Synthesis of Nanophase Materials for Thermodynamically Tuned Reversible Hydrogen Storage

Sonjong Hwang, David Abrecht and Channing Ahn
Caltech
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Project ID # STP_41_Ahn

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METAL HYDRIDE CENTER OF EXCELLENCE

Overview

Timeline

- Project start date:
  October 1, 2004
- Project end date:
  January 31, 2010

Percent complete: 80%

Budget

- Total project funding
  - DOE share $1M (5 yrs)
  - Contractor share $250k (5 yrs)
- Funding for FY07
  - DOE share $200k
  - Contractor share $50k
- Funding for FY08
  - DOE share $200k
  - Contractor share $50k

Barriers

(B) Weight and volume of on board hydrogen storage systems

(M) Reversibility of high capacity solid state storage materials

(N) Kinetics (fueling/refueling times) associated with current solid state storage materials

Partners

Interactions/ collaborations:

John Vajo, HRL Laboratories
Vitalie Stavila, Sandia Natl. Lab.
Karl Johnson, Univ. Pittsburgh
David Sholl, Georgia Inst. Tech.
J.C. Zhao, GE/Ohio State Univ.
Terry Udovic, NIST
Joseph Reiter, JPL
Craig Jensen, U. Hawaii

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Relevance

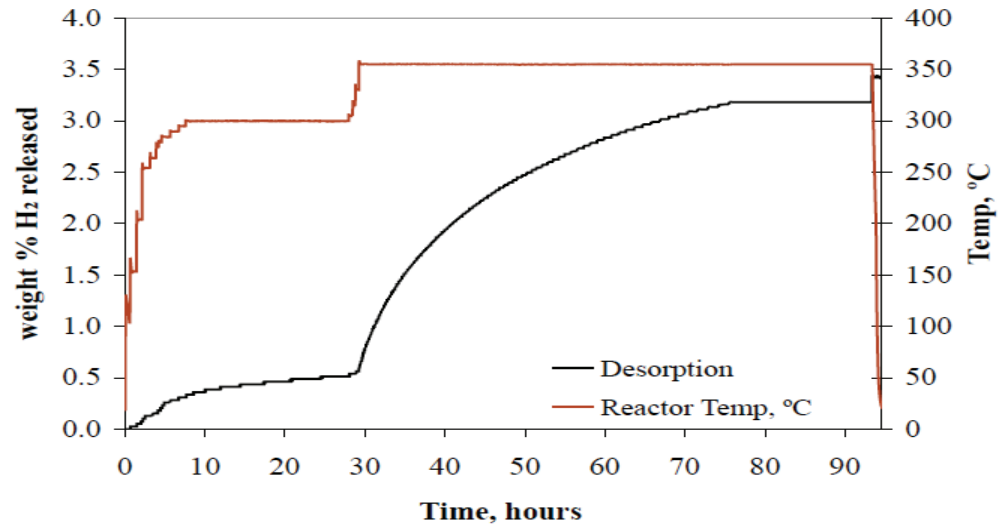
- To assess whether thermodynamically tractable reactions based on hydride destabilization, that should be reversible but appear not to be, are kinetically limited.
- To enable short hydrogenation times associated with refueling, that will require short solid-state and gas-solid diffusion path lengths.
- To address the problems associated with large, light-metal-hydride enthalpies (hydrogen fueling/refueling temperatures) and develop strategies to address thermodynamic issues surrounding the use of these materials through hydride destabilization. Systems of interest determined through “computational screening” by MHCoE partner members.
- To understand issues related to grain growth and surface/interface energies, which are vital in order to understand the kinetics of hydrogenation/dehydrogenation reactions.

