IV.C.9 High-Capacity and Low-Cost Hydrogen-Storage Sorbents for Automotive Applications

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Subcontractor:

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Project Start Date: August 1, 2015
Project End Date: July 31, 2018

Overall Objectives

- Produce materials capable of meeting or exceeding DOE's 2020 performance target of gravimetric capacity of 0.055 kg H_2/kg$_{system}$, volumetric capacity of 0.040 kg H_2/L$_{system}$ at a cost of \$333/kg_$H_{2\ stored}$.

- Study the effects of post-synthetic addition of metals to induce higher hydrogen binding affinities.

- Show that such materials are stable under the conditions expected of hydrogen sorbents.

- Show that these materials have appropriate sorption kinetics to quickly load and deliver hydrogen.

Fiscal Year (FY) 2016 Objectives

- Reproduce preliminary results of porous coordination network (PCN)-250 excess uptake of 6.75 wt%.

- Year 1 Go/No-Go: demonstrate an sorbent material with at least a reversible 1.5 wt% excess hydrogen per 500 m^2/g (1.5X greater than Chahine's rule) with at least 2,000 m^2/g specific surface area and 60 g/L total volumetric capacity (assuming single crystal density) at pressures less than or equal to 100 bar and 77 K. In addition, demonstrate repeatable activation procedures which result in some quantitative, known level of desolvation and no metal-bound water generation as validated by an independent lab directed by DOE.

- Show through advanced X-ray characterization the desolvation of open metal sites.

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

(O) Lack of Understanding of Hydrogen Chemisorption and Physisorption

(J) Thermal Management

Technical Targets

Metal-Organic Frameworks with Enhanced Hydrogen Storage: This project is generating materials for the express purpose of storing hydrogen in vehicular systems. The materials are targeted toward the project's end reach values which would allow them to be incorporated into systems meeting the DOE system targets.

- Excess gravimetric H_2 uptake:
  - Project Target: 10 wt% excess material basis
  - DOE 2020 Target: 5.5 wt% system basis
- Volumetric H_2 uptake:
  - Project Target: 0.055 kg H_2/L of material (total)
  - DOE 2020: Target 0.040 kg H_2/L of system
- Cost per kg/H_2 stored DOE 2020 Target: \$333/kg_$H_{2\ stored}$
- Increase material capacity and heat of adsorption >10% via post-synthetic modification

FY 2016 Accomplishments

- Observed that Fe_3O cluster based materials show changes indicating desolvation and possible reduction at temperatures above 150°C.

- Several new metal organic frameworks (MOFs) generated which show potential for increased capacity.

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INTRODUCTION

Hydrogen storage technology is critical for next generation energy conversion devices such as proton exchange membrane fuel cells. Further interest in the direct

use of hydrogen as a fuel source is driving a significant amount of research to find more efficient ways of storing and transporting hydrogen for consumer use. To be practical for transportation applications, the storage system should reach gravimetric capacity of 0.055 kg H_2/kg$_{—system}$, volumetric capacity of 0.040 kg H_2/L$_{—system}$ at a cost of \$333/kg_H_2 stored according to the performance targets set by DOE for 2020. No current technology meets all of these goals. Compared with chemical or metal hydride based approaches, sorption based technology has the advantages of (a) low parasitic energy consumption for desorption, (b) fast kinetics for storage and delivery, and (c) light material for high gravimetric and reasonable volumetric storage capacity. The main challenge, however, is its limited capacity even under low temperature, high pressure conditions. In general, the H_2 uptake by sorbents at liquid N_2 temperature follows the so called Chahine's rule, i.e., the excess gravimetric capacity increases proportionally at the rate of 1 wt% for every 500 m^2/g Brunauer-Emmett-Teller (BET) specific surface area (SSA). This is calculated based on the surface area required for an arrangement of non-interacting hydrogen atoms on a flat surface. Excessive increase of SSA, however, leads to the reduction of sorbent's density therefore reducing the volumetric storage capacity. Studies show that the volumetric capacity peaks near the BET SSA of 3,000 m^2/g, suggesting a ceiling of 6 wt% gravimetric capacity if the sorbent follows Chahine's rule strictly. To achieve DOE's 2020 gravimetric and volumetric capacity goals simultaneously, the new adsorbent must exceed this limitation. To reach these goals metal-organic frameworks are being pursued as high surface area and low density sorbents.

APPROACH

This project is a collaborative effort between Texas A&M University and Argonne National Laboratory in developing low-cost and high-capacity hydrogen-storage sorbents with appropriate stability, sorption kinetics, and thermal conductivity. The objective of this three-year project is to produce hydrogen storage materials that meet or exceed DOE's 2020 performance target. The proposal adopts approaches of rational design, novel synthesis, and engineering development of new sorbents, supported by studies of storage capacity, kinetics, and H_2–sorbent interaction using advanced characterization techniques. The proposed activities focus on the preparation of sorbents with improved hydrogen binding and the uptake capacity that surpasses the conventional cryogenic storage limit. The focus of these studies involves generating materials with uncoordinated metal sites and geometric features which increase the ability for the materials to adsorb hydrogen. This involves both initial material design to include such uncoordinated metal sites as well as post synthetic modification through atomic layer deposition to achieve increased binding site density.

