

## IV.C.3 Hydrogen Storage in Metal-Organic Frameworks

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### Subcontractors:

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- General Motors Corporation (GM), Warren, MI (Anne Dailly)

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Project End Date: March 31, 2015

### Overall Objectives

- Research and development of onboard systems that allow for a driving range greater than 300 miles.
- Materials sought with the potential for meeting the DOE targets of reversible uptake:
  - 2017 targets: 5.5% H<sub>2</sub> by mass, volumetric capacity of 40 g/L
  - “Ultimate full fleet” targets: 7.5% H<sub>2</sub> by mass, 70 g/L
- Synthesize new metal-organic frameworks (MOFs) capable of achieving the -20 kJ/mol adsorption enthalpy required for use as hydrogen storage materials operating 100 bar at ambient temperatures.

### Fiscal Year (FY) 2013 Objectives

- Synthesize MOFs exhibiting reversible H<sub>2</sub> uptake greater than 2.5 wt%.
- Prepare a high-valent MOF with an initial adsorption enthalpy greater than 12 kJ/mol (at 298 K and 300 bar).
- Synthesize new MOFs with the multifunctional ligands prepared in year one.

- Prepare at least two MOFs with the optimal 7 Å between opposing pore surfaces as predicted with *in silico* screening techniques.
- Demonstrate that improved understanding of MOF-H<sub>2</sub> interactions through inelastic neutron scattering experiments and new approaches to calculate observed spectra provide new insight into the governing physics of adsorption in porous media.
- Demonstrate the ability to determine H<sub>2</sub>-metal interactions in realistic systems containing low-coordinate metal cations.
- Demonstrate the correlation between high-pressure measurements and theoretical and spectroscopic predictions.
- Demonstrate the ability to measure H<sub>2</sub> adsorption in a test material up to 10 cycles at 298 K.
- Demonstrate the ability to measure H<sub>2</sub> adsorption in a test material up to 10 cycles at temperatures relevant to use in onboard vehicle applications.

### Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Fuel Cell Technologies Office Multi-Year Research, Development and Demonstration Plan:

(A) System Weight and Volume

### Technical Targets

Specific efforts are focused on the research and development of onboard systems that allow for a driving range greater than 300 miles. Materials are sought with the potential for meeting the 2017 DOE targets of reversible uptake and, subsequently, the “ultimate full fleet” targets (see Table 1).

### FY 2013 Accomplishments

- Published joint theory/experiment paper in *J. Am. Chem. Soc.* on the hydrogen storage properties of M-BTT (M = Cu, Mn, Fe, Zn), a MOF with open M<sup>2+</sup> cation sites.
- Synthesized five new MOFs with ligands prepared in year one.
- A new isostructural MOF series (M<sub>2</sub>dobdc') has been synthesized and characterized.
- The structure of M<sub>2</sub>(dobdc') and D<sub>2</sub> binding sites were elucidated via powder neutron diffraction.

TABLE 1. Progress towards Meeting Technical Targets for Onboard Hydrogen Storage for Light-Duty Vehicles

Storage Parameter	Units	2017 Target	Ultimate Target	2013 Status <sup>†</sup>
<b>System Gravimetric Capacity:</b> Usable, specific-energy from H <sub>2</sub> (net useful energy/max system mass) <sup>*</sup>	kWh/kg (kg H <sub>2</sub> /kg system)	1.8 (0.055)	2.5 (0.075)	(0.016 kg H <sub>2</sub> /kg adsorbent)
<b>System Volumetric Capacity:</b> Usable, energy density from H <sub>2</sub> (net useful energy/max system volume)	kWh/L (kg H <sub>2</sub> /L system)	1.3 (0.040)	2.3 (0.070)	(0.011 kg H <sub>2</sub> /L adsorbent)

<sup>\*</sup> Generally the full mass (including hydrogen) is used; for systems that gain weight, the highest mass during discharge is used. All capacities are net useable capacity able to be delivered to the power plant. Capacities must be met at end of service life.

