

IV.A.4n Reversible Hydrogen Storage Materials – Structure, Chemistry and Electronic Structure

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Introduction and Approach

We employ state-of-the-art characterization tools to investigate the microstructural and microchemical changes that occur in candidate material systems during the uptake and release of hydrogen. This investigation provides fundamental insight to the processes governing hydrogen uptake and release. The characterization is coupled with first-principles, electronic-structure and thermodynamic techniques to predict and assess meta-stable and stable phases. Electronic-structure calculations are used to enhance the understanding of Metal Hydride Center of Excellence (MHCoe) experimental characterization results on candidate systems.

These efforts enable a more efficient approach to designing a new system with the required properties. Partnerships have been formed with the following groups (Sandia National Laboratories, HRL, University of Pittsburgh, Carnegie Mellon University, and University of Reno-Nevada) and these fruitful partnerships will continue in the next fiscal year (FY).

Results

1. We have demonstrated how theory can interface with experiment and improve understanding of assessed properties. As shown in Figure 1, first-principles-based electronic-structure and

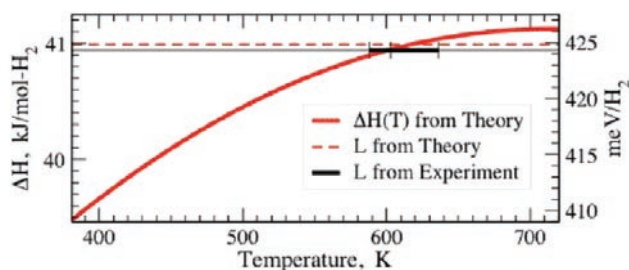


FIGURE 1. $\Delta H(T)$ from our DFT results compared to an assessed latent heat L of 41 kJ/mol- H_2 determined both from theory and experiment (the assessment from van't Hoff plot affects value of enthalpy). L from theory is insignificantly affected by including data from a larger temperature range, i.e. 381-636K.

thermodynamic calculations of the destabilized reaction $LiBH_4 + MgH_2$ were completed in FY 2006 (see publications). Key achievements were:

- Predicted the van't Hoff plot for assessment of latent heat of reaction and for direct comparison to HRL experiments.
 - Revealed that assessed latent heat is not the true enthalpy of reaction due to the affect of assessing discrete data and slopes on van't Hoff plot.
 - Revealed the importance of rotational modes in these molecular solids.
2. Acquisition of a vacuum transfer stage to observe environmentally sensitive samples in the transmission electron microscope (TEM) in furtherance of the previous FY goal. Results obtained, in association with several partners include:
- Within ball milled and Ti-doped $NaAlH_4$, the presence and location of the catalytic species (Ti) was identified by using energy dispersive x-ray spectroscopy (EDS) and electron energy loss spectroscopy (EELS). EELS peak shapes of Ti show, in general, that Ti is not oxidized to TiO_2 . Deconvolved EELS Ti peak shapes confirm that a majority of the Ti resides as Al_3Ti (Graetz *et al.*, 2003) and show the cubic form in 10 cycle material (Figure 2). This work was performed in conjunction with U. Hawaii during the last FY and is no longer part of the center activities.
 - The thermal stability of Mg/Si interfaces in ball milled $2 Mg + Si + 0.1 Nb_2O_5$ and "dilution milled" $Mg + 5 Si + 0.25 Ni$ was studied by using the in situ TEM annealing technique coupled with EDS and high resolution

