IV.E.3 Neutron Characterization in Support of the DOE Hydrogen Storage Sub-Program

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Project Start Date: June 2010
Project End Date: Project continuation and direction determined annually by DOE

Fiscal Year (FY) 2012 Objectives

- Support the DOE-funded hydrogen-storage projects by providing timely, comprehensive characterization of materials and storage systems using state-of-the-art neutron methods.
- Direct partner synthesis efforts based on the understanding gained through the use of these methods.
- Demonstrate the fundamental characteristics of useful hydrogen-storage materials.

Technical Barriers

This project addresses the following technical barriers from the Storage section (3.3) of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) System Weight and Volume
(P) Lack of Understanding of Hydrogen Physisorption and Chemisorption

Technical Targets

NIST provides important materials metrologies for DOE-funded projects using neutron-scattering measurements to understand and characterize hydrogen-substrate interactions of interest in a variety of materials ranging from H_2 adsorbed in nanoporous materials to H chemically bonded in complex-hydride materials. Insights gained from these studies will be applied toward the design and synthesis of hydrogen-storage materials that meet the following DOE 2017 storage targets:

- Specific energy: 1.8 kWh/kg
- Energy density: 1.3 kWh/L
- Cost: $2-$4/kWh net

FY 2012 Accomplishments

- Manuscript published on detailed measurements of temperature dependence of hydrogen adsorbed structures in Fe-MOF74 and its oxidized form.
- Manuscript accepted for publication concerning hydrogen spillover on single-walled carbon-nanohorns in collaboration with the Oak Ridge National Laboratory (ORNL) and Rice University.
- Manuscript submitted for publication concerning spillover speciation in an effort led by NREL.
- Manuscript published on synthesis and characterization of first metal hydrazinoborane and its hydrazine borane adduct.
- Manuscript submitted for publication on structural characterization of X-ray diffraction (XRD)-amorphous, aluminoborane compound AlB_4H_{11}.
- Manuscript published on BH_4^- reorientational mechanism in high-temperature hexagonal $LiBH_4$ phase.
- Manuscript submitted for publication on confinement effects on $LiBH_4$ and $NaAlH_4$ sequestered in ordered nanoporous carbon frameworks.

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Introduction

To obtain the DOE levels of hydrogen storage in a timely manner, it is imperative that trial-and-error testing of materials be avoided. Thus, the focus must be upon the rational design of new systems. From a thorough understanding of the physics and chemistry that governs the hydrogen-substrate interactions, we will be able to make a more concerted effort to push the frontiers of new materials. The key to improving materials is a detailed understanding of the atomic-scale locations of the hydrogen and determining how it gets there and how it gets out. Neutron scattering is perhaps the premier technique for studying hydrogen and the

NIST Center for Neutron Research is currently the leading facility in the U.S. for studying these materials.

Approach

NIST provides important materials characterization for DOE-funded, hydrogen storage projects using neutron-scattering measurements to probe the amount, location, bonding states, dynamics, and morphological aspects of (i) molecular hydrogen in carbon-based materials such as polymers, metal organic frameworks (MOFs), and carbonaceous materials such as carbon nanohorns, and (ii) atomic hydrogen in a variety of complex hydride materials including those containing boron and nitrogen, as well as their intermediates and by-products. NIST works directly with DOE and other partners that produce novel hydrogen storage materials to analyze the most promising samples and to help determine and resolve the fundamental issues that need to be addressed.

Results

In collaboration with U. California Berkeley, U. Maryland, U. Florida, Australian Nuclear Science and Technology Organisation, and the Rutherford Appleton Laboratory, we used several neutron-based techniques, including neutron powder diffraction (NPD) and neutron vibrational spectroscopy (NVS), to determine the hydrogen adsorption properties of Fe-MOF74 (Figures 1-2) and its oxidized derivative [1]. These two MOFs, which possess one-dimensional hexagonal channels decorated with unsaturated iron coordination sites, exhibit high initial isosteric heats of adsorption of −9.7(1) and −10.0(1) kJ mol^{-1}, respectively. NPD has allowed the identification of three D_2 binding sites within the two frameworks, with the closest contacts corresponding to Fe–D_2 separations of 2.47(3) and 2.53(5) Å, respectively. NVS spectra, obtained from *p*-H_2 (*para*-H_2) and D_2–*p*-H_2 mixtures adsorbed in Fe_2(dobdc), reveal weak interactions between two neighboring adsorption sites, a finding that is in opposition to a previous report of possible 'pairing' between neighboring H_2 molecules.

