Neutron Characterization and Calphad in support of the Metal Hydride Center of Excellence

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### Overview

#### Timeline
- Project start FY05
- Project end FY09
- 50% complete

#### Barriers addressed
- Characterization of structures and hydrogen bonding in new storage materials
- Lack of phase diagram data on potential new storage materials

#### Budget
- FY05 $125k
- FY06 $156k
- FY07 $276k
- FY08 (req.) $287k

#### Partners

NIST has provided over 420 instrument days to date and 2 FTE’s/year for the HSCoE and MHCoE combined.
Objectives

**Overall:** Support the development of hydrogen storage materials by providing timely, comprehensive characterization of Center-developed materials and storage systems using state-of-the-art neutron methods and Calphad. Help speed the development and optimization of storage materials that can meet the 2010 DOE system target of 6 wt% and 45 g/L capacities.

- Characterize structures, compositions, and absorption site interaction potentials for hydrogen in candidate materials.
- Provide Calphad calculations of phase relationships of potentially promising hydrides.
Approach

• **Neutron methods**
  – determine elemental compositions of materials (non-destructive prompt-gamma activation analysis of H stoichiometries)
  – 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)

• **Calphad methods**
  – develop a thermodynamic database from the available literature and first-principles calculations
  – incorporate database into an overall temperature-pressure-composition framework for multicomponent metal-hydrogen systems.
Technical Accomplishment

Structure Identification of Li$_4$Ge$_2$D and Li$_4$Si$_2$D

**Li$_4$Ge$_2$D**
- $R_{wp}=3.94\%$
- $R_p=3.34\%$
- $\chi^2=1.00$

**Li$_4$Si$_2$D**
- $R_{wp}=5.85\%$
- $R_p=4.84\%$
- $\chi^2=1.977$

Strong Li-H binding in Li$_4$Ge$_2$H and Li$_4$Si$_2$H is primarily responsible for the stabilization of these hydrides.

Note: LiH (Li-H ~ 2.038Å)
Technical Accomplishment

Measured neutron vibrational spectra for Li₄Ge₂H and Li₄Si₂H

Characterized the phonon modes with first-principles phonon calculations

Assignments of the phonon modes are consistent with NPD-observed Li-H bond lengths and the corresponding bond strength.

<table>
<thead>
<tr>
<th></th>
<th>Ge</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-Li1</td>
<td>2.091Å</td>
<td>2.087Å</td>
</tr>
<tr>
<td>H-Li2</td>
<td>2.007Å</td>
<td>2.016Å</td>
</tr>
<tr>
<td>H-Li3</td>
<td>1.939Å</td>
<td>1.881Å</td>
</tr>
</tbody>
</table>

(in preparation 2007)
Technical Accomplishment

Destabilization of the 2CaH$_2$ / Si system

\[ 2\text{CaH}_2 + \text{Si} \rightarrow \text{Ca}_2\text{Si} + 2\text{H}_2 \]

200-300°C

>500°C

Amorphous hydride phase

Hydrogen Induced Amorphization

NPD, NVS, and Isotherm Results

- Ca$_2$Si readily absorbs H$_2$ at P < 1 atm.
- Quite rapid absorption kinetics (few min)
- No obvious pressure plateau
- Formation of amorphous hydride upon hydrogenation

Easy H$_2$ absorption compared to hard-to-hydride Mg$_2$Si at 200-300°C.

“Amorphization” could be a way to accelerate the hydrogenation kinetics.

Technical Accomplishment

Destabilization of the CaH₂ / MgH₂ / Si system

- Add MgH₂ (higher H₂ storage capacity); possibly improve slow Mg₂Si kinetics
- Single-phase solid solution Ca₂₋ₓMgₓSn observed in (1-x)Ca₂Sn-(x)Mg₂Sn system

\[ \text{CaH}_2 + \text{MgH}_2 + \text{Si} \rightarrow \text{CaMgSi} + 2\text{H}_2 \]

(2-x) CaH₂ + x MgH₂ + Si → Ca₂₋ₓMgₓSi (0<x<1)

Intermediate compositions are Ca₂Si/CaMgSi two-phase mixture (distinct from Ca₂₋ₓMgₓSn)

J. Alloys Comp. in press (2007)
Hydrogenation Properties of $\text{Ca}_{2-x}\text{Mg}_x\text{Si}$

- $\text{CaMgSi}$ hardly absorbs $\text{H}_2$ under 0-70 atm at 200-300°C.
- Hydrogenation behavior of $(1-x)\text{Ca}_2\text{Si}-x\text{CaMgSi}$ compositions is dominated by $\text{Ca}_2\text{Si}$.

Isotherm measurements

<table>
<thead>
<tr>
<th>Composition</th>
<th>Neutron Counts</th>
</tr>
</thead>
</table>
| $\text{Ca}_{4/3}\text{Mg}_{2/3}\text{Si}$ $(x=2/3)$ | |}
| $\text{Ca}_{5/3}\text{Mg}_{1/3}\text{Si}$ $(x=1/3)$ | |}
| $\text{Ca}_2\text{Si}$ $(x=0)$ | |}

NVS

(After hydrogenation at 200°C 50 atm)

0.0 0.2 0.4 0.6 0.8 1.0 1.2 1.4 1.6 1.8 2.0 2.2

0 10 20 30 40 50 60

$P$ (atm)

$\text{Neutron Counts}$

$\text{Neutron Energy Loss (meV)}$

$\text{J. Alloys Comp. in press (2007)}$
Technical Accomplishment

Quaternary System: Na-Mg-Si-H

NaH + MgH₂ → NaMgH₃ (350°C, 50bar H₂)

