

## IV.C.4 New Carbon-Based Porous Materials with Increased Heats of Adsorption for Hydrogen Storage

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### Technical Targets

**TABLE 1.** Progress towards Meeting Technical Targets for Hydrogen Storage

Characteristic	2017 Targets	NU 2012 Status
System Gravimetric Capacity	0.055 kg H <sub>2</sub> /kg system at ambient T and 100 bar	0.14 kg H <sub>2</sub> /(kg sorbent + H <sub>2</sub> ) at 77 K and 70 bar
System Volumetric Capacity	0.040 kg H <sub>2</sub> /L system at ambient T and 100 bar	0.045 kg H <sub>2</sub> /L sorbent at 77 K and 70 bar

### FY 2012 Accomplishments

- Obtained external validation of 8 wt% excess hydrogen uptake in NU-100 at 77 K and 50 bar.
- Developed a new MOF material with over 6 wt% excess hydrogen uptake at 77 K and 35 bar.
- Demonstrated a high-throughput computational screening method capable of screening thousands of hypothetical MOF targets.



### Fiscal Year (FY) 2012 Objectives

- Obtain external validation of hydrogen uptake at 77 K in the metal-organic framework (MOF) NU-100, which was measured in our labs last year
- Develop high surface area materials for cryogenic hydrogen storage
- Develop high surface area materials containing functional groups that can bind hydrogen at room temperature
- Use computational modeling to understand existing materials and design new materials for hydrogen storage

### Technical Barriers

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

- (A) System Weight and Volume
- (F) Charging/Discharging Rates
- (P) Lack of Understanding of Hydrogen Physisorption and Chemisorption

### Introduction

One option for storing hydrogen on vehicles is to use tanks filled with porous materials that act as “sponges” to take up large quantities of hydrogen without the need for extremely high pressures. The materials must meet many requirements to make this possible. This project is developing two related classes of porous materials to meet these requirements. All materials are synthesized from molecular constituents in a building-block approach. This allows us to create a wide variety of materials in a tailorable fashion. The materials have extremely high surface areas, to provide many locations for hydrogen to adsorb. In addition, they are designed to contain cations that create large electric fields to bind hydrogen strongly but not too strongly.

### Approach

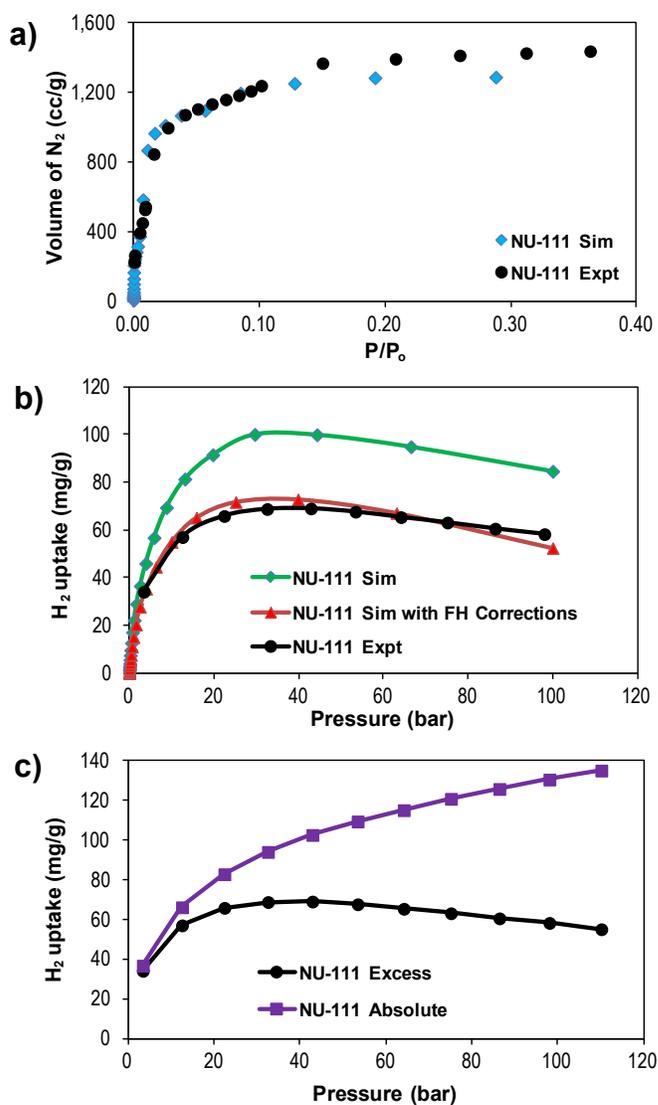
The approach in this project is to introduce cations into MOFs and polymeric-organic frameworks to increase the hydrogen heats of adsorption, which will, in turn, increase the amount of hydrogen that can be stored near room temperature. Many MOFs have enough surface area to meet the DOE hydrogen storage targets if the entire surface were covered with a monolayer of hydrogen. However, at room temperature, the energetic interactions between hydrogen and the surfaces are too weak to bind hydrogen. Thus, we are

focused on increasing these energetic interactions. A variety of synthetic chemistries are being explored to increase the chances of success. In addition, molecular modeling is used to help explain experimental observations and provide guidance to the synthetic efforts.

