

IV.C.4 HyMARC (Support): NREL Effort

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Project Start Date: October 1, 2015
Project End Date: Project continuation and direction
determined annually by DOE

- Demonstrate the ability to increase the binding energy and/or hydrogen desorption temperature in a sorbent material.
- Develop computational program to control the advanced cryostat controlled PCT apparatus.
- Determine the viability of boron and nitrogen doped materials for increased binding energy and capacities that could approach the 2020 DOE onboard hydrogen storage targets.
- Conduct a multi-laboratory PCT round-robin investigation to determine the volumetric and gravimetric capacities of two standard sorbent materials.
- Assist the DOE Hydrogen Materials – Advanced Research Consortium (HyMARC) seedling projects.

Technical Barriers

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

- (A) System Weight and Volume
- (B) System Cost
- (C) Efficiency
- (E) Charging/Discharging Rates
- (O) Lack of Understanding of Hydrogen Physisorption and Chemisorption
- (P) Reproducibility of Performance

Technical Targets

Hydrogen Storage Materials: This project is conducting validation studies of various framework materials, sorbents, hydrides and model compounds. Concurrently, the team also is developing new characterization tools for the rapid enhancement of materials development. Insights gained from these studies will be applied toward the design and synthesis of hydrogen storage materials that meet the following DOE onboard 2020 automotive usable hydrogen storage targets.

- 1.5 kWh/kg system (4.5 wt% H₂)
- 1.0 kWh/L system (0.030 kg H₂/L)
- Cost of \$10/kWh (\$333/kg H₂ stored)
- Operating at ambient temperatures (-40°C to 60°C)
- Onboard efficiency of 90% and minimum hydrogen delivery pressure of 5 bar
- Total refuel time of 5 min

Overall Objectives

- Develop a series of advanced characterization tools that allow for rapid advancement and in-depth understanding of next-generation hydrogen storage materials.
- Develop a hydrogen storage material with a total material-based capacity of greater than 45 g/L, at a temperature above 150 K and less than 100 bar, and reversible for multiple cycles.
- Develop a consensus protocol for the measurement and reporting of hydrogen gravimetric and volumetric capacities.
- Validate the performance of various hydrogen storage materials as requested by DOE.

Fiscal Year (FY) 2017 Objectives

- Develop new characterization tools (specifically: thermal conductivity and cryostat temperature control of pressure-concentration-temperature [PCT] apparatus).

FY 2017 Key Accomplishments

- Completed an NREL-led round robin study on the hydrogen adsorption measurements of two different carbon samples. The study included 13 laboratories, plus two DOE FCTO program participants.
- Established the ability to control the desorption temperature of hydrogen in pore-restricted sorbents with a resultant range from 80 K to 300 K.
- Modified carbon sorbents for introduction of metal sites with resultant high surface areas while increasing hydrogen desorption temperature.
- Utilized the thermal conductivity apparatus that can operate from 50 K to 380 K with gas overpressures up to 100 bar for preliminary experiments on MOF-5 (metal organic framework).
- Validated the adsorption capacities of multiple external laboratory materials under investigation for DOE.
- Initiated the protocols for reporting volumetric capacity of sorbent materials through DOE, U.S. DRIVE Tech Team, and international partner interactions.
- Established multiple experimental and modeling partnerships and collaborations with the HyMARC team.
- Correlated the theoretical and experimental binding energies for a series of boron substituted carbon-based sorbents (in collaboration with Pacific Northwest National Laboratory [PNNL]).
- Designed, constructed, and utilized the cryostat temperature controlled PCT apparatus for experiments from 50 K to 300 K under pressures up to 180 bar hydrogen.



INTRODUCTION

The Hydrogen Storage program supports research and development of technologies to lower the cost of near-term physical storage options and longer-term material-based hydrogen storage approaches. The program conducts research and development of low-pressure, materials-based technologies and innovative approaches to increase storage potential and broaden the range of commercial applications for hydrogen. These advanced-materials activities focus on development of core capabilities designed to enable the development of novel materials with the potential to store hydrogen near room temperature, at low-to-moderate pressures, and at energy densities greater than either liquid or compressed hydrogen. Key activities include improving the energetics, temperature, and rates of hydrogen release.

Advanced concepts include high-capacity metal hydrides, chemical hydrogen storage materials, and hydrogen sorbent materials, as well as novel material synthesis processes. The overarching goal of the FCTO Hydrogen Storage program is to develop and demonstrate viable hydrogen storage technologies for transportation, stationary, portable power, and specialty vehicle applications (e.g., material handling equipment, airport ground support equipment, etc.), with a key goal of enabling >300-mile driving range across all light-duty vehicle platforms, without reducing vehicle performance or passenger cargo space.