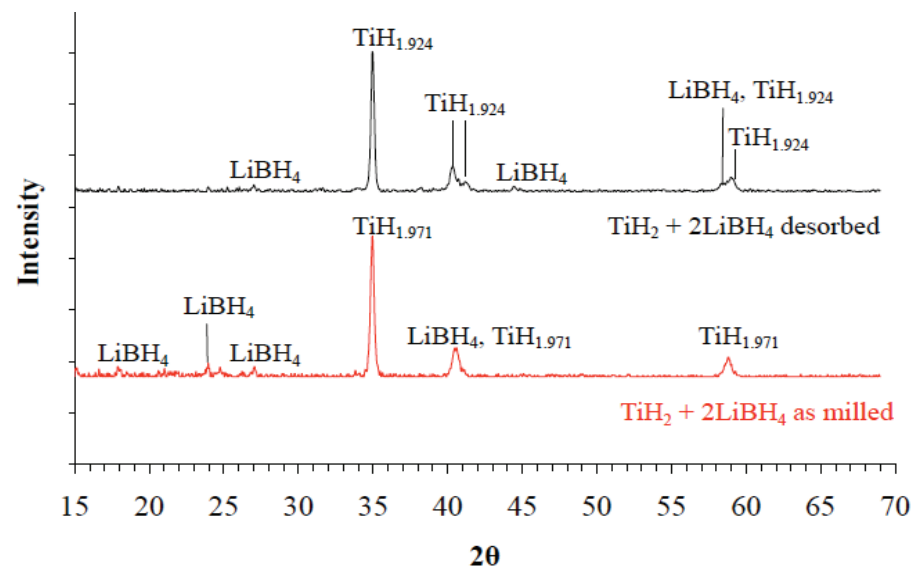
Approach

- Ball milling of destabilization candidates and gravimetric dehydrogenation and hydrogenation evaluation of thermodynamically appropriate systems, using Sieverts apparatus systems at Caltech and at JPL.
- Analysis of borohydride reaction pathway intermediates, like closo-boranes to seen if these structures can be destabilized.
- DFT calculations of specific hydride destabilization formation enthalpies and reaction enthalpies.
- X-ray diffraction for determining reaction product phases.
- NMR analysis (at the Caltech Solid State NMR facility) to determine bonding and phase formation in systems that lack long range crystallographic order.
- Transmission electron microscopy (at the Caltech Kavli Nanoscience Institute and the Material Science TEM facilities) and energy filtered imaging to determine microstructural evolution and phase inhomogeneities in scaffold based systems.

Technical Accomplishments and Progress: The $TiH_2 + 2LiBH_4 \rightarrow TiB_2 + 2LiH + 4H_2$ System: *Experimental Assessment of Chemical Destabilization*[a]

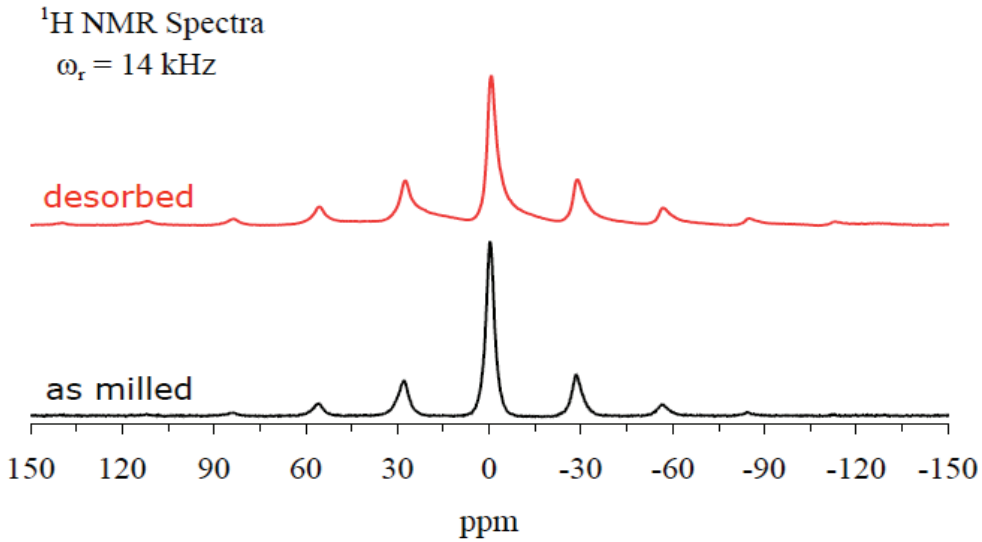
- We continue to pursue destabilization reactions with suitable thermodynamic properties based on computational screening by Center partners Johnson and Sholl (DFT). Of particular interest is the reaction $TiH_2 + 2LiBH_4 \rightarrow TiB_2 + 2LiH + 4H_2$, where:
  - ΔU_{0K} = 22.2 kJ/mol H_2[a]
  - 8.6 wt% capacity
- Isothermal kinetic desorption measurements of ball milled powders were taken at (350ºC shown at right) and we observed:
  - 3.5 wt% desorption over 95 hours
  - Desorption accounted for by decomposition of $LiBH_4$
- Powder XRD reveals only unreacted $LiBH_4$ and TiH_2 crystalline phases in desorption product, i.e. no reaction under these conditions between TiH_2 and $LiBH_4$, although ε phase of TiH_2 shown as peak splitting near 40 and 60 2Θ angle appears in product.
- Apparently, the stability of TiH_2 and TiB_2 do not allow activation under these conditions or kinetics are very slow for desired reaction.
- We note also that the TiH_2 appeared to "phase separate" under the conditions we applied, although a separate experiment appears to show wetting of $LiBH_4$ (shown subsequently) to TiH_2.



