Neutron Characterization in Support of the Hydrogen Sorption Center of Excellence

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Overview

Timeline
- Project start: FY05
- Project end: FY10
- 100% complete

Barriers
- Barriers addressed: Characterization of Hydrogen Physisorption and Chemisorption

Budget

<table>
<thead>
<tr>
<th>FY</th>
<th>HSCoE</th>
<th>MHCoE</th>
</tr>
</thead>
<tbody>
<tr>
<td>FY05</td>
<td>$130K</td>
<td>$125K</td>
</tr>
<tr>
<td>FY06</td>
<td>$208K</td>
<td>$156K</td>
</tr>
<tr>
<td>FY07</td>
<td>$216K</td>
<td>$276K</td>
</tr>
<tr>
<td>FY08</td>
<td>$225K</td>
<td>$287K</td>
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<tr>
<td>FY09</td>
<td>$234K</td>
<td>$298K</td>
</tr>
<tr>
<td>FY10</td>
<td>$234K</td>
<td>$298K</td>
</tr>
</tbody>
</table>

NIST provides access to neutron facilities and FTEs for the HSCoE and MHCoE

Partners
- **HS Center**
  Caltech, NREL, ORNL, LLNL, Penn State
- **External**
  UC Berkeley, U. Sydney, Monash Uni., General Motors, ISIS (U.K.)
Objectives and Relevance

Overall: Support the development of hydrogen storage materials by providing timely, comprehensive characterization of Center-developed materials and storage systems using neutron methods. Use this information to speed the rational development and optimization of hydrogen storage materials that can be used to meet the 2010 DOE system goal of 6 wt% and 45 g/L capacities.

• Provide Calphad calculations of phase relationships of potentially promising hydrides. (MHCoE only)

• Relevance

• Neutron scattering on a great variety of new hydrogen storage materials for various research groups contributes to a focusing on technical barriers

• We contribute within the Center and with external partners.
• **Neutron methods**
  – determine elemental compositions of materials (prompt-\(\gamma\) activation analysis)
  – determine location of H and crystal structures of materials (neutron diffraction superior to XRD for locating light elements)
  – 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)
We seek to understand hydrogen interactions with metal ions and focus on the rational synthesis of sorbents that can strongly bind di-hydrogen ligands for vehicular hydrogen storage.

**Problem**
- Graphene slit-pore structure not stable
- Need a “spacer molecule” to prop open layers

**Strategy**
- Insert alkali-metal (AM) atoms between graphite layers
- Nomenclature: “Graphite intercalation compounds”
- Pore-width controlled by size of AM atom

**Correlation between interlayer spacing and H₂ adsorption enthalpy**
- H₂ adsorption reversible at low temperatures (< 150 K); H₂ reacted chemically at higher temperatures (~195 K).

<table>
<thead>
<tr>
<th>Graphite Intercalation Compounds</th>
<th>Isosteric Heat(_{ave}) (kJ/mol)</th>
<th>Adsorption(_{max}) (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KC(_{24})(H₂)(_x)</td>
<td>9.2</td>
<td>1.24</td>
</tr>
<tr>
<td>RbC(_{24})(H₂)(_x)</td>
<td>12.6</td>
<td>1.03</td>
</tr>
<tr>
<td>CsC(_{24})(H₂)(_x)</td>
<td>14.9</td>
<td>0.85</td>
</tr>
</tbody>
</table>
Graphite Intercalation Compounds (Ahn, Caltech)

**Problem**

- How does hydrogen bind in these systems?
  - Can we apply this to GO/Graphene pores?
- In-plane structure of KC$_{24}$(H$_2$)$_{0.5}$ not well-known:
  - makes computation difficult

**QENS: Diffusional Dynamics**

The rate of H$_2$ diffusion in KC$_{24}$ is slower than in other types of carbon adsorbents.

**INS: Neutron spectroscopy**

- Multiple adsorption sites
- Strong rotational barrier (~130 meV)
- H$_2$-H$_2$ interactions
- Change in structure

Reduction of H$_2$ diffusion at larger concentration: site-blocking and correlation
We previously used neutron diffraction to locate hydrogen binding sites in TM-benzenetrizetrazole frameworks (TM= Mn, Cu).
- Initial high enthalpy of adsorption due to TM:H₂ interaction

Combinatorial search for reaction conditions allows new Fe²⁺-BTT to be characterized at U.C. Berkeley

Excess 3.7 wt% 30 bar; total: 4.1 wt% 95 bar 35 g/l (Crystal ρ); 2100 m²/g : (lower values than for Mn-BTT)
**Technical Accomplishment**

**Effect on transition metal on H$_2$-M interactions** (Long U.C. Berkeley)

- **Neutron diffraction** allows identification of adsorption sites with H$_2$ loading.