APPROACH

This national laboratory collaboration brings together internationally recognized leaders in hydrogen storage materials characterization and development at NREL, PNNL, Lawrence Berkeley National Laboratory, and NIST, as the HyMARC support team (also known as the Hydrogen Storage Characterization and Optimization Research Effort [HySCORE]). This collaboration is based on a synergistic approach to further validate hydrogen storage concepts and develop the key core capabilities necessary for accurate evaluation of hydrogen storage materials capacity, kinetics, and sorption/desorption physio-chemical processes. The overall approach involves parallel experimental and modeling efforts to utilize the core capabilities developed to rapidly define, model, synthesize, and characterize the appropriate materials necessary for achieving the 2020 Hydrogen Storage goals set forth by DOE. The approach is multifaceted to mitigate risk and ensure success as we bridge the gap between physisorption and chemisorption to provide the basis for a new generation of hydrogen storage materials technologies.

Our approach in FY 2017 (specifically NREL and NIST in this report) included efforts to develop state-of-the-art characterization techniques for hydrogen storage materials including advanced thermal conductivity, PCT, and neutron-based spectroscopic techniques. Through theoretical–experimental iterations, we focused on addressing questions and validating recent concepts and mechanisms related to materials-based hydrogen storage community including:

- Can multiple hydrogen molecules be adsorbed on an unsaturated metal center within a sorbent?
- Is it possible to enhance the kinetics of hydride formation with additives?
- Does the incorporation of boron sites improve the binding energy of carbon-based sorbents?
- How can one alter/increase the hydrogen binding energies for physisorption in non-crystalline and crystalline sorbents?

Our team directly interacts with and supports the entire HyMARC core team, as well as the HyMARC seedling projects.

KEY RESULTS

Volumetric Round Robin Study

The NREL-led round robin study involved the hydrogen adsorption measurements of two different carbon samples. Participants were asked to measure and calculate capacities at ambient temperature and liquid nitrogen temperatures. Detailed instructions and protocols were provided. The data comes from 13 different laboratories: one industry, eight government, and four academic institutions. The participants included four international laboratories and nine laboratories within the United States. Due to the large amount of data, we have decided to write two manuscripts: (1) presentation of the data with comparative analysis, and (2) in-depth analysis of the data including modeling to adjust data based on possible errors. Our current focus is to publish the first manuscript, which is in draft form.

To highlight some of the analysis and data, Figures 1–3 show the final compilation of the data taken at ambient temperature for Sample 1. This includes excess gravimetric capacity (Figure 1), excess volumetric capacity (Figure 2), and total volumetric capacity (Figure 3). The data shown in Figure 1 includes 16 different volumetric measurements and one gravimetric measurement. The data in Figures 2 and 3 are all based on volumetric measurements. The data were corrected by the participants for any obvious calculation errors that were discovered. One set of data was removed because of system contamination issues. The full manuscript will present all data for Sample 1 and 2 at both temperatures.

We are currently utilizing multiple statistical approaches to analyze the variability in the data. One approach is displayed in Figure 4, where each data set is interpolated to a common pressure in order to calculate statistics and evaluate the range of error. The error bars shown in Figure 4a are larger for Sample 2 than Sample 1. This is expected because Sample 2 is a powder while Sample 1 is pelletized. Experimentally, it is more difficult to determine sample mass, packing density, etc., in a powder sample than a pelletized sample. The error bars associated with the total volumetric capacity in Figure 4b are larger at higher pressures for