<sup>†</sup> Since the project deals with the development of storage materials, the performance status is given in terms of storage capacity for storage materials, not the whole storage system.



## INTRODUCTION

MOFs are promising solid sorbents for storage of H<sub>2</sub> at room temperature. They can be tailored to incorporate a large number of selected metal ions, thereby tuning the H<sub>2</sub> binding energy. The overall aim of the project is to synthesize new MOFs capable of achieving the  $-20$  kJ/mol adsorption enthalpy required for use as hydrogen storage materials operating under 100 bar at ambient temperatures.

## APPROACH

This research involves investigators with a range of capabilities—including synthesis and characterization of new materials, electronic structure calculations, neutron diffraction and scattering studies, and high-pressure gas sorption measurements. The team performs work in four areas: Task 1) Synthesis of Metal-Organic Frameworks (Long-LBNL), Task 2) Characterization of Framework-H<sub>2</sub> Interactions (Brown-NIST), Task 3) First-Principles Calculations of Hydrogen Binding Enthalpies (Head-Gordon-LBNL), and Task 4) High-Pressure H<sub>2</sub> Adsorption Measurements (Dailly-GM).

## RESULTS

In order to address the system weight and volume technical barriers from the Hydrogen Storage section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan we are synthesizing a number of new metal-organic frameworks with the potential to reversibly adsorb large quantities of H<sub>2</sub> at modest pressures and temperatures. To reach these goals two separate approaches are being used. The first is maximizing H<sub>2</sub> uptake by preparing MOFs with optimal opposing pore surface distances. Theoretical calculations have shown that to maximize H<sub>2</sub> uptake materials with opposing surfaces 7 Å apart are needed. In order to rapidly screen the pore size of a large number of MOF structures for this optimal 7 Å distance we have developed an *in silico* screening tool that calculates

opposing surface distances as a function of surface area from crystallographic information files. MOF-5, for example, features a large fraction of surface area outside the 7 Å distance (Figure 1).

In addition to maximizing pore size and opposing pore distances, we are currently rigorously investigating MOFs with coordinatively unsaturated metal cation sites. The majority of work thus far has been devoted to the synthesis and characterization of the M<sub>2</sub>(dobdc<sup>+</sup>) (M = Mg<sup>2+</sup>, Mn<sup>2+</sup>, Fe<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>) (dobdc<sup>+</sup> = 2,4-dioxido-1,5-benzenedicarboxylate) (“dobdc-prime”) metal-organic framework series as well as other MOF-74 analogs (Figure 2). These materials are similar in structure to the already reported, and well studied, M<sub>2</sub>(dobdc) (M = Mg<sup>2+</sup>, Mn<sup>2+</sup>, Fe<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup>) (dobdc<sup>+</sup> = 2,5-dioxido-1,4-benzenedicarboxylate) or MOF-74 structure. The synthesis of H<sub>4</sub>dobdc<sup>+</sup> is extremely simple compared to H<sub>4</sub>dobdc and can be realized by the direct carboxylation of resorcinol with CO<sub>2</sub> in the presence of potassium carbonate. An analogous synthesis with hydroquinone to produce H<sub>4</sub>dobdc is not possible thus more expensive, solvent

