HyMARC: Technical Activities at NIST

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Overview

Timeline and Budget

• **Timeline:**
  Phase 1: 10/1/2015 to 9/30/2018
  Phase 2: 10/1/2018 to 9/30/2022

• **Budget:**
  2 post-docs are provided for this effort through HyMARC/NREL

• **Barriers Addressed:**
  General:
  A. Cost; B. Weight and Volume; C. Efficiency;
  E. Refueling Time;
  **Reversible Solid-State Material:**
  M. Hydrogen Capacity and Reversibility;
  N. Understanding of Hydrogen Physi- and Chemisorption;
  O. Test Protocols and Evaluation Facilities;

• **HyMARC Collaborators**
  • LBNL – Jeff Long, Martin Head-Gordon
  • PNNL – Tom Autrey, Mark Bowden
  • SNL – Vitalie Stavila
  • LLNL – Brandon Wood
  • HyMARC seedling - Eric Majzoub (Univ. Missouri-St. Louis)
An synergistic collaboration and research effort among HyMARC participants to:

- **develop** and **enhance** hydrogen-storage core capabilities, i.e. characterization techniques
- **validate** claims, concepts, and theories of hydrogen-storage materials
- **double** hydrogen storage energy density (increase from 25g/L to 50 g/L)
Relevance: Impact of Neutron Analyses

- Neutrons provide unique specificity towards determination of hydrogen properties
  - Enables identification of isotopically-labelled hydrogen location within complex structures
  - Enables identification of hydrogen dynamics within complex structures

http://www.ne.ncsu.edu/nrp/npdf.html
Approach: Neutron Scattering

Utilize neutrons to characterize and validate hydrogen storage media

NIST provides neutron-scattering-based characterization of materials of interest within HyMARC and other DOE-funded projects

- Solvent addition as a solution for enhancing hydrogen storage properties of magnesium borohydride ($\text{Mg(BH}_4\text{)}_2$)
- Quantum rotational tunneling of $\text{BH}_4^-$ anions in lithium benzimidazolate-borohydride $\text{Li}_2(\text{bIm})\text{BH}_4$
- $\text{H}_2$ adsorption in a Cu(I) MOF

HyMARC (PNNL/LBNL/NREL)

- NIST

U.C. Berkeley/NIST
Accomplishments and Progress:
Enhancing hydrogen storage properties of Mg(BH$_4$)$_2$

Mg(BH$_4$)$_2$  $\xrightarrow{5 \text{ weeks}}$  1/3 Mg(B$_3$H$_8$)$_2$ + 2/3 MgH$_2$ + 2/3 H$_2$

L – solvent: tetrahydrofuran (THF)

Mg(BH$_4$)$_2$ • L  $\xrightarrow{24 \text{ h}}$  1/5 MgB$_{10}$H$_{10}$ • L + 4/5 MgH$_2$ + 11/5 H$_2$

$\text{Mg(BH}_4\text{)}_2\cdot3\text{THF}$

“...The modified coordination may play a role in the dehydrogenation mechanism...”$^1$

Objective: Look into the fundamental properties of Mg(BH$_4$)$_2$ • L and try to explain how the solvent coordination might have the beneficial effect of enhancing dehydrogenation kinetics.

$^1$ M. Chong et al. Inorganics 2017, 5, 89.
Accomplishments and Progress: Enhancing hydrogen storage properties of Mg(BH$_4$)$_2$

Samples: Mg(BH$_4$)$_2$·L were prepared by adding an excess of solvent to Mg(BH$_4$)$_2$ at room temperature.

Reference samples:
- Tetrahydrofuran (THF)
- Tetrahydrofuran-d$_8$ (TDF)

Selective Deuterium deuteration
Accomplishments and Progress: Enhancing hydrogen storage properties of Mg(BH$_4$)$_2$

Methods:

- Neutron powder diffraction (NPD): structure and phases
- Neutron vibrational spectroscopy (NVS): vibrational modes
- Quasielastic neutron scattering (QENS): reorientational dynamics
Accomplishments and Progress: Enhancing hydrogen storage properties of Mg(BH$_4$)$_2$

Neutron powder diffraction measurements of Mg(BH$_4$)$_2$·3TDF upon heating from 5 K to 298 K indicate a phase transition in the temperature range between 175 and 225 K, from triclinic ($P$-1) to monoclinic ($C2/c$) structure.
Accomplishments and Progress:
Enhancing hydrogen storage properties of Mg(BH$_4$)$_2$

- Vibrational properties are strongly influenced by the THF environment.
- In particular, there is a shift towards lower energies of the BH$_4^-$ librational and bending modes with THF present as a result of changes in the bond lengths and force constants. Splitting in spectral features is also observed and explained by the lowering of the overall symmetry of Mg(BH$_4$)$_2$·3THF.
Accomplishments and Progress: Enhancing hydrogen storage properties of Mg(BH$_4$)$_2$

- Orientational mobilities of the BH$_4^-$ anions obtained from QENS are not particularly sensitive to the presence of THF or TDF and compare well with the mobilities of BH$_4^-$ anions in unsolvated Mg(BH$_4$)$_2$.
- the THF molecules in Mg(BH$_4$)$_2$·3THF are also found to be orientationally mobile, undergoing 180° reorientational jumps around their $C_2$ molecular symmetry axis.
Accomplishments and Progress: Enhancing hydrogen storage properties of Mg(BH$_4$)$_2$

- Computational results for the solid state using the crystal structures suggest the static binding energy of each THF molecule averages to -27 kJ/mol THF. On the other hand, DFT calculations for the hypothetical Mg(BH$_4$)$_2$·1THF complex suggests the binding energy is greater for the first THF, then the subsequent ·2THF and ·3THF adducts.