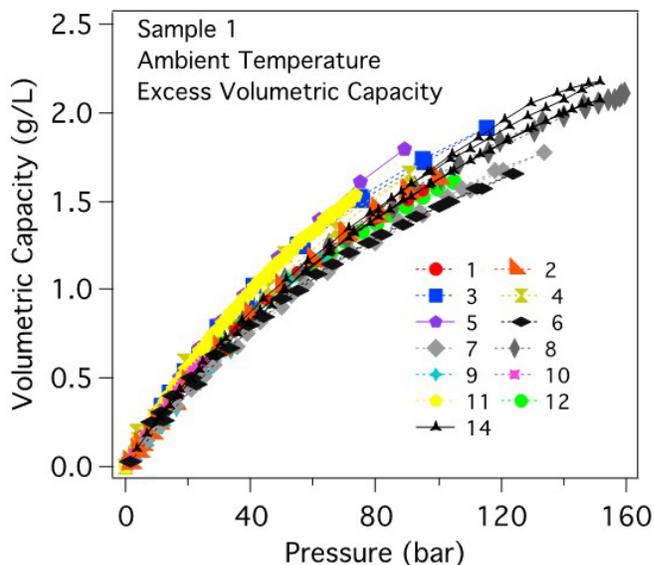


FIGURE 2. Excess volumetric capacity at ambient temperature for sorbent Sample 1

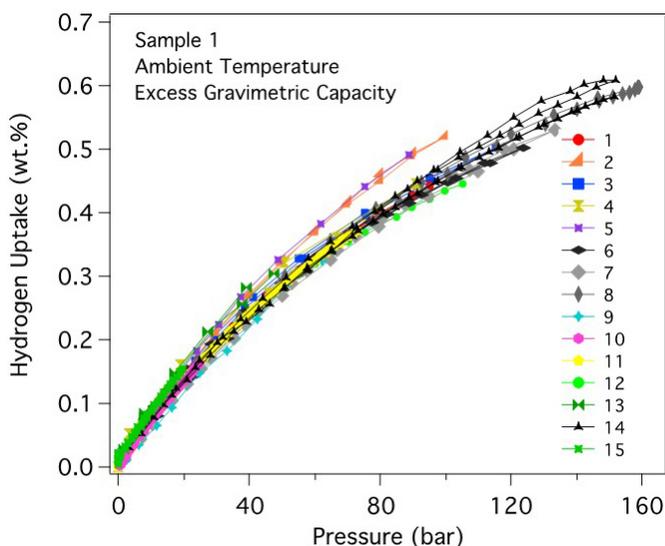


FIGURE 1. Excess gravimetric capacity at ambient temperature for sorbent Sample 1