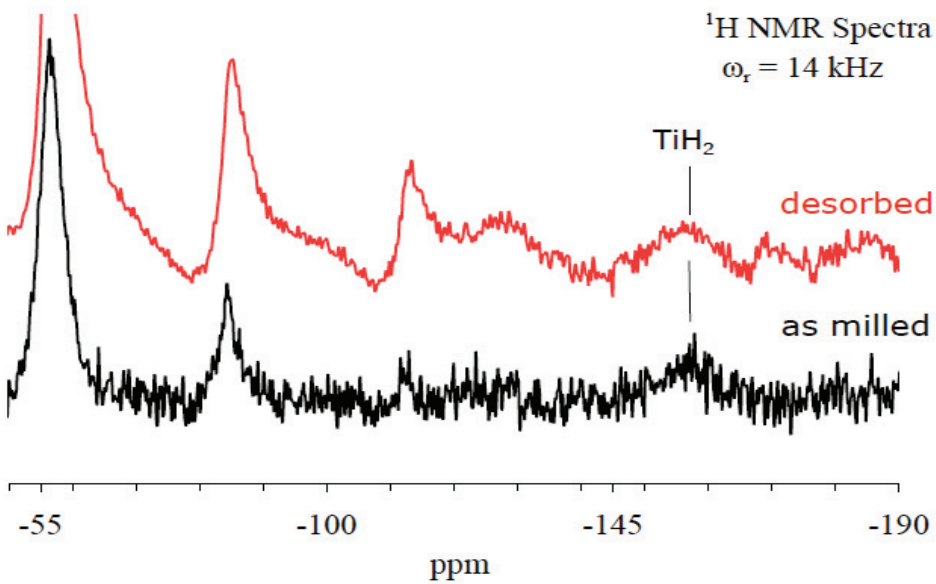


[a]Calculated by Center partner David Sholl and published as Alapati, S. V.; Johnson, J. K.; Sholl, D. S., J. Phys. Chem. C 2008, **112,** 5258-5262.

Technical Accomplishments and Progress: The TiH_2+2$LiBH_4$ → TiB_2 + 2LiH + 4H_2 System (continued): *MAS-NMR Spectroscopy*