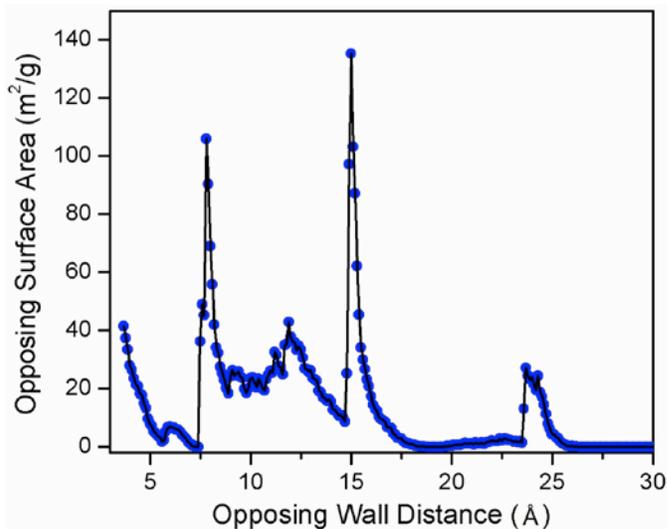
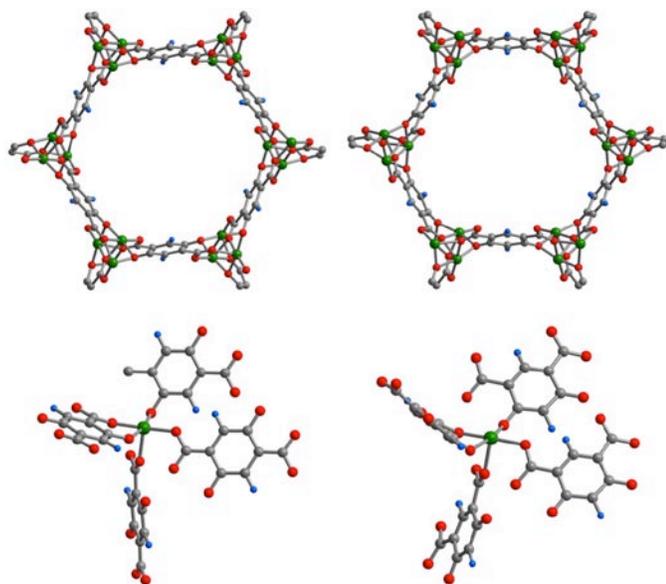


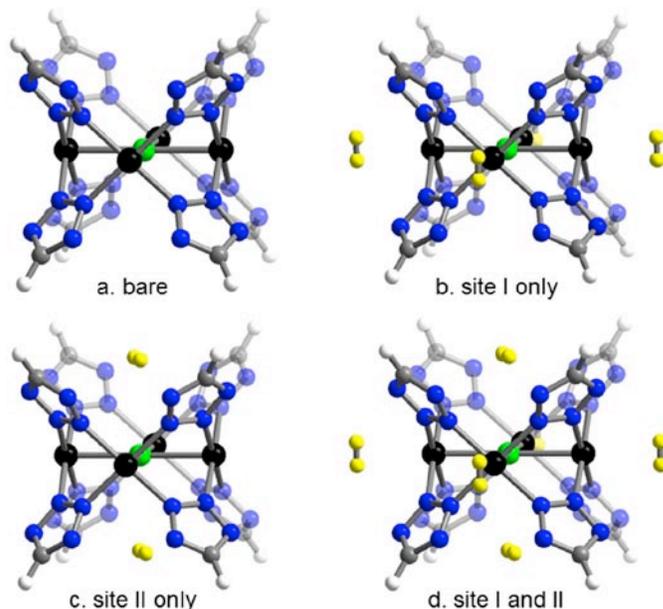
FIGURE 1. Opposing surface area distribution for Zn<sub>4</sub>O(BDC)<sub>3</sub> as calculated with a 3.68-Å probe molecule diameter and a 0.1-Å step size.



**FIGURE 2.** (upper) Crystal structures of  $\text{Ni}_2(\text{dobdc})$  (left) and  $\text{Ni}_2(\text{dobdc}')$  (right) as viewed down the (0,0,1) direction. Green, red, gray, and blue represent nickel, oxygen, carbon, and hydrogen atoms, respectively. (lower) Close up of the coordination environment of  $\text{Ni}^{2+}$  in  $\text{Ni}_2(\text{dobdc})$  (left) and  $\text{Ni}_2(\text{dobdc}')$  (right).

intensive synthetic techniques are required. It was our hope that the MOF-74 structure type could be synthesized with this new ligand as the synthesis of large amounts of MOF based on it would be significantly cheaper and have far less environmental impact than the synthesis of  $\text{H}_4\text{dobdc}$ , which is currently made via far less green methods. Furthermore, both  $\text{Ni}_2(\text{dobdc}')$  and  $\text{Co}_2(\text{dobdc}')$  exhibit low coverage isosteric heats of  $\text{H}_2$  adsorption of approximately -12.0 kJ/mol, on track with the FY 2013 target. Future work with these materials will focus on further characterization of M- $\text{D}_2$  and M- $\text{H}_2$  interactions via neutron scattering techniques and theoretical calculations.