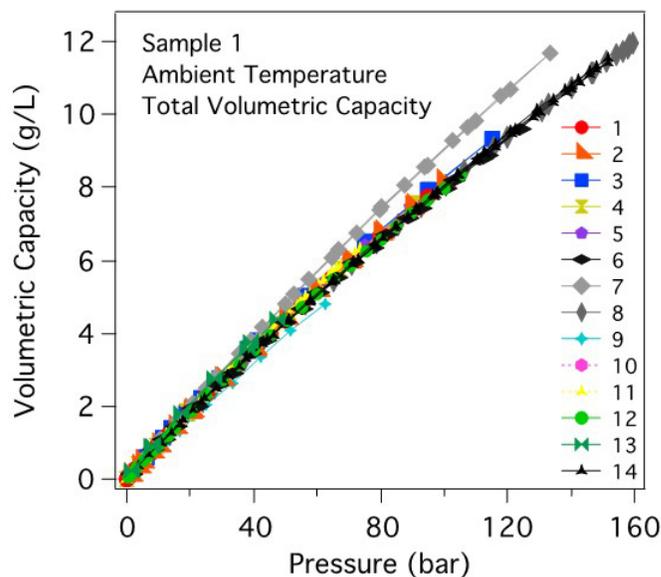


FIGURE 3. Total volumetric capacity at ambient temperature for sorbent Sample 1

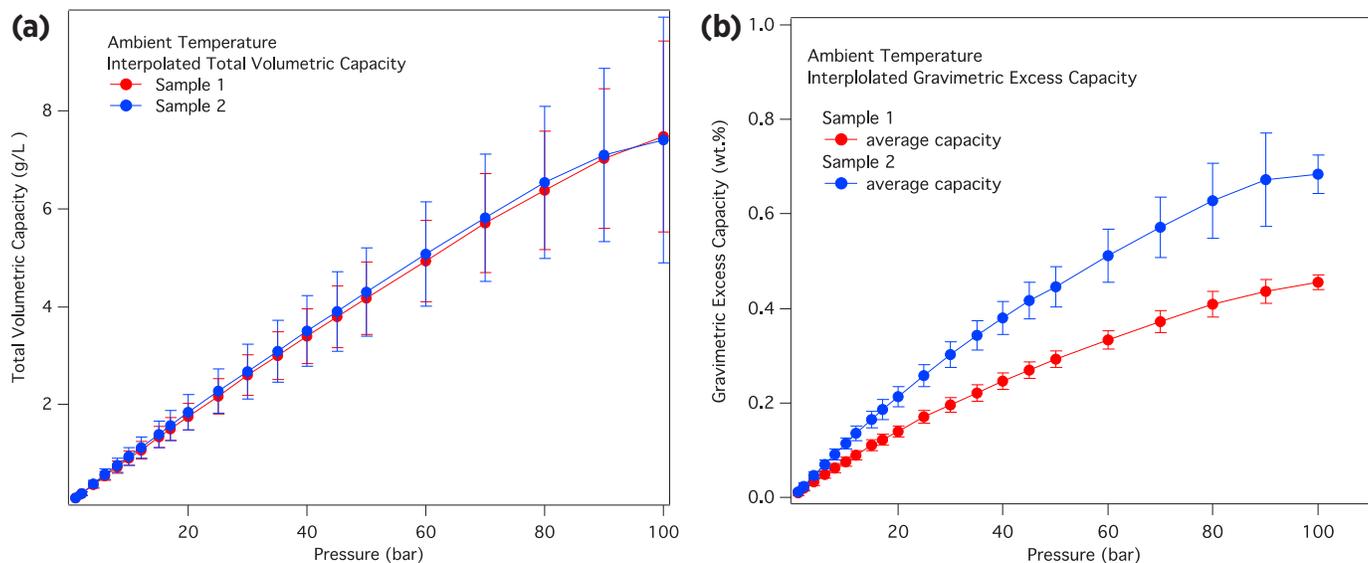


FIGURE 4. The average of interpolated data for the excess gravimetric capacity (a), and the total volumetric capacity (b) at ambient temperature for sorbent Sample 1 and Sample 2

both samples. This can be attributed to the variation in the packing density measured by different laboratories. We continue to analyze the data and work closely with the study participants to make sure all details are reported and conveyed in the coming manuscripts. In summary, it appears that the community at large has improved in the reporting of viable hydrogen adsorption data, especially with gravimetric capacities. There still needs to be improvement in developing a standard protocol for the determination of excess volumetric capacity of less dense powder samples to reduce the relative range in results observed in this study.

Control of Hydrogen Desorption Temperature

In our attempts to control the desorption temperature of the hydrogen from sorbents in FY 2016, we investigated a series of oxo-carbon species with different metal centers. The most interesting of these materials turned out to be calcium oxalate, which exhibited a highly unusual hydrogen adsorption behavior (Figure 5). While the Brunauer–Emmett–Teller surface area was only 4 m²/g, the material still adsorbed 1.2 wt.% hydrogen at 200 K, but only <0.01 wt.% at 77 K. As shown in Figure 5, the reversible desorption peak of the hydrogen appears at 180 K with a binding energy of ~19 kJ/mol as determined by variable heating rate temperature programmed desorption. To better understand this odd behavior, Lawrence Berkeley National Laboratory modeled the hydrogen binding in calcium oxalate, and computationally identified the binding site and computed the interaction energy. It was predicted that within the oxalate framework there were non-specific interactions that were dispersion dominated in the ultramicroporous structure. The calculated binding energy was 24 kJ/mol, which was very close to the experimental value. This work

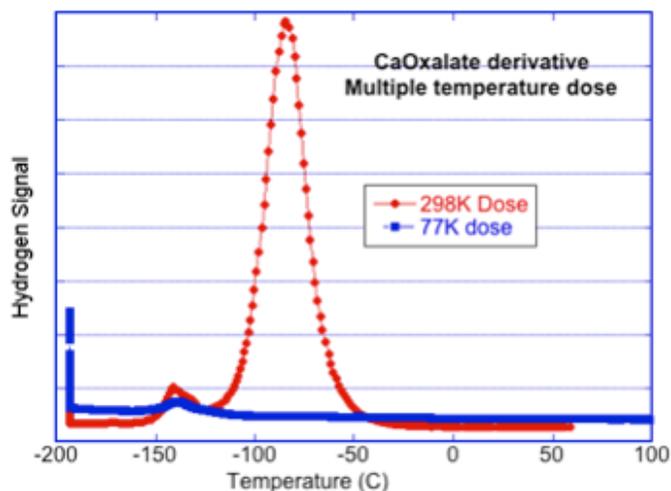


FIGURE 5. Temperature programmed desorption spectra of calcium oxalate hydrogen sorption experiments. In the red curve the material was dosed for 10 minutes with 1.4 bar hydrogen at 298 K and then quenched to 77 K, while the blue curve was dosed at 77 K. The heating rate was 15 K/min.

is the first demonstration of how small pores can control both the thermodynamics and kinetics of hydrogen sorption mechanisms. We are planning to submit a full part on this result and further investigate other materials with higher capacity but similar dispersion interactions.