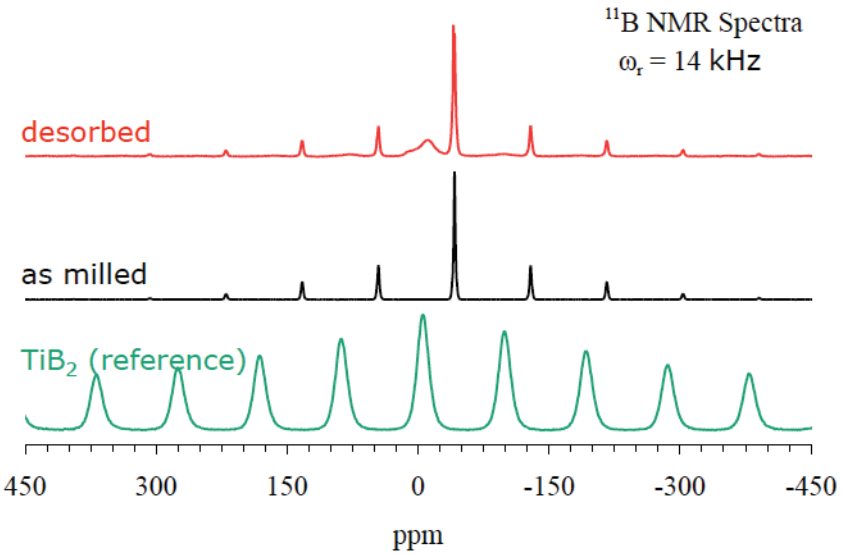


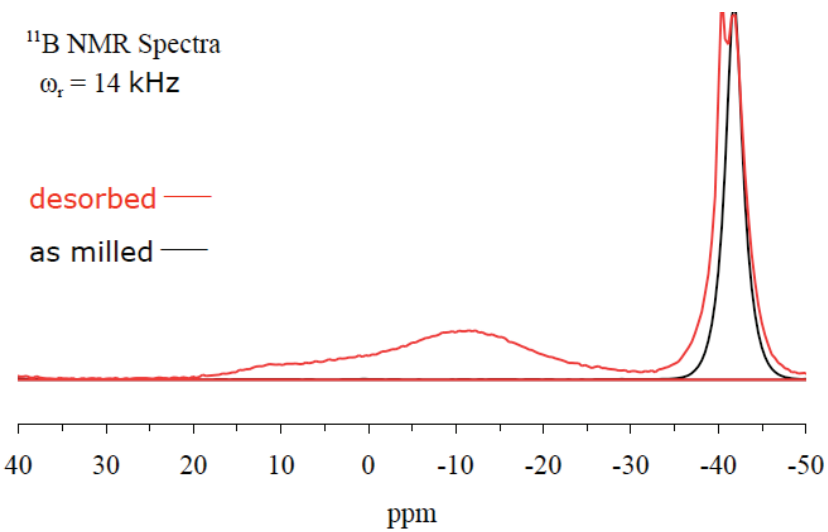
(a) ^{1}H MAS NMR spectra shown at left, of the as-milled TiH_2+2$LiBH_4$ system and the desorption product. Spectrum of desorbed phase shows a small decrease in the $LiBH_4$ peak intensity centered at 0 ppm shift. The peaks tail toward negative shift in the desorbed product, possibly due to LiH formation.



(b) The same ^{1}H MAS NMR spectra as above is shown at left, blown up to show the TiH_2 peaks at -159 ppm. No apparent decrease in the peak intensity was observed, indicating no change in the TiH_2 content after dehydrogenation.

Technical Accomplishments and Progress: The TiH_2+2$LiBH_4$ → TiB_2 + 2LiH + 4H_2 System (continued): *MAS-NMR Spectroscopy*





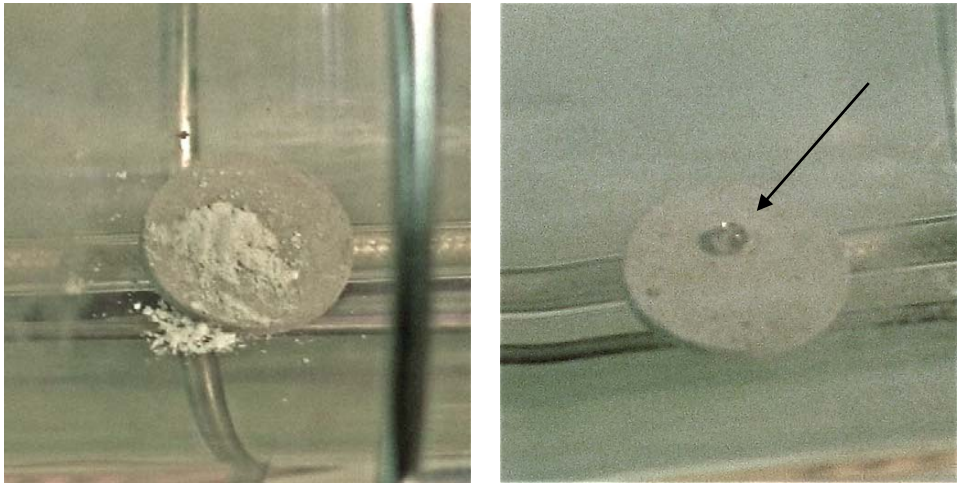
- Bloch ^{11}B MAS NMR also shows a small decrease in peak intensity for $LiBH_4$ after the desorption reaction. Formation of peaks at -12 ppm and 9-10 ppm indicate formation of $Li_2[B_{12}H_{12}]$* and amorphous boron, respectively.
- No formation of TiB_2, which produces a main peak shift at -5 ppm, is observable within the spectra of the other compounds.