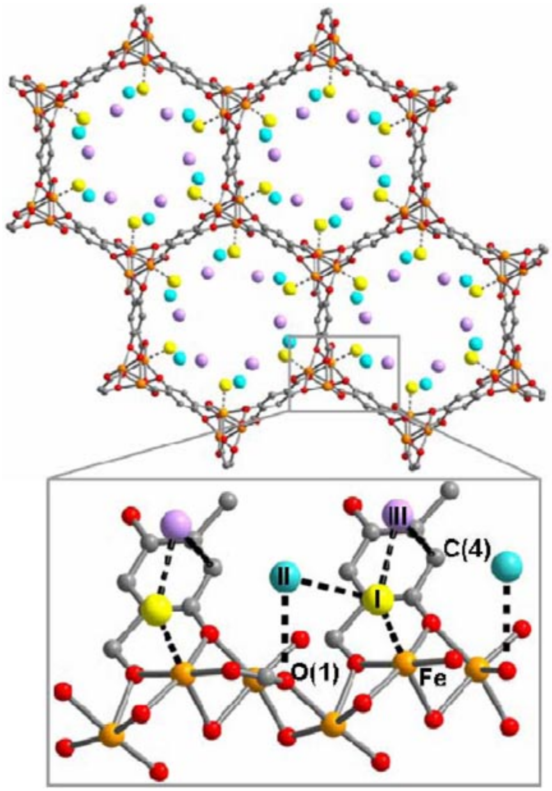

FIGURE 1. Fe-MOF74 loaded with 2.25 D_2 per Fe^{2+}, viewed along the [001] direction. Orange, gray, and red spheres represent Fe, C, and O atoms, respectively. The box contains a close-up view of the framework wall, showing the closest D_2-D_2 and D_2-framework interactions (drawn as dotted lines) along the channel. Three D_2 sites, determined by NPD, are labeled as I, II, and III in order of binding strength.

In collaboration with U. Delaware, U. Indianapolis, Rice U., Chase Corp., ORNL, and Siberian State Tech. U., NVS and Sievert's method measurements were combined with temperature-cycling to assess the role of temperature-

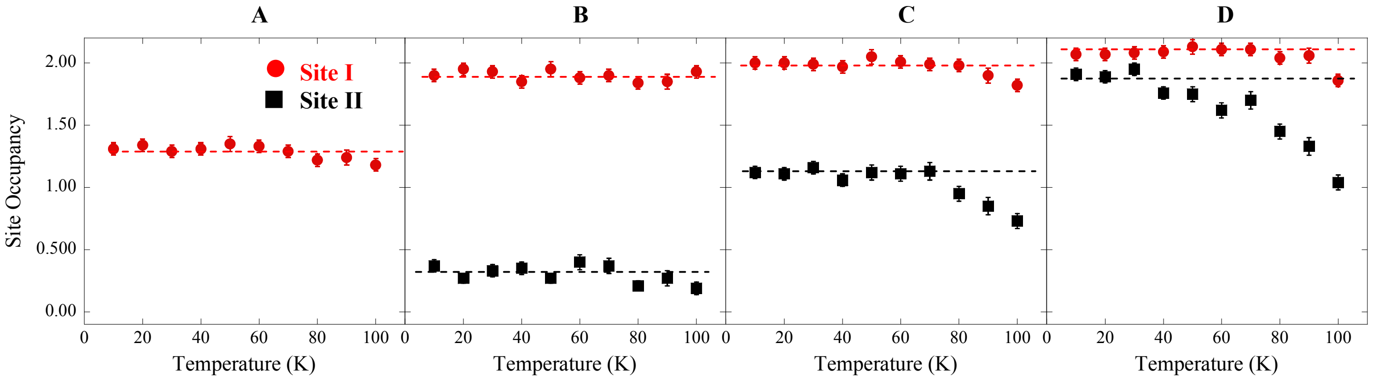

FIGURE 2. Occupancy of H_2 in Fe-MOF74 at site **I** (red) and **II** (black) plotted as a function of temperature for four different D_2 loadings, including (A) 0.5, (B) 1.0, (C) 1.5, and (D) 2.0 D_2 molecules per Fe^{2+}.

