Neutron Characterization in support of the DOE Hydrogen Storage Sub-Program

Terrence J. Udovic
Craig M. Brown
Dan A. Neumann

National Institute of Standards and Technology
Technology Administration, U.S. Department of Commerce

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Overview

Timeline
• Project start date: 10/2010
• Project end date: 10/2014*
  *Project continuation and direction determined annually by DOE

Barriers addressed
A. System Weight and Volume
O. Lack of Understanding of Hydrogen Physisorption and Chemisorption

Budget
• FY14 DOE Funding: $200K
• Planned FY15 DOE Funding: $200K
• Total DOE Funds Received to Date: $800K

NIST continues to provide access to neutron facilities and FTEs for the DOE Hydrogen Storage Projects.

Partners
Caltech, Delaware, GM, HRL, Maryland, Michigan, Missouri-St. Louis, Molecular Foundry, NREL, Ohio State, Penn, Penn State, RCB Hydrides, Sandia, UC Berkeley, Utah, Washington U.-St. Louis

NIST Associates
John J. Rush       Hui Wu
Matt Hudson        Wei Zhou
Zeric Hulvey       Wan Si Tang
Objectives and Relevance

Overall: Support the DOE-EERE-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.
Approach

Neutron methods

- determine elemental compositions of materials (prompt-γ activation analysis and neutron reflectometry of H stoichiometries and profiles)

- determine location of H and crystal structures of materials (neutron diffraction superior to XRD for “seeing” light H and D)

- determine bonding of absorbed H (unlike IR and Raman, neutron vibrational spectroscopy “sees” all H vibrations for straightforward comparison with first-principles calculations)

- elucidate H diffusion mechanisms (faster dynamics timescale of neutron quasielastic scattering complements NMR; transport mechanisms gleaned from momentum transfer dependence)
Neutron methods, synthesis expertise, and DFT computations were used to further the goals of the DOE Hydrogen-Storage Sub-Program.
Motivation: investigating new materials potentially promising for hydrogen storage

MSiH₃ (M=K, Rb, Cs) stores hydrogen reversibly through an MSi/MSiH₃ equilibrium, yielding a 0.1 MPa H₂ equilibrium pressure at ~410 K.

Agreement between neutron vibrational spectroscopy and density functional theory corroborates β-MSiH₃ structures determined by diffraction methods.
Characterization of Alkali-Metal Silanides

Motivation: investigating new materials potentially promising for hydrogen storage

Quasielastic neutron scattering data for CsSiH$_3$ corroborate the change to a more three-dimensional SiH$_3^-$ reorientation mechanism upon transformation to the disordered cubic $\alpha$-phase.

Fixed-window scans indicate that:

- SiH$_3^-$ anions attain high reorientational mobilities ($\gg 10^{10}$ H jumps/s) that increase with cation size.
- there are hysteretic order-disorder phase changes that affect the SiH$_3^-$ reorientation mechanism and mobilities.

likely H motion in ordered $\beta$-phase

likely H motion in disordered $\alpha$-phase
Characterization of Decaborane

Motivation: Determining the chemical nature of thermally treated decaborane

The neutron vibrational spectrum of $^{11}\text{B}_{10}\text{H}_{14}$ (black) is in good agreement with the DFT-simulated 1-phonon (gray) and 1+2-phonon (red) spectra.

Currently, neutron prompt-gamma activation analysis is being used to obtain B/H ratios in different thermally treated samples of $\text{B}_{10}\text{H}_{14}$.

We successfully established the baseline spectroscopic signature for $\text{B}_{10}\text{H}_{14}$ to be used later for comparison with polymerized versions after thermal treatments and lithiation.
Motivation: determining products of hydrogenated Li$_3$N in nanoporous carbon

Neutron vibrational spectroscopy confirms that both LiNH$_2$ and LiH are hydrogenation products from carbon-nanoconfined Li$_3$N, with no obvious presence of Li$_2$NH.
Characterization of Anion Dynamics in Na$_2$B$_{12}$H$_{12}$

Motivation: investigating potential borohydride dehydrogenation products

Quasielastic neutron scattering measurements of disordered Na$_2$B$_{12}$H$_{12}$ indicate rapid (>10$^{11}$ jumps/s), mainly (small-angle) uniaxial, reorientational motions of the B$_{12}$H$_{12}^{2-}$ anions. N. Verdal et al., J. Phys. Chem. C 118, 17483 (2014).
Characterization of Li$_2$B$_{10}$H$_{10}$

Motivation: investigating potential borohydride dehydrogenation products

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Li$_2$B$_{10}$H$_{10}$ was found to exhibit hexagonal symmetry to best stabilize the ionic packing of the relatively small Li$^+$ cations and large ellipsoidal B$_{10}$H$_{10}$$^{2-}$ anions.

Characterization of Li$_2$B$_{10}$H$_{10}$

Motivation: investigating potential borohydride dehydrogenation products

Collaboration with Maryland, Sandia National Laboratories

Neutron-Elastic-Scattering Fixed-Window Scans

Differential Scanning Calorimetry for Li$_2$B$_{10}$H$_{10}$

Fixed-window scans of $^7$Li$_2$$^{11}$B$_{10}$H$_{10}$ indicate a transition to an unknown phase by 680 K with highly reorientationally mobile B$_{10}$H$_{10}^{2-}$ anions, possibly similar in character to Na$_2$B$_{10}$H$_{10}$.