*NMR Confirmation for Formation of $[B_{12}H_{12}]^{2-}$ Complexes during Hydrogen Desorption from Metal Borohydrides, Son-Jong Hwang, Robert C. Bowman, Jr., Joseph W. Reiter, Job Rijssenbeek, Grigorii L. Soloveichik, Ji-Cheng Zhao, Houria Kabbour, and Channing C. Ahn, J. Phys Chem. C, 112, 3164-3169, 2008.

Technical Accomplishments and Progress: Analysis of $LiBH_4$ wetting for aerogel scaffold destabilization reactions

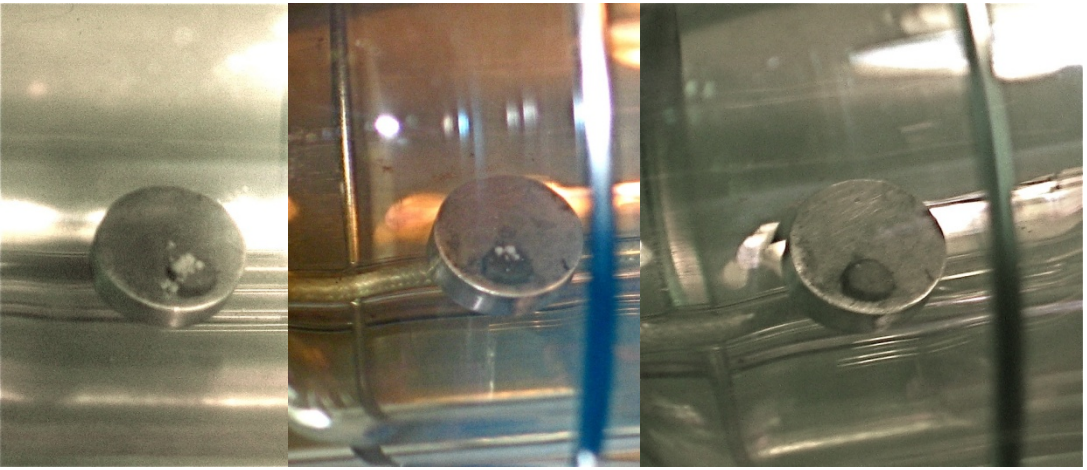
Assessing surface reactivity will be crucial in promoting destabilization reactions in carbon aerogel scaffolds. In an effort to determine the intrinsic reactivity of constituents that might affect the ability to incorporate hydrides into scaffolds and ultimately, the kinetics of destabilization, wetting experiments of $LiBH_4$ were performed over compressed disks of MgH_2 and TiH_2.

MgH_2 was examined as a collaboration with Center partner HRL Laboratories, in order to account for difficulties encountered in discerning kinetic enhancement of $LiBH_4$ incorporation into MgH_2 coated aerogel scaffolds. The figures to the right show that $LiBH_4$ does not wet the surface of MgH_2, a result that is consistent with spatially resolved Raman data that showed phase segregation in this system[a].



Images above show melting behavior of $LiBH_4$ over a milled and compacted MgH_2 powder. $LiBH_4$ forms a bead strongly on the surface, with a large contact angle.

$LiBH_4$ was also investigated over TiH_2 in an attempt to explain apparent issues involved in phase segregation during dehydrogenation, but $LiBH_4$ appears to wet easily, a TiH_2 compress.



Images at left show melting of $LiBH_4$ over a TiH_2 compacted powder mounted on an aluminum disk.