activated, metal-assisted hydrogen storage in Pt-decorated single-wall carbon nanohorns (Pt-SWCNHs) [2]. NVS measurements on single samples of SWCNHs decorated with 2–3 nm Pt nanoparticles showed a 0.17% mass fraction loss of molecular hydrogen after the sample was loaded at 77 K then cycled to room temperature (at a pressure of about 0.5 MPa) and back to 4 K. However, no loss in hydrogen was observed when it was cycled only up to 150 K. Control samples using undecorated SWCNHs did not display any loss of adsorbed H_2 measured at 4 K after cycling to room temperature. Similar measurements involving temperature cycling of Pt-decorated SWCNHs charged with 5 MPa of H_2 at 77 K using a Sievert's apparatus also indicated a measurable quantity (≈0.08% mass fraction) of metal-assisted hydrogen adsorption caused by cycling samples to room temperature. These measurements present evidence for additional excess storage measured at low temperatures induced by metal-assisted activated processes at room temperature. Density functional theory (DFT) calculations were performed to predict signature NVS spectra for C–H libration and bending modes for various conformations of carbon with hydrogen attached in different configurations. However, NVS spectra revealed a near-continuum spectrum, different from the predicted sharp peaks by our DFT calculations, indicating a lack of one preferred binding site if chemically-bonded H occurred in these samples.

In collaboration with U. Maryland, U. Penn, and GM, the first example of a metal hydrazinoborane, $LiN_2H_3BH_3$ (Figure 3), and its hydrazine borane ($N_2H_4BH_3$, HB) adduct, $LiN_2H_3BH_3{\cdot}2N_2H_4BH_3$, were synthesized, and their structures and bonding were characterized [3] via XRD, molecular dynamics simulated annealing methods, and NVS. The metal hydrazinoboranes exhibit dramatically improved dehydrogenation over pristine HB with nearly complete dehydrogenation in a mild temperature range (323–498 K) with minimal toxic gas (i.e., NH_3 or N_2H_4) release. The metal cation replaces one H on the middle N in the HB molecule, leading to the formation of $[NH_2NHBH_3]^-$. In particular, the extent and purity of H_2 released from $LiN_2H_3BH_3$ exceed even the best performance reported for hydrolysis of HB with catalysts. The electronic and structural changes from $N_2H_4BH_3$ to $[N_2H_3BH_3]^-$ are likely the main reasons for the observed improved hydrogen release properties for the metal hydrazinoboranes.

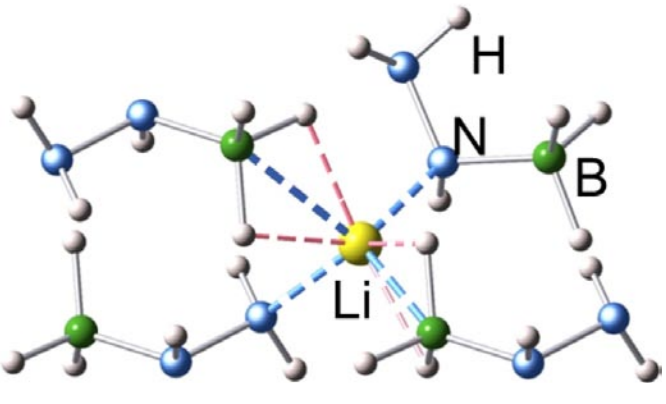

FIGURE 3. The local structure of $LiN_2H_3BH_3$

In collaboration with Ohio State U., Northwestern U., U. Maryland, the Savannah River National Laboratory, and ORNL, we used NVS to help characterize the novel, XRD-amorphous, aluminoborane compound AlB_4H_{11}. The structure was identified by coupling a first-principles, DFT-based approach with infrared (IR), NVS, and NMR measurements. The AlB_4H_{11} structure was found to contain distinct $[BH_4]$ and $[B_3H_7]$ units without any $[AlH_4]$ units. It forms a $-[B_3H_7]-Al(BH_4)-$ polymer chain with the $[BH_4]$ units twisted relative to each other perpendicular to the chain direction and bonded to Al, and a chain backbone consisting of $[B_3H_7]$ and Al where the $[B_3H_7]$ unit exhibits a triangular boron configuration. The computed lowest-energy structure shows good agreement with IR, NVS, and NMR spectra.