- From this combined experimental and computational study of THF adducts of Mg(BH$_4$)$_2$, we find little direct interaction between the THF and the BH$_4^-$ anion. We propose that using fractions of THF to Mg(BH$_4$)$_2$ is beneficial in (i) preventing weakly bound THF from coming free from the Mg$^{2+}$ cation and (ii) disrupts the stability of crystalline phase leading to a lower melting point and enhanced kinetics.
Accomplishments and Progress:
Quantum BH₄⁻ Rotational Tunneling in Li₂(bIm)BH₄

- Reorientational BH₄⁻ motion is known to contribute strongly to the balance of energies determining the thermodynamic stability of borohydrides.
- Therefore, information on the reorientational dynamics is important for understanding the fundamental properties of these compounds.
- The hydrogen dynamics in lithium benzimidazolate-borohydride, Li₂(bIm)(BH₄) (bIm = C₇H₅N₂) was studied using various neutron scattering techniques and DFT calculations, in order to get better insights into the possible application of this material in hydrogen storage.
Accomplishments and Progress:
Quantum BH\textsubscript{4}⁻ Rotational Tunneling in Li\textsubscript{2}(bIm)BH\textsubscript{4}

Neutron-elastic-scattering fixed-window scan on the High-Flux Backscattering Spectrometer (HFBS) upon heating at 1 K min\textsuperscript{-1} from 4 K to 385 K at 1.2 Å\textsuperscript{-1} neutron momentum transfer.
Accomplishments and Progress:
Quantum BH$_4^-$ Rotational Tunneling in Li$_2$(bIm)BH$_4$

Arrhenius-type plots of the derived jump correlation frequencies $\tau_1^{-1}$ versus $1/T$ from the various QENS and NMR results for the much more rapid three-fold reorientations of the three H atoms associated with the $-$BH$_3$ fragment, as well as for the much slower exchange of these H atoms with the remaining, Li$_4$-anchored H atom.
Accomplishments and Progress: Quantum BH$_4^-$ Rotational Tunneling in Li$_2$(blm)BH$_4$

It is a rare observation of rotational tunneling of the BH$_4^-$ anion via neutron scattering, and possibly the second neutron-spin-echo (NSE) observation of tunnelling phenomena after an early work on dimethylacetylene.

Both NMR and neutron scattering results for Li$_2$(blm)(BH$_4$) are described in terms of a gradual transition from the regime of low-temperature quantum dynamics (rotational tunneling of BH$_4^-$ anions) to the regime of classical three-fold uniaxial jump reorientations at higher temperatures.
Accomplishments and Progress: 
H₂ adsorption in a Cu(I) MOF

Gas adsorption isotherms and Infra-red spectra indicate a strong temperature dependence of H₂ adsorption characteristics in a Cu(I) MOF.

We performed variable-temperature diffraction to monitor how the H₂ is interacting with the framework.

- The bare framework shows a moderate negative thermal expansion (NTE).
- 0.75 D₂:Cu dosed at 77 K and then cooled to base (prior to heating) shows a strong NTE.
- Recooling to base shows a large hysteresis away form the physisorbed system at low temperature. Rietveld refinement is consistent with two types of H₂, one being much closer to the Cu(I) site.
Summary

- Orientational mobilities of the BH$_4^-$ anions in Mg(BH$_4$)$_2$·xTHF adducts are found not to be particularly sensitive to the presence of THF and compare well with the mobilities of BH$_4^-$ anions in unsolvated Mg(BH$_4$)$_2$. The THF molecules in Mg(BH$_4$)$_2$·3THF are also found to be orientationally mobile, undergoing 180° reorientational jumps around their $C_2$ molecular symmetry axis.

- Both NMR and neutron scattering results for Li$_2$(bIm)(BH$_4$) are described in terms of a gradual transition from the regime of low-temperature quantum dynamics (rotational tunneling of BH$_4^-$ anions) to the regime of classical three-fold uniaxial jump reorientations at higher temperatures. This uncommon behavior is due to the unique BH$_4^-$ coordination in this compound.

- Gas adsorption isotherms and infra-red spectra of H$_2$ in a Cu(I) MOF indicate a strong temperature dependence of the H$_2$ adsorption behavior. Rietveld refinement analysis of complementary diffraction data is consistent with two types of H$_2$, one being much closer to the Cu(I) site.
Collaboration and Coordination

• NREL/NIST collaboration
  – Characterizing ultra-microporous materials using neutron diffraction and neutron spectroscopy

• NREL/NIST collaboration with LBNL and PNNL
  – Characterizing hydrogen adsorption in metal organic framework materials using neutron diffraction and neutron spectroscopy
  – Characterizing various hydrogen storage materials at the Advanced Photon Source
  – Various neutron scattering characterization of Mg(BH₄)₂·xTHF
Project was not reviewed last year.
Proposed Future Work

• Perform QENS measurements on recently synthesized Mg\(^{11}\text{BH}_4\)\(_2\)\(\cdot x\text{THF}\) and Mg\(^{11}\text{BH}_4\)\(_2\)\(\cdot x\text{TDF}\) materials to gain insights into the reorientation dynamics and mobilities of BH\(_4^-\) anions and provide more information on the interaction between THF and Mg\(\text{BH}_4\)\(_2\).

• Continue neutron diffraction/NVS characterizations of new MOF materials

Any proposed future work will depend on the available funding.
Publications


Presentations

3. M. Dimitrievska: “Carbon Incorporation and Anion Dynamics as Synergistic Drivers for Ultrafast Diffusion in Superionic LiCB$_{11}$H$_{12}$ and NaCB$_{11}$H$_{12}$”, MRS Spring meeting, Phoenix, AR, Apr. 2018.