Variable Temperature PCT Apparatus

NREL has developed a variable temperature PCT apparatus to facilitate hydrogen capacity measurements at pressures up to 200 bar over a wide temperature range (50 K to 350 K). It consists of a modified PCTPro 2000 integrated

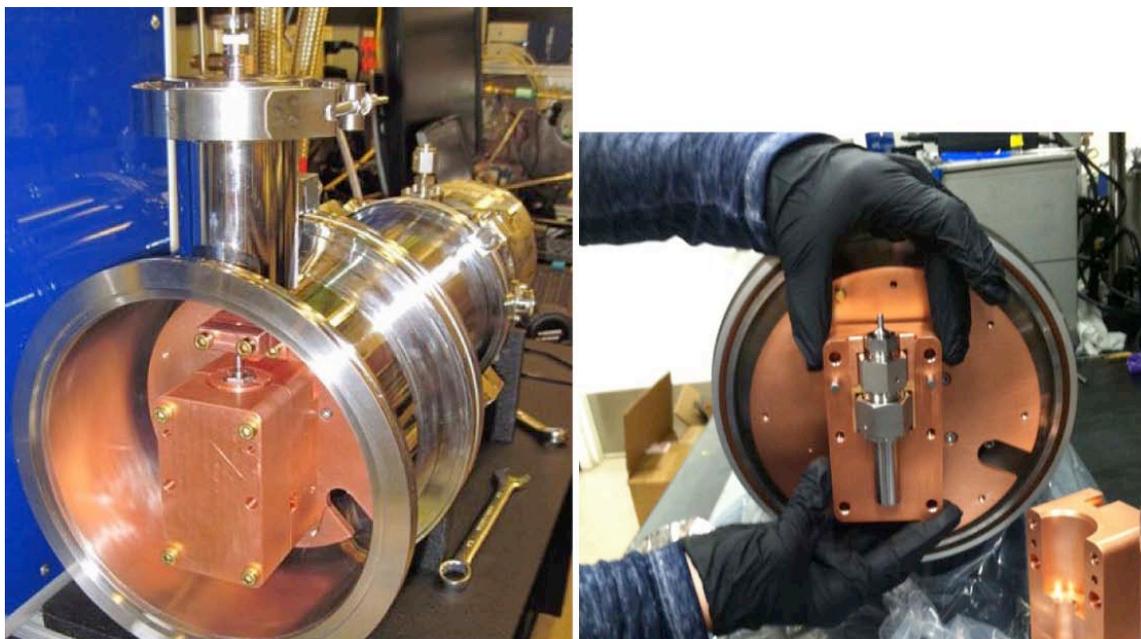


FIGURE 6. Cryostat attached to the NREL PCT system. Left: complete isothermal copper jacket; right: the sample cell within the copper jacket.

with a heavy-duty cryocooler used for the temperature control and a custom made isothermal sample holder that was designed to minimize temperature gradients at the sample (Figure 6). At the time of this report, verification of its operation is in progress and will show that this new apparatus will produce accurate and reliable measurements. Initial verification efforts consist of null measurements to show acceptable results at all temperatures and pressures and indeed, these initial results are acceptable. Future efforts will integrate new data acquisition software into the instrument and validate isosteric heat of adsorption measurements.

Boron-Doped Materials

The goal of this work is to incorporate B functionalities into carbon materials for enhanced hydrogen binding using vapor phase synthesis and/or modification. The boron incorporation (BC_x) has been predicted to enhance the hydrogen binding energy (to the range of 10–15 kJ/mol) through strain-induced distortion of the sp^2 network to produce sp^3 -like boron. This is termed “graphitic puckering” and is depicted in Figure 7. Increased puckering is expected to promote H_2 – BC_x interactions with higher binding energy.

Near edge X-ray absorption fine structure (NEXAFS) measurements conducted at end station 10-1 at the Stanford Synchrotron Radiation Lightsource (SLAC) National Accelerator Laboratory confirm the presence of non-planar boron consistent with the puckered sp^2 – sp^3 structure. Figure 7 shows boron 1s NEXAFS data for a BC_x material compared to hexagonal boron nitride (h -BN). The BC_x NEXAFS data shows three peaks in the π^* region labeled 1, 2, 3. Peaks 1