In collaboration with U. Maryland, quasielastic neutron scattering (QENS) spectra were measured for $LiBH_4$ in the high-temperature hexagonal crystal phase. The elastic incoherent structure factor (EISF) associated with the rapid BH_4^- anion reorientations was determined at 400 K, 410 K, and 420 K for momentum transfers as high as 4.2 Å^{-1} (Figure 4). The results strongly suggest a BH_4^- reorientational mechanism approaching quasi-free, trigonal-axis rotation of

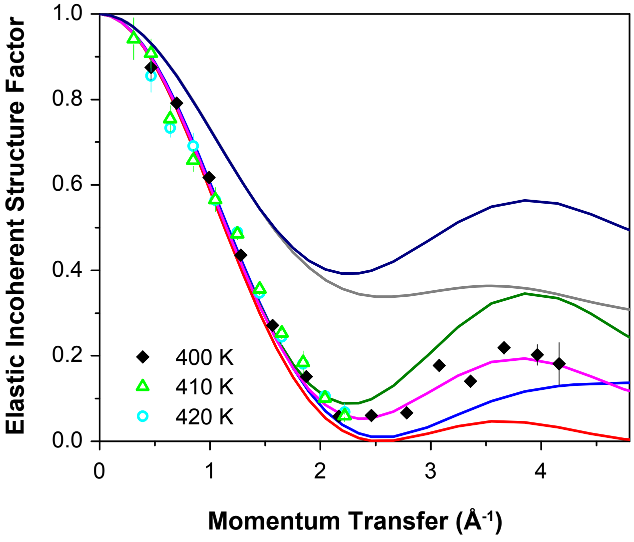

FIGURE 4. EISF data derived from QENS measurements for $LiBH_4$ at 400 K (black diamonds), 410 K (green triangles), and 420 K (cyan circles) compared with calculated curves for various BH_4^- reorientation models, from top to bottom: (dark blue) uniaxial three-fold reorientational jumps, (gray) continuous rotation of three H's around the trigonal axis with a fixed axial H, (green) tetrahedral tumbling among four sites, (magenta) continuous rotation around the trigonal axis combined with jump exchanges with the axial H, (blue) cubic tumbling among eight sites, and (red) isotropic rotational diffusion.

three borohydride H atoms, combined with reorientational jump exchanges between these delocalized “orbiting” H atoms and the remaining axial borohydride H atom [4]. This mechanism is consistent with previously reported diffraction and spectroscopy studies.

Continuing a collaboration with U. Missouri-St. Louis, Washington U.-St. Louis, Sandia National Laboratories, and Caltech, a comparison was made between $LiBH_4$ sequestered inside an ordered-nanopore carbon (NPC) scaffold and bulk $LiBH_4$. Consistent with NMR observations of two translationally distinct BH_4^- populations for $LiBH_4$ in NPC with 4-nm diameter cylindrical pores, analysis of QENS spectra reveal two reorientationally distinct populations of BH_4^- anions. Such a spectrum at 400 K is shown in Figure 5. The quasielastic scattering from this material is best represented by two Lorentzian functions, with linewidths differing by nearly an order of magnitude. Analogous to the translationally slower interior and more rapid interface BH_4^- anions observed by NMR, the narrower and broader Lorentzian components are associated with the reorientational motions of the less mobile, more bulk-like interior and more mobile, interface BH_4^- anions, respectively. Activation energies for reorientation of 15±1 kJ/mol and 11.3±0.8 kJ/mol for the former and latter BH_4^- populations were determined from an Arrhenius plot of the Lorentzian linewidths. The respective reorientation jump rates from the Arrhenius fits varied from ~2.6×10^{9} s^{1} and 5.6×10^{10} s^{1} at 193 K to ~3.5×10^{11} s^{1} and 2.1×10^{12} s^{-1} at 400 K. The reorientation rates and activation energy of the less mobile population are similar to those for bulk $LiBH_4$. The well-behaved Arrhenius-type dependence of the two Lorentzian linewidths from 193 K to 400 K are inconsistent with the presence of a solid-solid phase transition in this region.