- MgH₂/Si system is hard to hydride
- NaH/Si system reversibly absorbs H₂
- NaH/MgH₂ forms a NaMgH₃ phase

So, we tried MgH₂/NaH/Si system

**Desorption:** 350°C evac.
NaH + 2MgH₂ + 2Si → Mg₂Si + NaSi

**Hydrogenation:** 350°C 50 atm
NaSi + Mg₂Si + H₂
→ (1-x)Mg₂Si + (1-x)NaH + Si + xNaMgH₃

Mg₂Si can partially absorb H₂ through the formation of NaMgH₃

Reversible hydrogenation/dehydrogenation
NaMgH₃ ↔ Na + Mg + 3/H₂ (350°C)
For $\text{Ca}(\text{BH}_4)_2$ synthesized at Sandia, the neutron vibrational spectrum is in agreement with first-principles phonon calculations based on the published $\text{Ca}(\text{BH}_4)_2$ structure.
Destabilization of LiBH₄ with ScH₂ and CaH₂

• 2LiBH₄/ScH₂

Isotherm proposed: \[ 2\text{LiBH}_4 + \text{ScH}_2 \rightarrow \text{ScB}_2 + 2\text{LiH} + 4\text{H}_2 \uparrow \] (8.9 wt%)

• Moderate desorption (~6 h to complete)
  but: 1. dehydrogenation only above 380°C
  2. no noticeable absorption observed during the rehydrogenation step

• 6LiBH₄/CaH₂

Isotherm proposed: \[ 6\text{LiBH}_4 + \text{CaH}_2 \rightarrow \text{CaB}_6 + 6\text{LiH} + 10\text{H}_2 \uparrow \] (11.7 wt%)

• Moderate desorption (~2-3 h to complete)
• Complete rehydrogenation can be achieved at 380°C / 50 bar H₂
  but: 1. dehydrogenation only above 380°C
  2. relatively slow hydrogenation kinetics (1 day to complete)

Subsequent results from other partners suggest that the dehydrogenation of the borates leads to elemental boron, not borides.
Technical Accomplishment

Calphad Computations

- Developing Calphad database for H-Li-Mg-Ca-B-Si with thermodynamic descriptions of the constituent subsystems
  - 15 binary total: 11 full descriptions available, 3 provisional in development, 1 under development
  - 20 ternary total: 2 full descriptions available, 1 partial description available
- Challenge: lack of available experimental data
  - Incorporate data from ab initio calculations by MHCoE partners

Results: Quaternary System: Mg-Li-B-H

2 LiBH$_4$ + MgH$_2$  
4 LiBH$_4$ + MgH$_2$  
7 LiBH$_4$ + MgH$_2$  

2 LiBH$_4$ + MgH$_2$ is the most promising composition with a large amount of available hydrogen (11.5%) at the lowest reaction temperature (188°C).

We are currently in the process of expanding to include N in the overall database as well as to investigate Na-K-B-H phases.
Future Work

Remainder of FY 2007:

- Scale up for higher hydrogenation pressure capability (<1000 atm) and use to investigate new ternary and quaternary systems via neutron methods.
- Continue thin-film characterizations using neutron reflectometry.
- Continue efforts to synthesize $^{11}$B labelled hydrogen-storage materials.
- Complete thermodynamic assessments for systems with provisional descriptions (Li-B intermediate phases).
- Include descriptions for ternary and quaternary hydrides as data become available.
- Identify systems with MHCoE partners for future neutron scattering studies and Calphad database development.

FY 2008:

- Perform neutron scattering characterizations of new materials in conjunction with the needs of the other partners, emphasizing materials synthesized at high pressures.
- Continue to expand Calphad database (evaluate literature for data, identify data needs and systems with MHCoE partners for future database development).
- Initiate feasibility studies of unique neutron imaging of H distribution and transport in storage beds for candidate materials.
Neutron methods and Calphad computations provided crucial, non-destructive characterization and predictive tools for the Metal-Hydride Center of Excellence.

• Combined neutron and first-principles studies reveal novel ternary structures and H bonding for hydrided Li and Ca alloyed with Si (Ge). Nonetheless, the formation of these structures decreases the maximum H uptake expected for these destabilized materials. Also the H desorption temperature is still too high for practical applications.

• Hydrogen-induced amorphization (HIA) observed for Ca$_2$Si suggests a possible pathway for developing new hydride materials with improved absorption kinetics and warrants further examination.

• Attempts to make Mg$_2$Si more hydridable by alloying with Ca$_2$Si or NaSi were only partially successful. Although the CaMgSi alloy that routinely formed using Ca$_2$Si could not be hydrided under normal conditions, some of the Mg$_2$Si hydrided when NaSi was present to form NaMgH$_3$. This suggests that proper doping of Mg$_2$Si with additional elements can render the Mg component more reactive.

• Neutron methods confirm the formation of Ca(BH$_4$)$_2$ from the high-pressure hydrogenation of CaH$_2$ and CaB$_6$. These high-pressure syntheses may provide an alternate means of incorporating neutron-transparent $^{11}$B into various borohydrides to enable better neutron measurements.

• Hydrogen cycling measurements of promising destabilizing combinations of LiBH$_4$ with ScH$_2$ and CaH$_2$ indicate that they may be hindered by the formation of elemental boron during dehydrogenation.

• A Calphad database for H-Li-Mg-Ca-B-Si-N with thermodynamic descriptions of the constituent subsystems is being developed from binary data from the literature and *ab initio* calculations. So far, 2 LiBH$_4$ + MgH$_2$ is the most promising composition with respect to hydrogen availability and reaction temperature.