimuli-response to gas pressure led by Andy Lipton
- National Institute of Standards and Technology
  - Neutron diffraction studies for identification of H_2 adsorption sites in porous materials led by Craig Brown
- Lawrence Livermore National Laboratory
  - Computational examination of H_2 adsorption and stimuli-response behavior led by Brandon Wood
- Sandia National Laboratory
  - Single-crystal X-ray diffraction of porous adsorbent led by Vitalie Stavila

Remaining Challenges and Barriers

- Objective: Increase hydrogen delivery working capacity, while simultaneously lowering energy consumption during on- and off-loading, through development of stimuli-responsive porous adsorbent materials with high capacity "step-shaped" adsorption–desorption profiles in relevant pressure and temperature regimes.
- Remaining Challenges
  - Develop thorough understanding of stimuli-responsive behavior of the porous material. This information will promote logical and rapid material modification to achieve desired delivery performance
  - Through ligand modifications, tune H_2-induced stimulus response of porous material to occur below 200 bar near room temperature
  - Through metal node substitution, increase the working capacity of H_2 delivery by increasing the total capacity of the porous material

Proposed Future Work

- Variable temperature H_2 adsorption–desorption measurements with known materials (i.e. ZIF-7 and CdIF-13)
  - Will develop the baseline performance metrics of initial materials, guiding our modifications to the material structure
- Computational characterization of H_2-induced stimulus-response in known materials
  - Understanding of structural parameters that control step-shaped behavior will allow our synthetic team to logically tune the material to achieve modified adsorption–desorption behavior
- Empirical characterization of structural transition in stimuli-responsive porous material
  - Through solid-state NMR spectroscopy and single-crystal X-ray diffraction, we will corroborate computationally predicted structures, towards complete insight into structural features that control H_2 adsorption–desorption behavior
- Synthesis of stimuli-responsive porous materials with modified chemical structure
  - Using insight gained through above work, modified materials will be synthesized and characterized, and their H_2 adsorption–desorption behavior will be measured towards achieving high working capacities of deliverable H_2 below 200 bar at room temperature
- These combined efforts will help meet upcoming milestones, including the M15 Go/No-Go of step-shaped adsorption at 195 K below 180 bar.

Technology Transfer Activities

- We are not currently undertaking technology transfer activities
- For desirably performing materials developed over the course of this project, our team will appropriately apply for patent protection.

Summary

- Objective: Increase hydrogen delivery working capacity, while simultaneously lowering energy consumption during on- and off-loading, through development of stimuli-responsive porous adsorbent materials with high capacity “step-shaped” adsorption–desorption profiles in relevant pressure and temperature regimes.
- Relevance:
  - By moving away from extreme pressurization or cryogenic conditions for high capacity hydrogen delivery, energy expenditure will be reduced, lowering the cost of delivery.
  - Porous materials can achieve high capacities of deliverable hydrogen with a reduced footprint under parallel temperature and pressure conditions, lowering requirements for storage tank footprint.
- Approach: Establishing step-shaped adsorption–desorption behavior for H_2 with known stimuli-responsive porous materials that display step-shaped behavior with more strongly adsorbing gases. Followed by structural modifications, influenced by extensive characterization, to desirably tune adsorption–desorption behavior.
- Accomplishments: Characterization of H_2 adsorption in the known stimuli-responsive porous adsorbent ZIF-7 (sod-Zn(benzimidazolate)$_2$)
- Collaborations: Established collaborations with various HyMARC team members at LBNL, LLNL, PNNL, NREL, SNL and NIST.
- Towards the M15 Go/No-Go, we have established the ability of known stimuli-responsive porous materials to adsorb H_2