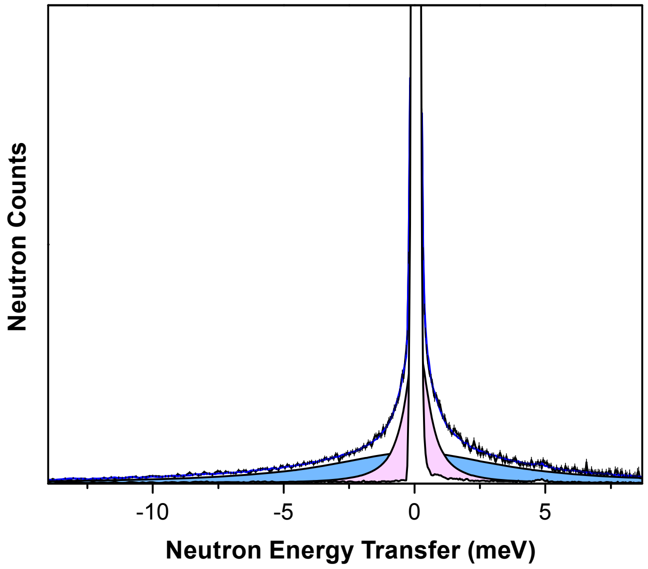

FIGURE 5. QENS spectrum of $LiBH_4$ in NPC at 400 K and 3 $Å^{-1}$ momentum transfer. The spectrum is fit to an elastic line with instrumental resolution (white) and two Lorentzian functions (narrower: pink and broader: blue) that reflect two different BH_4^- reorientational dynamics.

Conclusions and Future Directions

- Neutron methods have provided crucial, non-destructive characterization tools for the DOE Hydrogen Storage Sub-Program.
- The Fe-MOF74 system provided a rare opportunity to observe reduction-oxidation chemistry at the unsaturated metal sites in a MOF.
- Our measurements confirm the loss of adsorbed H_2 and significant metal-assisted hydrogen storage on Pt-SWCNHs that are activated at T >150 K, which is consistent with hydrogen spillover.
- The first example of a metal hydrazinoborane was synthesized and characterized. Further studies need to be conducted in expanding the range of metals used, tuning the reactivity of B–H and/or N–H through inducing polar species such as strong electropositive cations or highly active anions, exploring the role of dopants or catalysts in controlling dehydrogenation, and understanding the dehydrogenation mechanism.
- The successful characterization of AlB_4H_{11} demonstrates the usefulness of the structure prediction approach for determining the local structures of even XRD-amorphous compounds.
- We continued to characterize various aspects of nanoconfinement in an attempt to understand its effect on the hydrogen cycling of $LiBH_4$ and were able to observe two dynamically distinct populations of BH_4^- anions associated with $LiBH_4$ regions next to and away from the pore walls.
- We will continue to support the DOE Hydrogen Storage Sub-Program where needed.

Special Recognitions & Awards/Patents Issued

1. Craig M. Brown received the 2012 Arthur S. Flemming Award, administered by George Washington University, for his seminal contributions to our understanding of new materials suited for hydrogen energy storage in next-generation, clean automobiles.

2. Wendy L. Queen won the NIST chapter of Sigma-Xi Postdoctoral Poster Competition (Materials Category) for her poster: “Reducing Energy Costs of Industrial Gas Separations Using Metal-Organic Framework Based Solid Adsorbents”.

FY 2012 Publications/Presentations

1. N. Verdal, W. Zhou, V. Stavila, J.-H. Her, M. Yousufuddin, T. Yildirim, and T.J. Udovic, “Alkali and Alkaline-Earth Metal Dodecahydro-*Closo*-Dodecaborates: Probing Structural Variations via Neutron Vibrational Spectroscopy,” J. Alloys Compds. 509S, S694 (2011).