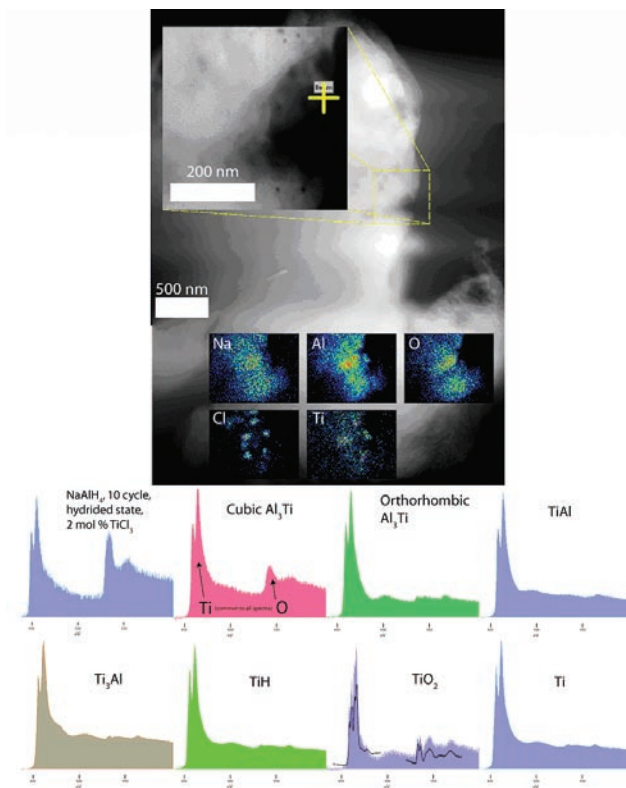


FIGURE 2. Electron energy loss spectra from indicated region in 10 cycle NaAlH_4 , 2 mol% TiCl_3 doped. (Overlaid Ti edge spectra in TiO_2 form, Ahn *et al.*, overlaid O edge spectra from Leapman *et al.*)

imaging. Dynamic studies of the ball-milled material show no elemental segregation even at differential thermal analysis (DTA)-reported hydrogen desorption temperatures (Figure 3). Why higher annealing temperatures are needed in these experiments is not known and is unusual as reaction temperatures are often lower in this type of experiment. Additionally, Nb and Ni do not appear to be well distributed after ball milling. Future work will verify the effectiveness of dilution milling in the Ni-catalyzed system. This work is being performed in conjunction with HRL Laboratories.

- The reaction products produced during the cycling of the $\text{CaH}_2/\text{CaB}_6$ system has been examined. Initial investigation was to investigate the elemental distribution in the particles. Found unanticipated reaction products on a sample that had been through three cycles (Figure 4). Energy dispersive analysis has been used to identify the chemistry of the particles and microdiffraction to determine the crystal structure. Degradation products do not appear in material that has not been cycled. Preliminary analysis has been performed but the results are proprietary;

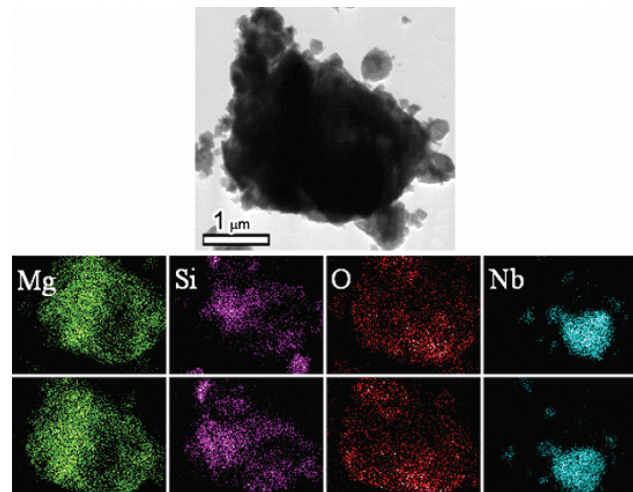


FIGURE 3. Image and EDS maps of $2 \text{Mg} + \text{Si} + 0.1 \text{Nb}_2\text{O}_5$, ball milled for 30 minutes. Upper maps show elemental distribution at room temperature, and lower maps show elemental distribution at 240°C . Distribution is not homogenous at either temperature, and does not agree with differential thermal analysis performed by HRL.

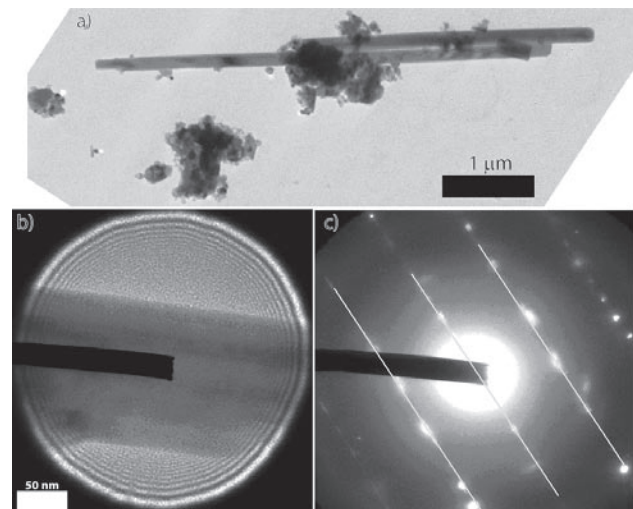


FIGURE 4. a) TEM bright field image of large "prismatic" degradation crystals in 3 cycle catalyzed $2 \text{CaH}_2 + \text{CaB}_6$, b) the location of the nanobeam on a prismatic crystal, and c) a representative nanobeam diffraction pattern showing both layer lines and spot patterns from b). Work to fully identify these crystals is ongoing, as both EDS and EELS do not give expected elemental compositions for these products.

further work will be performed in the next FY to complete the identification of these products. This work is being performed in conjunction with SNL.