RESULTS

The initial goal of reproducing the previously reported hydrogen capacity of PCN-250 was the primary focus at the outset of the program. Initial difficulties resulted in the use of PCN-250(Fe) rather than PCN-250(Co) to ensure homogeneity within the samples. For the mixed metal species it is possible that all iron clusters could be present in the samples. However as shown in Figure 1, the validation test performed by National Renewable Energy Laboratory gave a value of 4.85 wt%, which was well below that previously measured for the Fe_2CoO based cluster [1]. The measured surface area of the material of 1,750 m^2/g predicts a value of 3.5 wt% excess based on Chahine's rule. Thus this material still exceeded the expected excess gravimetric capacity by 50%, indicating that there are still structural features in PCN-250 which provide advantageous hydrogen sorption. Several of these materials show gravimetric excess uptakes of >2 wt% at 1 bar and 77 K. These are undergoing synthesis for high-pressure measurements. However, by generating structures which retain pore shape and volume similar to PCN-250 while also increasing the pore size slightly, it is hypothesized that the overall capacity of these materials can be increased. MOFs with significantly larger pores yielded low hydrogen excess uptake values and would likely give exceedingly low volumetric values. A zirconium system, which at present has below the Quarter 3 target of 1,500 m^2/g with a BET SSA of 1,359 m^2/g, shows excess gravimetric uptake of ~2.2 wt% and volumetric uptake of 25.8 g/L at 77 K and 1 bar. At high pressure we expect it to exceed 2.7 wt% (based on Chahine's rule) and it may have a high volumetric uptake as well. The ligands shown in Figure 2 are of the most current interest (Figure 2a is the ligand for PCN-250, Figure 2b and Figure 2d are pyrazolate and triazolate ligands respectively, which provide a different connectivity giving us access to different pore profiles, and Figure 2c being the ligand for the new zirconium system).

In situ X-ray absorption spectroscopy experiments were conducted by the Argonne National Laboratory team for three MOF samples received from Texas A&M including: PCN-250-Fe$_3$, PCN-250-Fe$_2$Co and PCN-250-Fe$_2$Ni. For this experiment, we designed an in situ reactor consisting of a quartz tube flow reactor and a stainless steel sample holder. X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure spectroscopic data near Fe K-edge (7.1109 KeV) were taken continuously as the temperature increased to record the oxidation state and coordination structural changes. Figure 3a shows the change of iron XANES spectra of PCN-250-Fe$_3$ during the thermal activation. A common feature among all the spectra is the presence of dominant white line peak near 7,125 eV for the as-prepared samples which indicates a higher oxidation state induced by the binding of oxygenate functional group from solvent. With the increase of temperature, the white line peak in PCN-250-Fe$_3$ gradually reduces its intensity with
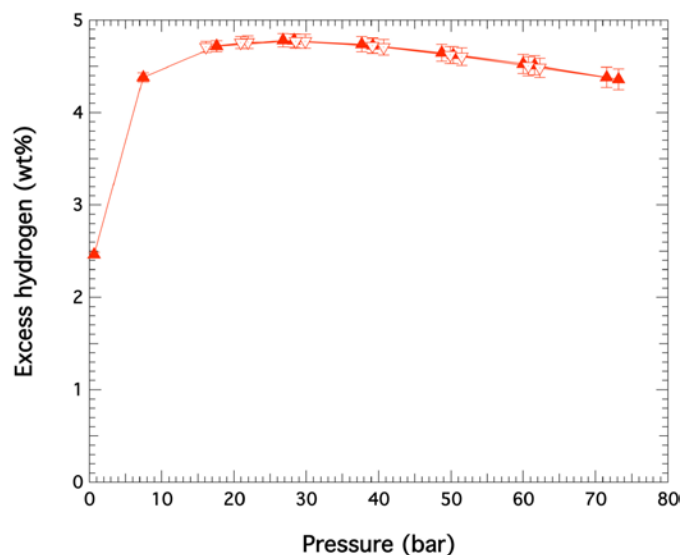
FIGURE 1. High-pressure H_2 isotherm at 77 K measured by National Renewable Energy Laboratory
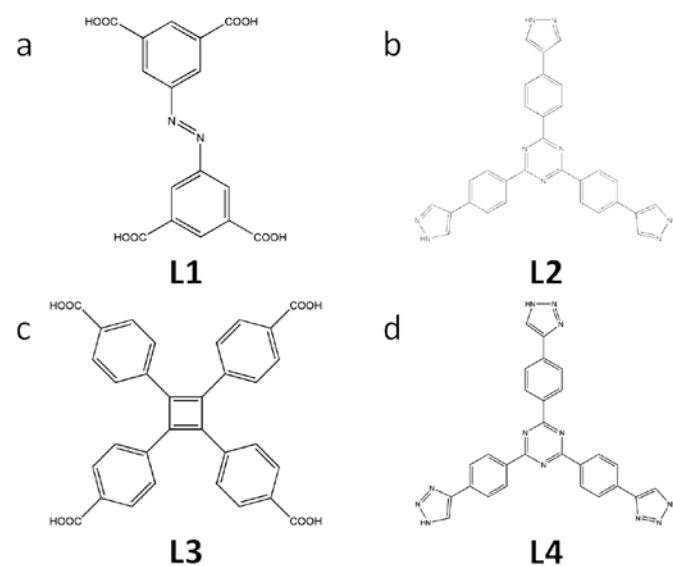