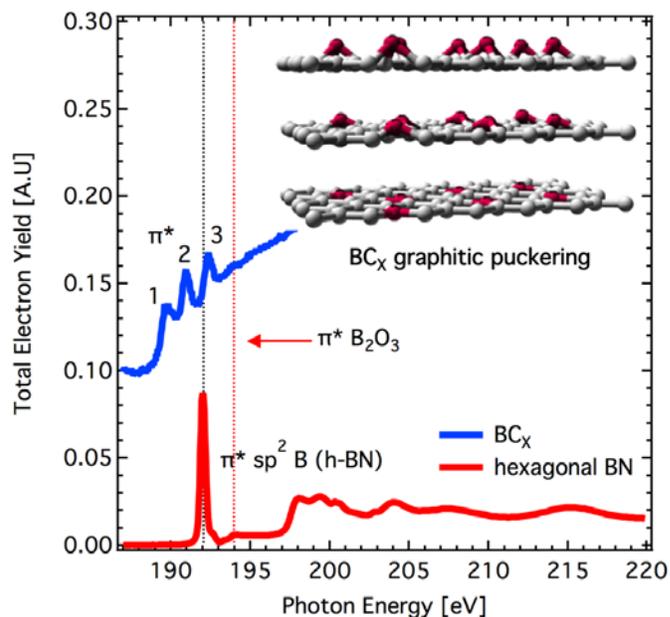


FIGURE 7. Boron 1s NEXAFS data for BC_x carbon and schematic of BC_x graphitic puckering. π^* Peaks 1 and 2 denote BC_x species with non-planar structure indicative of puckering. π^* Peak 3 is consistent with sp^2 B within hexagonal boron nitride. The red dashed line denotes the position of boron–oxygen species.

and 2 are consistent with non-planar boron that is attributed to a puckering structure. The π^* Peak 3 aligns to the π^* peak of h -BN which is consistent with the sp^2 structure for boron. No boron–oxygen species could be detected by NEXAFS

where the red dashed line denotes the position of the $B_2O_3 \pi^*$ peak. Neutron prompt gamma analysis performed on BC_x seeds and BC+PECVD materials yielded a 0.47 mol% B and 2.2 wt% B, respectively. The results are a promising indication that sp^3 boron is being incorporated.

PNNL has conducted a new series of theoretical predictions of the binding energies for hydrogen after the incorporation of boron, and found that a binding energy of 7–8 kJ/mol is predicted. For the materials described above, variable temperature programmed desorption found a binding energy of ~ 7 kJ/mol. We have recently conducted a second synthetic approach to incorporate more boron throughout the sample; the analysis will be complete by the end of the fiscal year.

Thermal Conductivity

In collaboration with Troy Semelsberger (LANL), we discovered unusual behavior while measuring the thermal conductivity of MOF-5 under a variety of temperatures and pressures. We conducted measurements on two sets of MOF-5 samples under helium pressures ranging from 0.03 bar to 100 bar, and at temperatures ranging from 40 K to 400 K.

Figure 8 shows the measured thermal conductivity and diffusivity of MOF-5 at various temperatures and pressures. Two different MOF-5 sample sets (a set consists of two pucks) were measured. In Figure 8, the two sets are called “NREL MOF” and “LANL MOF,” with the name indicating the laboratory where each was first measured. Both sets were provided by Mike Veenstra at Ford and are expected to have the same thermal properties. The “@ NREL” and “@ LANL” in the legend indicate where the measurements were made. Note that the LANL MOF has been measured at 77 K by both LANL and NREL, and the results show good agreement between the two instruments.

At sub-ambient temperatures, both the thermal conductivity and diffusivity show a pronounced peak, which

shifts to lower pressure as the temperature decreases. For all investigated temperatures, the peak in thermal diffusivity occurs at lower pressure than the peak in the thermal conductivity. Though the room temperature and elevated temperature conductivity data do not roll over in the range of pressures measured, they may follow the trend if the pressure were further increased.

To understand the source of the non-monotonic behavior observed in the MOF-5+He system, we will be measuring the thermal conductivity of MOF-5 in the presence of other gases at different pressures and temperature. Troy Semelsberger at LANL has measured MOF-5 in hydrogen at both room temperature and at 77 K, and did not observe a peak in the thermal conductivity as a function of pressure at either temperature. In the coming weeks, we will measure MOF-5 samples in the presence of hydrogen to confirm this result and in the presence of argon at a variety of temperatures.

CONCLUSIONS AND UPCOMING ACTIVITIES

We have validated several key aspects of hydrogen storage materials that were first reported in FY 2016. These include:

- Conducting an international round robin to establish the validity of the proposed protocol for hydrogen sorption measurement.
- Binding two hydrogen molecules to a metal center in a framework material.
- Controlling the binding energy by changing metal centers in several sorbent species.
- Increasing the binding energy in carbon sorbents by the introduction of catecholates and metal centers.
- Validating several models/predictions of materials' performance.