## Results

Previously we had reported [1] on the design, synthesis, and computational modeling of a micro- and mesoporous MOF material, NU-100, that displayed an extraordinarily high internal surface area and very high uptake of molecular hydrogen at 77 K. Experimentally we had obtained a Brunauer-Emmett-Teller (BET) surface area of 6,160 m<sup>2</sup>/g, in good agreement with predictions from modeling (i.e. ~6,600 m<sup>2</sup>/g). In addition, we measured an excess uptake of 99 mg of H<sub>2</sub> per gram of NU-100, corresponding to 9.0 wt% at 77 K, and we estimated the total hydrogen uptake (at the pressure of maximum excess H<sub>2</sub> sorption) to be 164 mg/g, or 14.3 wt%. During the past year, we worked closely with Phil Parilla at NREL to obtain external validation of these hydrogen uptake numbers. At NREL we observed a maximum excess uptake of 87 mg of H<sub>2</sub> per gram of NU-100, corresponding to 8.0 wt%. These values are ~12% lower than found earlier at Northwestern (with a separate preparation of NU-100). The differences can be traced to difficulties in fully activating the material and in maintaining a moisture-free environment, rather than to measurement discrepancies. The activation problems were reflected in surface area measurements that likewise returned values ~12% lower than obtained under optimum experimental conditions.

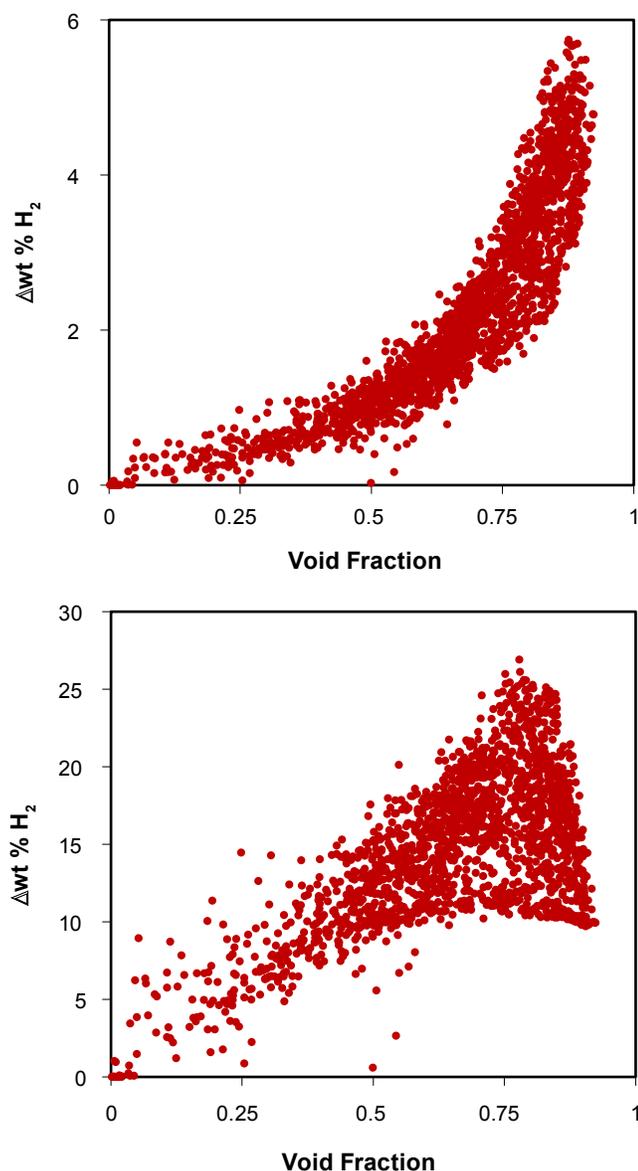
We also investigated the question of whether phenyl rings or carbon-carbon triple bonds are better for creating ultra-high surface area materials that can be functionalized for high hydrogen uptake. In the course of investigating this question, we synthesized a new MOF, NU-111, from a new hexa-carboxylic acid linker that contains triple bond spacers [2]. The material has an experimental BET surface area of 5,000±80 m<sup>2</sup>/g and a total pore volume of 2.38 cm<sup>3</sup>/g. The material was sent to NREL for high-pressure hydrogen uptake measurements, and the results are shown in Figure 1B. The excess hydrogen uptake of NU-111 is 21 mg/g at 1 bar and 69 mg/g at 32 bar. By using the N<sub>2</sub>-derived pore volume (2.38 cm<sup>3</sup>/g) and the bulk phase density of H<sub>2</sub>, the total H<sub>2</sub> uptake at 110 bar and 77 K was calculated to be 135 mg/g (Figure 1C). The uptake of NU-111 is within range of the system gravimetric target for onboard H<sub>2</sub> storage, 5.5 wt% (= 58 mg/g), albeit at cryogenic rather than ambient temperature. The simulated H<sub>2</sub> isotherm of NU-111 is in only qualitative agreement with the experimental H<sub>2</sub> measurements using the classical force field model (Figure 1B). However, incorporating the Feynman-Hibbs corrections for quantum diffraction effects results in excellent agreement with the experimental isotherm. The