Li$_2$B$_{10}$H$_{10}$, similar to its polyhedral cousin Li$_2$B$_{12}$H$_{12}$, completes an order−disorder phase transition by ~680 K. This information further elucidates the important Li-B-H phase diagram.

Characterization of $\text{Na}_2\text{B}_{10}\text{H}_{10}$

Motivation: investigating potential borohydride dehydrogenation products

Using neutron scattering methods in conjunction with DFT, we have corrected structural errors in the previously published, monoclinic ordered $\text{Na}_2\text{B}_{10}\text{H}_{10}$ structure.

H. Wu et al., CrystEngComm (in press) doi:10.1039/c5ce00369e
Motivation: characterizing conductivity properties of cubic Na$_2$B$_{10}$H$_{10}$

NPD pattern for disordered cubic Na$_2$B$_{10}$H$_{10}$ at 410K and inset showing the orientationally disordered B$_{10}$H$_{10}^{2-}$ anions (H atoms omitted) and the array of partially occupied Na$^+$ cation sites (red, yellow, and blue).

AC impedance measurements for Na$_2$B$_{10}$H$_{10}$ and related materials vs. temperature.

An improvement over Na$_2$B$_{12}$H$_{12}$, Na$_2$B$_{10}$H$_{10}$ exhibits dramatic superionicity above its ~360 K phase transition, aided by the large mobile anions and the appearance of cation vacancies.

Collaborations

**U.S. Partners (Type of Institution): What we provide to them**

**CalTech** (Univ.): neutron measurements of various porous materials and borohydrides.

**Delaware** (Univ.): neutron measurements of various zeolites.

**GE** (Industry): neutron characterization of complex hydrides.

**GM** (Industry): neutron characterization of complex hydrides.

**HRL** (Industry) neutron measurements of BH$_4^-$ dynamics in nanoconfined metal borohydrides.

**Maryland** (Univ.): neutron and x-ray measurements of alanates, borohydrides, and related materials.

**Michigan** (Univ.): neutron measurements of BH$_4^-$ dynamics in neat and nanoconfined metal borohydrides.

**Missouri-St. Louis** (Univ.): neutron measurements of various alanates, borohydrides, and related materials.

**NREL** (Gov.): neutron measurements / isotherm measurements of various spillover related materials.

**Ohio State** (Univ.): neutron and x-ray measurements of borated compounds.

**Penn** (Univ.): neutron measurements of amidoboranes and other storage-related materials.

**Penn State** (Univ.): neutron measurements of various boron doped carbons.

**RCB Hydrides** (Industry): neutron and x-ray measurements and DFT calculations of various alanates, borohydrides, and related materials; neutron imaging of hydrogen-storage beds.

**Sandia** (Gov.): neutron measurements and DFT calculations of various alanates, borohydrides, and related materials.

**Molecular Foundry** (Gov.): neutron measurements of various metal-organic framework materials

**U.C. Berkeley** (Univ.): neutron measurements of various alanates, borohydrides, and related materials.

**Utah** (Univ.): neutron characterization of complex and metal hydrides.
Future Work

Remainder of FY2015:

• Continue to perform neutron-based structural and spectroscopic characterizations of new materials in conjunction with the needs of the DOE-funded projects, including novel bulk and nanoconfined complex hydride materials.

• For example, continue characterization work on hydrogenated/dehydrogenated Li$_3$N in nanoporous carbon, metal borides, and decaborane-based materials (with Sandia National Laboratories, HRL, and U. Missouri-St. Louis); start characterization work on mixed-alkali-metal silanides.
Summary

Neutron methods continue to provide crucial, non-destructive characterization tools for the DOE Hydrogen-Storage Sub-Program.

• Agreement between neutron vibrational spectroscopy and density functional theory corroborates β-MSiH$_3$ structures determined by diffraction methods.

• Quasielastic neutron scattering data for CsSiH$_3$ corroborate the change to a more three-dimensional SiH$_3^-$ reorientation mechanism upon transformation to the disordered cubic α-phase.

• We successfully established the baseline spectroscopic signature for B$_{10}$H$_{14}$ to be used later for comparison with polymerized versions after thermal treatments and lithiation.

• Neutron vibrational spectroscopy confirms that both LiNH$_2$ and LiH are hydrogenation products from carbon-nanoconfined Li$_3$N, with no obvious presence of Li$_2$NH.

• Quasielastic neutron scattering measurements of disordered Na$_2$B$_{12}$H$_{12}$ indicate rapid (>10$^{11}$ jumps/s), mainly (small-angle) uniaxial, reorientational motions of the B$_{12}$H$_{12}^{2-}$ anions.

• Li$_2$B$_{10}$H$_{10}$ was found to exhibit hexagonal symmetry to best stabilize the ionic packing of the relatively small Li$^+$ cations and large ellipsoidal B$_{10}$H$_{10}^{2-}$ anions.

• Li$_2$B$_{10}$H$_{10}$, similar to its polyhedral cousin Li$_2$B$_{12}$H$_{12}$, completes an order−disorder phase transition by ~680 K. This information further elucidates the important Li-B-H phase diagram.

• Using neutron scattering methods in conjunction with DFT, we have corrected structural errors in the previously published, monoclinic ordered Na$_2$B$_{10}$H$_{10}$ structure.

• An improvement over Na$_2$B$_{12}$H$_{12}$, Na$_2$B$_{10}$H$_{10}$ exhibits dramatic superionicity above its ~360 K phase transition, aided by the large mobile anions and the appearance of cation vacancies.