FIGURE 2. Ligands of high interest for increased H_2 sorption

FIGURE 3. XANES progression during heating (a) and radial distribution function of Fe-O distances (b)

the process accelerated between 150°C to 180°C. Figure 3b shows the radial distribution function derived from the extended X-ray absorption fine structure spectra taken at selected temperatures. Radial distribution function can be interpreted as the "shells" of atoms surrounding to the center Fe atom.

CONCLUSIONS AND FUTURE DIRECTIONS

Based on the uptake measurements for PCN-250, hydrogen adsorption saturates at ~28 bar meaning that no improvement in hydrogen capacity is achieved after this
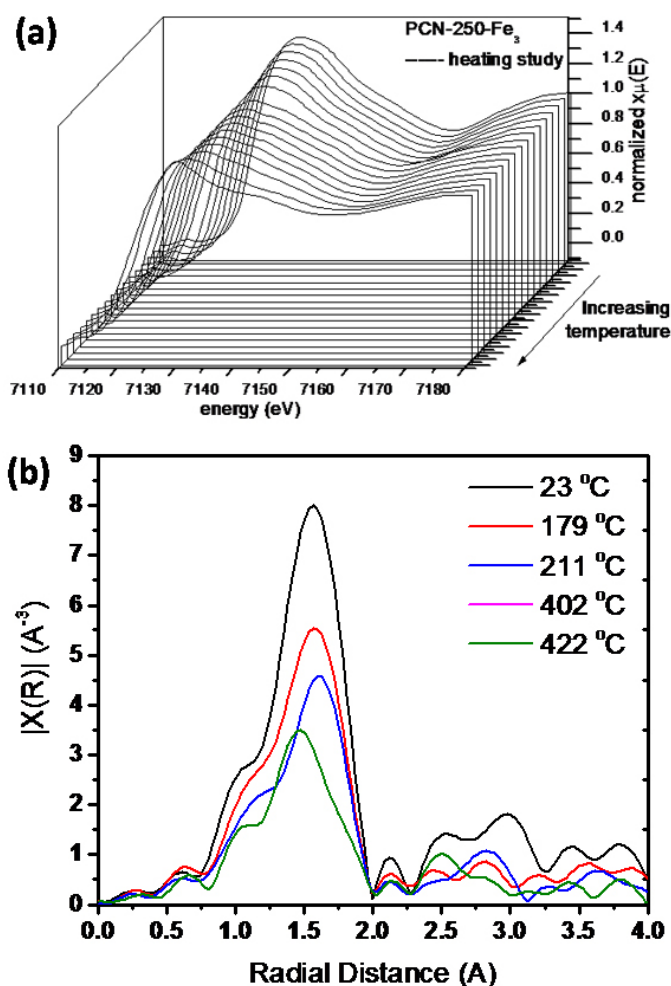
point. This indicates that the pore volume is likely filled meaning that a material with larger pores will be necessary to meet the DOE's goals. As a result of the lower than expected performance of PCN-250, new materials were tested at sub-ambient pressures. Further, based on the initial X-ray studies, the metal choice, solvent exchange, and desolvation criteria as observed for the M_3O cluster based materials must be carefully controlled to fully activate the materials and avoid decomposing them. The application of atomic layer deposition in Year 2 to increase the content of uncoordinated metal sites in the materials will be investigated as a way to compensate for the typical disadvantages of larger pores such as poor volumetric capacity by increasing the materials' affinity for hydrogen. The zirconium system shows promise and though it does not meet our current targets, it may provide a structural avenue towards creating MOFs with more favorable hydrogen affinities. If we can achieve a structural analogue using a first row transition metal, the performance should increase on a gravimetric basis and may meet the project goals.

REFERENCES

1. Feng, et al., "Kinetically tuned dimensional augmentation as a versatile synthetic route towards robust metal–organic frameworks," *Nature Communications* 5, 5723. 2014.