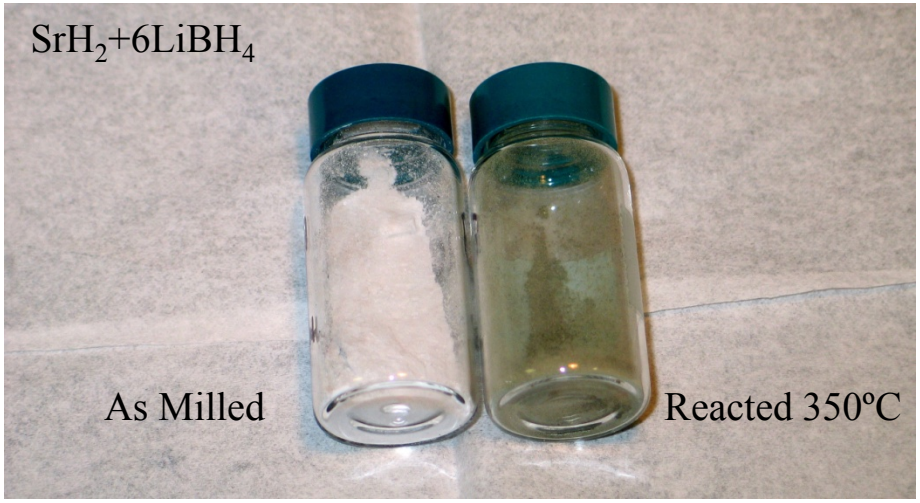
Left: $LiBH_4$ powder on TiH_2, before heating
Middle: Partially melted $LiBH_4$. No beading occurs, and the melted powder appears to wet the surface of the TiH_2
Right: After complete melting. Only small traces of $LiBH_4$ remain on the surface. The bulk has melted into the TiH_2

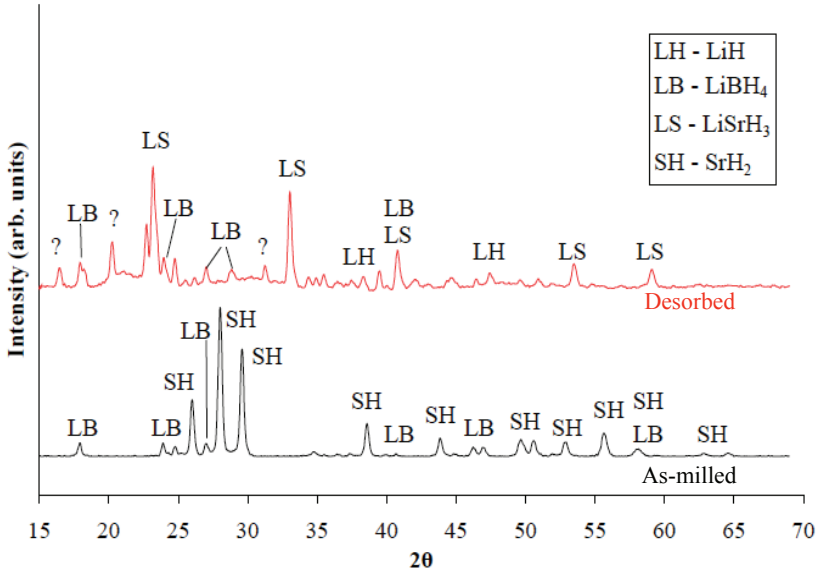
[a]A. Borgschulte, S. Kato and A. Zuttel, "Thermodynamic limitations of Reactive Hydride Composites," MH2008, Reykjavik, June, 2008.