2. N. Verdal, T.J. Udovic, J.J. Rush, R.L. Cappelletti, and W. Zhou, "Hydrogen Dynamics of the Dodecahydro-*Closo*-Dodecaborate Crystals", Proc. Am. Chem. Soc., Div. Fuel Chem. 56, (2) 181 (2011).

3. N. Verdal, T.J. Udovic, J.J. Rush, V. Stavila, H. Wu, W. Zhou, and T. Jenkins, "Low-Temperature Tunneling and Rotational Dynamics of the Ammonium Cations in $(NH_4)_2B_{12}H_{12}$," J. Chem. Phys. 135, 094501 (2011).

4. N. Verdal, H. Wu, T.J. Udovic, V. Stavila, W. Zhou, and J.J. Rush, "Evidence of a Transition to Reorientational Disorder in the Cubic Alkali-Metal Dodecahydro-*Closo*-Dodecaborates," J. Solid. State Chem. 184, 3110 (2011).

5. J.-H. Her, H. Wu, N. Verdal, W. Zhou, V. Stavila, and T.J. Udovic, "Structures of the Strontium and Barium Dodecahydro-Closo-Dodecaborates," J. Alloys Compds. 514, 71 (2012).

6. N. Verdal, T.J. Udovic, and J.J. Rush, "The Nature of BH_4^- Reorientations in Hexagonal $LiBH_4$," J. Phys. Chem. C 116, 1614 (2012).

7. N. Verdal, T.J. Udovic, and J.J. Rush, "Correction to 'The Nature of BH_4^- Reorientations in Hexagonal $LiBH_4$'," J. Phys. Chem. C 116, 5275 (2012).

8. Y.S. Chua, H. Wu, W. Zhou, T.J. Udovic, G. Wu, Z. Xiong, M.W. Wong, and P. Chen, "Monoammoniate of Calcium Amidoborane - Synthesis, Structure and Hydrogen-Storage Properties," Inorg. Chem. 51, 1599 (2012).

9. M.M. Barsan, I.S. Butler, D.F.R. Gilson, R.O. Moyer, Jr., W. Zhou, H. Wu, and T.J. Udovic, "Raman, FTIR, Photoacoustic-Infrared and Inelastic Neutron Scattering Spectra of Ternary Metal Hydride Salts A_2MH_5 (A=Ca, Sr, Eu; M=Ir, Rh) and their Deuterides," J. Phys. Chem. A 116, 2490 (2012).

10. H. Wu, W. Zhou, F.E. Pinkerton, T.J. Udovic, T. Yildirim, and J.J. Rush, "Metal Hydrazinoborane $LiN_2H_3BH_3$ and $LiN_2H_3BH_3 \cdot 2N_2H_4BH_3$: Crystal Structures and High-Extent Dehydrogenation," Energy Environ. Sci. 5, 7531 (2012).

11. W.L. Queen, E.D. Bloch, C.M. Brown, M.R. Hudson, J.A. Mason, L.J. Murray, A.J. Ramirez-Cuesta, V.K. Peterson, and J.R. Long, "Hydrogen Adsorption in the Metal-Organic Frameworks Fe_2(dobdc) and $Fe_2(O_2)$(dobdc)," Dalton Trans. 41, 4180 (2012).

12. Y. Liu, C.M. Brown, D.A. Neumann, D.B. Geohegan, A.A. Puretzky, C.M. Rouleau, H. Hu, D. Styers-Barnett, P.O. Krasnov, B.I. Yakobson "Inelastic Neutron Scattering and High Pressure Gas Adsorption Measurements of Hydrogen Spillover on Pt-decorated Single-Walled Carbon Nanohorns," Carbon 50, 4953 (2012).

13. W.L Queen, C.M. Brown, M.R. Hudson, K. Sumida, E.D. Bloch, L.J. Murray, J.R. Long, D.K. Britt, and O.M. Yaghi "Gas Adsorption in Metal-Organic Frameworks With Coordinatively Unsaturated Metal Sites", 2011 Meeting of the American Crystallographic Association, New Orleans, LA (May 2011).