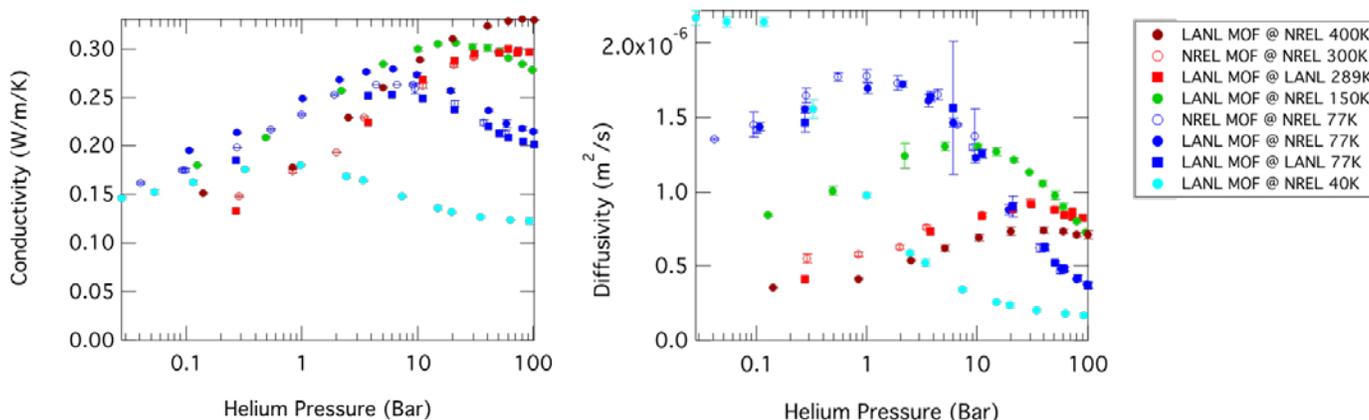


FIGURE 8. Thermal conductivity of MOF-5 in helium as a function of pressure at different temperatures

- Developed advanced characterization techniques that have already had a significant impact in the community and established the effect of systematic error on the reported capacities of standard carbon materials.

Taken together these results have established a multitude of possible solutions for advanced hydrogen storage materials—both sorbents and hydrides. Our upcoming activities will be to continue our development of the PCT cryostat system that will be essential to the DOE FCTO hydrogen storage programs. We will finish our validation of the concepts associated with the claims that boron doped sorbents are materials with the potential to display increased binding energies of physisorption. Finally, we will continue to interact with the theoreticians on various materials' matrix possibilities as we strive to increase the capacity of a new genre of hydrogen sorbents and improve the reversibility kinetics of possible hydrides. These iterative interactions will help to answer the following questions.

- Does the insertion of calcium into framework materials increase binding energy as predicted?
- Is it possible to bind more than two hydrogen molecules per open metal site?
- Through the control of pore size and chemistry, can we manipulate binding energies?
- Can we manipulate the binding energy with improved capacity?
- Can heterolytic cleavage of hydrogen be utilized as a possible mechanism to reach the 2020 targets?

SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

1. Katherine Hurst (NREL) attended the International Symposium Hydrogen & Energy in Hawaii, March 2017 and won the award for best poster.
2. Mira Dimitrievska (NIST/NREL), "Neutron scattering applications in materials for hydrogen energy storage," 23rd Annual Sigma Xi Postdoctoral Poster Presentation, Gaithersburg, USA, February 2017 received the most outstanding poster award.
3. Thomas Gennett, Steve Christensen, "*Nanostructured Composite Metal Hydrides*," U.S. provisional patent application was filed on May 17, 2017 at the United States Patent & Trademark Office and has received Application No. 62/507,354.

FY 2017 PUBLICATIONS

1. M. Dimitrievska, J.L. White, W. Zhou, V. Stavila, L.E. Klebanoff and T.J. Udovic, **Phys. Chem. Chem Phys.**, 18, 25546 (2016).
2. W.S. Tang, M. Dimitrievska, J.-N. Chotard, W. Zhou, R. Janot, A.V. Skripov, and T.J. Udovic, **J. Phys. Chem. C**, 120, 21218 (2016).
3. V. Soloninin, M. Dimitrievska, R.V. Skoryunov, O.A. Babanova, A.V. Skripov, W.S. Tang, V. Stavila, S. Orimo, and T.J. Udovic, **J. Phys. Chem. C**, 121, 1000 (2017).