We have also recently published work on combined theoretical/experiment work with metals of the  $\text{M}_3[(\text{M}_4\text{Cl})_3(\text{BTT})_8]_2$  (M-BTT;  $\text{BTT}^{3-} = 1,3,5\text{-benzenetristetrazolate}$ ,  $\text{M} = \text{Cu, Mn, Fe, Zn}$ ) structure type (Figure 3). Variable-temperature infrared spectroscopy studies of Mn-BTT, Fe-BTT and Cu-BTT, for which the thermodynamics of  $\text{H}_2$  adsorption is experimentally probed was complemented by a detailed density functional theory study, in which molecular fragments representing the metal clusters within the extended solid are simulated to obtain a more thorough description of the structural and thermodynamic aspects of  $\text{H}_2$  adsorption at the strongest binding sites. The close agreement between the theoretical and experimental data confirmed that the theoretical model is able to accurately describe the binding environments for  $\text{H}_2$  within the M-BTT structure type. The effect of substitutions at the metal cluster, namely the identity of the metal ion or the anion within the tetranuclear cluster



**FIGURE 3.** Representative density functional theory structural models of the hypothetical  $[\text{M}_4\text{Cl}(\text{tz})_8]^-$  ( $\text{M} = \text{Mn, Cu, Zn}$ ;  $\text{tz}^- = 5\text{-}H\text{-tetrazolate}$ ) molecule and its  $\text{H}_2$ -bound variants calculated for assessment of the  $\text{H}_2$  binding energies. For each of the metals surveyed, four structures were calculated. Starting with the parent molecule shown in (a),  $\text{H}_2$  molecules were introduced to (b) site I, (c) site II, or (d) site I and II. Black, green, white, gray and blue spheres represent M, Cl, H, C, and N atoms, respectively, while the H atoms of the bound  $\text{H}_2$  molecules are displayed as yellow spheres for clarity.

showed that the configuration of this unit indeed plays an important role in determining the affinity of the framework towards  $\text{H}_2$ . Interestingly, the theoretical study has identified that the Zn-based analog would be expected to facilitate an adsorption profile that is enhanced over the compounds that have been synthesized experimentally to date, highlighting the importance of a combined experimental and theoretical approach to the design and synthesis of new MOFs for  $\text{H}_2$  storage applications.

## CONCLUSIONS AND FUTURE DIRECTIONS

- The recently completed opposing surface area distribution program will be used to down select MOFs for room-temperature  $\text{H}_2$  storage.
- We have shown excellent agreement between experimental data and theoretical calculations; this will further be used to inform the synthesis of new MOF materials.
- Fruitful collaboration between researchers at NIST and LBNL has led to a better understanding of metal-hydrogen interactions in a number of new frameworks.
- Promising samples will be sent to GM for high-pressure hydrogen adsorption and cycling measurements.

**FY 2013 PUBLICATIONS/PRESENTATIONS**

1. “Opposing Surface Area Distribution (OSAD) as a Characterization Tool for Microporous Metal-Organic Frameworks”  
Sumida, K.; Rogow, D.L.; Herm, Z.R.; Long, J.R. *Langmuir* submitted.
2. “Impact of Metal and Anion Substitutions on the Hydrogen Storage Properties of M-BTT Metal-Organic Frameworks”  
Sumida, K.; Stuck, D.; Mino, L.; Chai, J.-D.; Bloch, E.D.; Zavorotynska, O.; Murray, L.J.; Dinca, M.; Chavan, S.; Bordiga, S.; Head-Gordon, M.; Long, J.R. *J. Am. Chem. Soc.* **2013**, *135*, 1083-1091.