14. N. Verdal, T.J. Udovic, V. Stavila, and J.J. Rush, "Characterization of Destabilized and Ultra-Stable Hydrogen Storage Materials Using Neutron Scattering Techniques," Hydrogen-Metal Systems Gordon Conference, Stonehill College, Easton, MA (Jul. 2011).

15. C.M. Brown, "Probing Adsorption in Microporous Materials using Neutrons," Braggspeaks, ANSTO, Sydney, Australia (Jul. 2011) (Invited).

16. C.M. Brown, "Physical Aspects of Gas Adsorption in Microporous Materials," PACRIM9, Cairns, Australia (Jul. 2011) (Invited).

17. N. Verdal, T.J. Udovic, J.J. Rush, R.L. Cappelletti, and W. Zhou, "Hydrogen Dynamics of the Dodecahydro-Closo-Dodecaborate Crystals," National Meeting of the American Chemical Society, Denver, CO (Aug. 2011).

18. W.L. Queen, "Utilizing Neutron Scattering Techniques in the Characterization of Metal-Organic Frameworks", University of California Berkeley, Berkeley CA, (Aug. 2011) (Invited).

19. W.L. Queen, C. M. Brown, and M. R. Hudson, "Physical Aspects of H_2 Storage in Microporous Materials", 2011 Fall National Meeting of the American Chemical Society, Denver, CO (Aug. 2011) (Invited).

20. C.M. Brown, "Probing Adsorption in Microporous Materials using Neutrons," University of Sydney Chemistry Department School Seminar, Sydney, Australia (Aug. 2011) (Invited).

21. C.M. Brown, "Probing Adsorption in Microporous Materials using Neutrons," Monash University Faculty of Engineering Seminar, Melbourne, Australia (Sep. 2011) (Invited).

22. C.M. Brown, "Probing Adsorption in Microporous Materials using Neutrons," CSIRO Seminar, Melbourne, Australia (Sep. 2011) (Invited).

23. C.M. Brown, "Probing Adsorption in Microporous Materials using Neutrons," University of Adelaide Chemistry and Physics Seminar, Adelaide, Australia (Sep. 2011) (Invited).

24. C.M. Brown, "Gas Storage in Porous Materials," IUPAC International Conference on Novel Materials, Shanghai, China (Oct. 2011) (Keynote and Session Chair).

25. C.M. Brown, "Structure and Properties of Advanced Materials through Neutron Scattering," Geophysical Laboratory Seminar, Carnegie Institute, Washington, DC (Nov. 2011) (Invited).

26. W.L. Queen, C.M. Brown, M.R. Hudson, E.D. Bloch, and J.R. Long, "Reducing Energy Costs of Industrial Gas Separations Using Metal-Organic Framework Based Solid Adsorbents", 19th Annual Postdoctoral Poster Competition sponsored by the NIST Chapter of Sigma Xi, Gaithersburg, MD (Feb. 2012).

27. T.J. Udovic, "Neutron Scattering Studies of the Structure, Spectroscopy, and Reorientational Dynamics of Borohydride-based Materials," Spring Meeting of the Materials Research Society, San Francisco, CA, (Apr. 2012) (Invited).

28. C.M. Brown, "Gas Storage in Porous Materials," Advanced Seminar on "Perspectives for Neutron Science in Novel & Extreme Conditions," Zaragoza, Spain (May 2012) (Invited).

29. N. Verdal, X. Liu, T.J. Udovic, and E.H. Majzoub, "Understanding the Destabilizing Mechanism of Nanoporous Carbon Using Inelastic Neutron Scattering," American Conference on Neutron Scattering, Washington, DC (Jun. 2012).

30. W.L. Queen, M.R. Hudson and C.M. Brown, "What Neutrons Tell Us about Industrially Important Adsorption Processes," American Conference on Neutron Scattering, Washington, DC (Jun. 2012).

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1. Y. Liu, *et al*., Carbon **50**, 4953 (2012).

2. W. Queen, *et al*., Dalton Trans. **41,** 4180 (2012).

3. H. Wu, *et al*., Energy Environ. Sci. **5**, 7531 (2012).

4. N. Verdal, *et al*., J. Phys. Chem. C **116**, 1614 (2012).