4. W.S. Tang, K. Yoshida, A.V. Soloninin, R.V. Skoryunov, O.A. Babanova, A.V. Skripov, M. Dimitrievska, V. Stavila, S. Orimo, and T.J. Udovic, **ACS Energy Lett.**, 1, 659 (2016).
5. H. Wu, W.S. Tang, W. Zhou, J.D. Tarver, V. Stavila, C.M. Brown, T.J. Udovic, **Journal of Solid State Chemistry**, 243, 2016, 162–167.
6. Y. Tulchinsky, C.H. Hendon, K.A. Lomachenko, E. Borfecchia, B.C. Melot, M.R. Hudson, J.D. Tarver, M.D. Korzynski, A.W. Stubbs, J.J. Kagan, C. Lamberti, C.M. Brown, M. Dinca, **Journal of the American Chemical Society**, 139, 2017, 5992–5997.
7. K.E. Hurst, T. Gennett, and P.A. Parilla, "A Multi-Laboratory Measurement Comparison Study of Hydrogen Sorption," in preparation, 2017.
8. K.E. Hurst, T. Gennett, and P.A. Parilla, "Lessons Learned based on Analysis of a Multi-Laboratory Measurement Study of Hydrogen Sorbent Materials," in preparation, 2017.
9. P.A. Parilla, T. Gennett, and K.E. Hurst, "Systematic Error from Using a Popular but Flawed Model for Manometric Instruments," in preparation, 2017.

FY 2017 PRESENTATIONS

1. Jacob Tarver and Craig Brown (NREL/NIST), "Using Neutrons to Probe Hydrogen Storage in Metal-Organic Frameworks," presented at 11th Intl Symp Hydrogen and Energy (February 2017).
2. Jacob Tarver and Craig Brown (NREL/NIST), "Using Neutrons to Probe Hydrogen Storage in Metal-Organic Frameworks," presented at Gordon Research Conference, Metal Hydrogen Systems (July 2017).
3. Katherine Hurst, Philip Parilla, and Thomas Gennett, "A Multi-laboratory Comparison Study of Volumetric Hydrogen Adsorption Measurements on Sorbents," International Hydrogen and Energy Symposium, Waikoloa Village, HI, March 1, 2017.
4. Katherine Hurst, Philip Parilla, and Thomas Gennett, "HYSCORE/NREL Opportunities for Collaboration," IEA Task 32 Experts Meeting, Waikoloa Village, HI, March 3, 2017.
5. Katherine Hurst, Thomas Gennett, and Philip Parilla, "Update on NREL's Validation Efforts: Inter-Laboratory Comparison," Hydrogen Storage Tech Team Meeting, Southfield, MI, March 16, 2017.
6. Katherine Hurst, Steven Christensen, Noemi Leick, and Thomas Gennett, "Modification of Hydride Materials for Hydrogen Storage by ALD," ALD2017, Denver, CO, July 15–18, 2017.
7. Mirjana Dimitrievska and Terrence Udovic, "Anion Dynamical Behaviors and Their Possible Relationship to Superionic Conductivities in Hydro-Closo-Borate Salts of Lithium and Sodium," MRS Fall meeting, Boston, USA, December 2016.
8. Mirjana Dimitrievska and Terrence Udovic, "Neutron scattering applications in materials for hydrogen energy storage," 23rd Annual Sigma Xi Postdoctoral Poster Presentation, Gaithersburg, USA, February 2017.
9. Philip Parilla, Katherine Hurst, and Thomas Gennett, "Update on the Inter-Laboratory Comparison on Volumetric Capacity Determination," Task 32 IEA HIA Expert Meeting, December 2016, Berlin, Germany.

- 10.** Thomas Gennett, “HySCORE, an Overview,” International Hydrogen and Energy Symposium, Waikoloa Village, HI, March 1, 2017.
- 11.** Thomas Gennett, “HySCORE, an Overview,” ECS International Meeting, New Orleans, LA, May 31, 2017.
- 12.** Philip Parilla, Katherine Hurst, and Thomas Gennett, “Hydrogen Sorbent Measurement Qualification and Characterization,” AMR, Washington, D.C., June 2017.
- 13.** Mirjana Dimitrievska, Jacob Tarver, Thomas Gennett, Terrence Udovic, and Craig Brown, “HySCORE: Technical Activities at NIST,” AMR, Washington, D.C., June 2017.