3. Initial metal hydrides properties and modeling database construction completed in summer FY 2005 and further improvements continue through FY 2006 (see <http://data.mse.uiuc.edu>).

- Advances in development of the alloy thermodynamic toolkit to study thermodynamic stability have been made. While tested early FY 2006, significant changes have been made for usability and generality. The toolkit utilizes data in the Structural Database to predict stability via DFT database.

Conclusions and Future Directions

Conclusions

- Demonstrated how theory can interface with experiment and improve understanding of assessed properties (see Figure 1).
- Used experiment to improve understanding of and to assess processing strategies and reliability.
- Developed a successful approach for examining environment sensitive materials in state-of-the-art analytical equipment (see Figures 2 and 3).
- Studied the $\text{CaH}_2/\text{CaB}_6$ system (with SNL).
- Assessed effectiveness of ball milling strategies for Li/Mg/destabilized systems (with SNL).
- Add modifications of Structural Database (current care-and-feeding at NCSA). Maintain database of candidate systems and reactions. Expand use, scope, and vetting reliability (with all partners).
- Completed studies of the phases and phase stabilities in complex metal-hydride LiBH_4 destabilized hydrogen-storage reactions, including calculating and assessing van't Hoff plot (with HRL and U. Pittsburgh/Carnegie Mellon University).

Future Directions

For FY 2007 we will continue experimental studies of the microchemical and microstructural changes occurring in different candidate systems that are supplied by the various partners. In addition to EDS analysis, electron energy loss spectroscopy will be used to investigate the chemistry and where appropriate to examine the nature of the bonding through examination of the near edge structure.

The structural database will be made available for use by partners. Further studies on the electronic-structure calculations on the bulk phase of LiBH_4 in the ground-state orthorhombic phase and room temperature hexagonal phase were completed, along with H_2 , hexagonal MgB_2 , MgH_2 and LiH will be conducted with

input from the HRL group. The results of these studies may require experimental verification. Additional calculations will be performed with input from partners regarding key issues.

In brief, plans include:

- Determine chemical/structural changes during (de)hydriding cycles (with SNL, HRL, U. Hawaii).
- Structure and energy of combined magnesium/borohydrides (with GE).
- Complete study of $\text{CaH}_2/\text{CaB}_6$ (with SNL) and NaAlH_4 (with U. Hawaii).
- Structure and chemistry of contaminant layers on (de)hydriding cycle (U. Nevada).

FY 2006 Publications/Presentations

- D.D. Johnson (UIUC) "Using DFT Methods: the good, bad and ugly". Theory Tutorial to MHCoe: Capabilities and background of first-principles modeling to the experimentalists (Aug. 17, 2005).
- Duane Johnson (UIUC) colloquium at Pittsburgh (Nov. 16-17, 2005).
- N. Zarkevich (UIUC), A. S. Alapati (Carnegie Mellon U.), D.D. Johnson (UIUC), "First-principles prediction, and proper comparison to experiment, of enthalpies and van't Hoff plots of complex metal-hydride destabilized hydrogen-storage reactions," submitted to J. Phys. Chem. B (Letters), May 2006.
- Podium presentation at the annual Hydrogen Review Meeting. Washington, D.C., May 2006.
- D. D. Graham (UIUC), I.M. Robertson (UIUC), L. F. Culnane (U. Hawaii), C. Jensen (U. Hawaii), M. Sulic (U. Hawaii), "Combining Electron Energy Loss Spectroscopy and Energy Dispersive Spectroscopy for Identification of Catalytic Species in Hydrogen Storage Materials," Hydrogen Meeting, Hawaii, October 2006.
- D.D. Johnson, "Calculating enthalpies of hydrogen storage complex-metal hydrides," Hydrogen Meeting, Hawaii, October 2006.

References

- Graetz, J., *et al.* *Applied Physics Letters*, **85** (3) (2004) 500-502.
- Leapman, R. D., *et al.* *Physical Review B (Condensed Matter)*, **26** (2) (1982) 614-35.
- Ahn, C. C., *et al.*, *EELS atlas*. Gatan, Inc.: 1983.