  Correlation of adsorption strength: Fe$^{2+}$ > Mn$^{2+}$ > Cu$^{2+}$
  with TM-H$_2$ distance: Fe$^{2+}$ < Mn$^{2+}$ < Cu$^{2+}$
  [2.17(5) < 2.27 < 2.47 Å]

  but not ionic radius*: Mn$^{2+}$ > Fe$^{2+}$ > Cu$^{2+}$

- **Primary adsorption sites** @TM have highest enthalpy
  - Shortest TM-D$_2$ distance found so-far is in Fe-BTT
  - INS consistent with strong H$_2$:Fe interaction at low loading
  - Fe$^{2+}$ site catalyzes hydrogen conversion to para-H$_2$
    (complete at low loading, partially at high loading)

*MOF-74 isostructural series has been predicted to have $\Delta$H(TM-H$_2$) distance varying
~PROPORTIONAL (INVERSE) with ionic radius. Zhou et al. JACS, 130, 15268, 2008

**At Fe$^{2+}$-site(I), 30% blocked by methanol**

**INS: H$_2$ rotational spectra**
Neutron diffraction and INS indicate electrostatic origins of interaction, no discrete orbital bonding-back bonding observed in character or strength.
Technical Accomplishment

Boron substituted carbons (M. Chung, Penn State Uni.)

- INS data shows, for the first time, a large rotational splitting indicative of enhanced H\textsubscript{2} interactions in a substituted carbon.

- Variable temperature, high pressure isotherms → Consistent with a model of hindered H\textsubscript{2} rotation barrier ~13 meV

- NMR indicates 6 at% B:C

- Clearly demonstrate the need to include isotherms at a range of temperatures to obtain robust ΔH values.

• INS data shows, for the first time, a large rotational splitting indicative of enhanced H\textsubscript{2} interactions in a substituted carbon.
Technical Accomplishment

Hydrogen diffusion in templated carbons (Webley, Monash Uni.)

- Platinum loading decreases surface area, excess adsorption
- Pore structure well defined (TEM and BET pore size analysis)
- Surface chemistry (XPS) and $\Delta H$ differs on Pt loading
Technical Accomplishment

Imaging H₂-adsorption in an activated carbon—Pfeifer, U Missouri

- Real-time observation of loading profiles as a function of pressure
- Quantitative information

Hydrogen scatters neutrons reducing intensity where adsorbed
Profile shows cylindrical profile of briquettes

Neutron Sensitive CCD camera

H₂-gas
sample
Neutrons

2 bar H₂

5 bar H₂
Collaboration with HRL, Lawrence Livermore, Maryland, and Michigan

Motivation: to characterize the properties of nanoconfined LiBH$_4$

NV spectra of LiBH$_4$ in 13 nm carbon aerogels

SANS suggests that the smallest pores fill first, and there is no change in apparent mesopore geometry with filling

Small-angle neutron scattering (SANS) data

LiBH$_4$ vibrational modes in the carbon aerogel exhibit a minor (~10%) broadening compared to bulk LiBH$_4$ modes

* We need to understand the relationship between pore morphology and filling behavior of nanoconfined storage materials.
Characterization of Nanoconfined Systems

Motivation: to investigate borohydride dynamics perturbations in carbon aerogels

- Bulk LiBH$_4$ undergoes a phase transition at 390 K

- Under conditions of confinement, we observe indications of a phase transition at 360 K

- Low-temperature dynamics due to hydrogen reorientation appear on the nanosecond timescale at 200 K in the bulk and fully-loaded aerogel

- This temperature is decreased by 75 K in the partially-loaded carbon aerogel

* Nanoconfinement appears to perturb the bulk thermodynamic properties

![Graph showing T dependence of BH$_4^-$ rotational jump frequency for nanoconfined LiBH$_4$ (4% loading in carbon aerogel)]
Collaborations

Partners:

CalTech (University/HSCoE, joint) Alkali intercalated graphite, high surface area MOFs

Monash Uni. (University, primary) Dynamics of $H_2$ in templated carbons

U. C. Berkeley (University, primary) Neutron measurements on various MOFs

Penn. State (University/HSCoE, primary) Composition and $H_2$ interactions in B-substituted carbons

NREL (Federal/HSCoE, primary) Neutron measurements on candidates for ‘strong interactions’ and B-substituted carbons

Missouri (University/HSCoE, primary) Imaging of storage media

ISIS (U.K. central facility, primary) INS measurements in MOFs
This was the final year of the HSCoE. See the final Center report for key achievements and areas requiring further study.
Summary

We have continued our primary task of performing various neutron characterization measurements in support of other HSCoE members.

Characterized the hydrogen environment upon adsorption in graphite intercalation materials despite lack of periodic crystal structure.
Characterized the hydrogen diffusion mechanism and geometry.

Determined multiple binding sites for H$_2$ in one of an isostructural series of BTT compounds. Partial understanding of the local adsorption potential is obtained from the current INS data.

For the first time we have observed a significant perturbation of the hydrogen rotational levels in a high surface area B:carbon.

Further understood the surface chemistry and hydrogen adsorption capacities in zeolite-templated carbons loaded with Pt nanoparticles. Failed to observe any spillover in these materials.

Performed preliminary test-bed work on a macroscopic imaging of hydrogen adsorption in a high surface area carbon.