**FIGURE 1.** Adsorption isotherms in NU-111 at 77 K: a) N<sub>2</sub> isotherms, b) excess H<sub>2</sub> isotherms, showing comparison of simulation and experiment, c) excess and absolute (total) H<sub>2</sub> isotherms

stability of NU-111 was examined by running multiple cycles of high-pressure hydrogen adsorption at room temperature, and it showed no loss of capacity. In addition, the N<sub>2</sub> isotherms for NU-111 was measured before sending the sample to NREL and upon receiving the sample back from NREL. The N<sub>2</sub> isotherm showed no loss of porosity during the shipping and measurements.

Significant efforts were devoted to introducing divalent metal cations into MOFs and porous organic polymers. A variety of synthetic strategies were tested to introduce cations via linker functionalization. Successful metal incorporation was demonstrated in multiple types of materials. The observed H<sub>2</sub> heats of adsorption increase upon metal incorporation, but at present they are lower than expected



**FIGURE 2.** Preliminary results from high-throughput computational screening of MOFs, showing that deliverable gravimetric capacity increases with void fraction and that deliverable volumetric capacity has a maximum around 0.75 void fraction

from our computational work, perhaps due to residual solvent molecules blocking access to the metal atoms.

In the computational part of the project, we pursued three goals. First, we tested how the degree of metal functionalization (metal loading) affects hydrogen storage in MOFs. As expected, higher metal loading leads to an increase in the absolute (total)  $H_2$  uptake. The deliverable capacity (defined in this work as hydrogen uptake at a pressure of interest minus hydrogen uptake at 2 bar) does not necessarily increase with higher metal loading. From the results so far, it is difficult to make any generalization

except to say that for each material there will be an optimum metal loading and that higher metal loading is not always better for the deliverable hydrogen capacity. Second, we investigated how incorporation of Mg-alkoxide functionality affects the rate of hydrogen diffusion in MOFs. Using molecular dynamics simulations, we calculated the diffusion coefficients of hydrogen in several MOFs of different topology. The main conclusion is that the Mg-alkoxide groups have only a small effect on hydrogen diffusion (less than one order of magnitude) and should not adversely affect rates of hydrogen uptake and release.

Finally, we demonstrated a method for high-throughput computational screening of MOFs for hydrogen storage. This work builds on our related work on natural gas storage [3] and previous work from this project on modeling hydrogen adsorption in metal-functionalized MOFs [4]. We combined these methods to screen over 16,000 MOFs with Mg-functionalized linkers for their ability to store and deliver hydrogen. In addition to identifying promising synthetic targets, the method provides useful structure/property relationships, as shown in Figure 2.

## Conclusions and Future Directions

### Conclusions

- We obtained external validation of 8 wt% excess hydrogen uptake in NU-100 at 77 K and 50 bar.
- We developed a new MOF material, NU-111, with over 6 wt% excess hydrogen uptake at 77 K and 35 bar.
- We tested a variety of synthetic strategies for introducing exposed divalent cations into MOFs and porous organic polymers as a means to increase the hydrogen enthalpy of adsorption.
- We demonstrated a high-throughput computational screening method capable of screening thousands of hypothetical MOF targets. This is a promising strategy for identifying new MOFs that may meet DOE hydrogen storage targets.

### Future Directions

- Test hydrogen uptake in recently synthesized materials.
- Complete modeling study of hydrogen diffusion in Mg-functionalized MOFs.
- Write up results for publication.

## FY 2012 Publications/Presentations

1. A.P. Katsoulidis, M.G. Kanatzidis, "Phloroglucinol microporous polymeric organic frameworks with -OH functional groups and high  $CO_2$  capture capacity," *Chem. Mater.*, **23**, 1818-1824, (2011).

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3. D. Yuan, R.B. Getman, Z. Wei, R.Q. Snurr, H.-C. Zhou, “Stepwise adsorption in a mesoporous metal-organic framework: Experimental and computational analysis,” *Chem. Commun.* **48**, 3297-3299 (2012).
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2. O.K. Farha, C.E. Wilmer, I. Eryazici, B.G. Hauser, P.A. Parilla, K. O’Neill, A.A. Sarjeant, S.T. Nguyen, R.Q. Snurr, J.T. Hupp, “Designing higher surface area metal-organic frameworks: Are triple bonds better than phenyls?” *J. Am. Chem. Soc.*, **134**, 9860-9863 (2012).
3. C.E. Wilmer, M. Leaf, C.Y. Lee, O.K. Farha, B.G. Hauser, J.T. Hupp, R.Q. Snurr, “Large-scale screening of hypothetical metal-organic frameworks,” *Nature Chem.*, **4**, 83-89 (2012).
4. R.B. Getman, J.H. Miller, K. Wang, R.Q. Snurr, “Metal alkoxide functionalization in metal-organic frameworks for enhanced ambient temperature hydrogen storage,” *J. Phys. Chem C* **115**, 2066-2075 (2011).