Technical Accomplishments and Progress: The CaH_2+6$LiBH_4$ → CaB_6 + 6LiH + 10H_2 Analogues

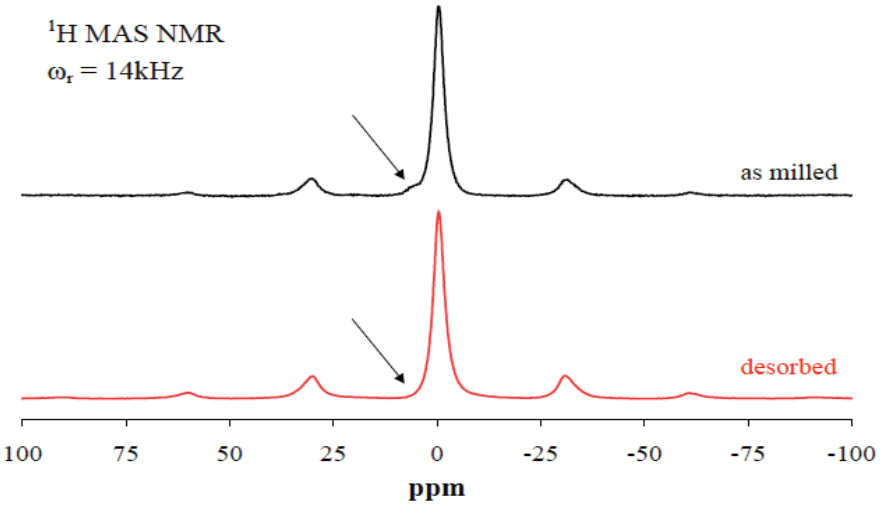
- Above destabilization reaction with appropriate gravimetric density but relatively high reaction enthalpy as determined by Center partners Johnson and Sholl[a]
  - ΔU_{0K} = 62.1 kJ/mol H_2
  - 11.6 wt% capacity
- Approach - Substitute higher MW elements for Ca in same periodic column as suggested by Center partner Vajo.
- Our own DFT calculations show with CaH_2 substituted by SrH_2 that:
  - ΔU_{0K} = 38.2 kJ/mol H_2 so attractive enthalpy
  - 9.1 wt% capacity so small weight penalty with Sr.
- Larger electron densities may translate to weaker bonds and better thermodynamics and/or kinetics.
- Initial work on a Sr analog shows that after desorption at 350ºC, sample changes to strong green colored powder.
- Powder XRD of desorption product shows unanticipated reaction paths producing phases, including:
  - $LiSrH_3$ trivalent
  - SrB_6 in very broad peaks = small reaction phase
  - Unreacted $LiBH_4$
  - LiH
  - 3.5 wt% release in initial desorption.
- Attractive enthalpy makes this a system of interest but further assessment of reaction pathway kinetics still needed.

[a]Calculated by Center partners and published as Alapati, S. V.; Johnson, J. K.; Sholl, D. S., J. Phys. Chem. C 2008, **112,** 5258-5262.



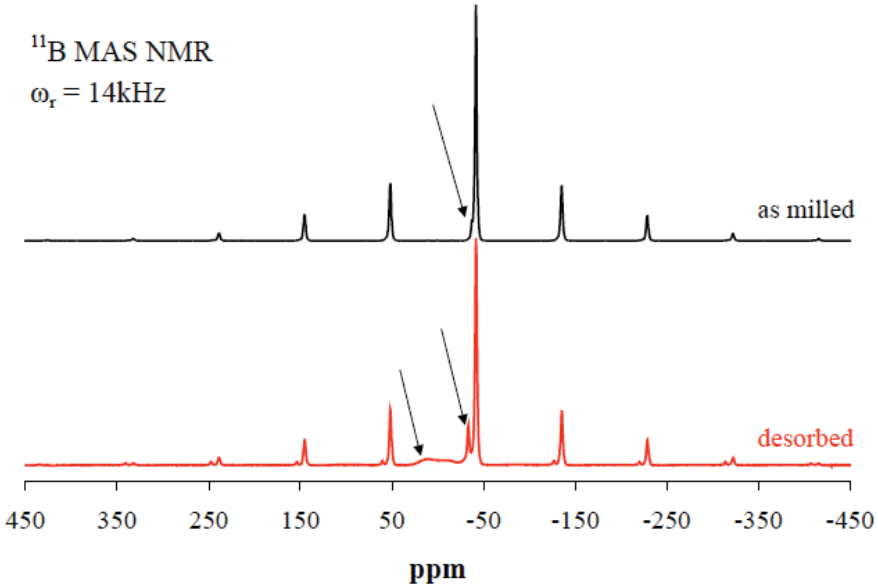


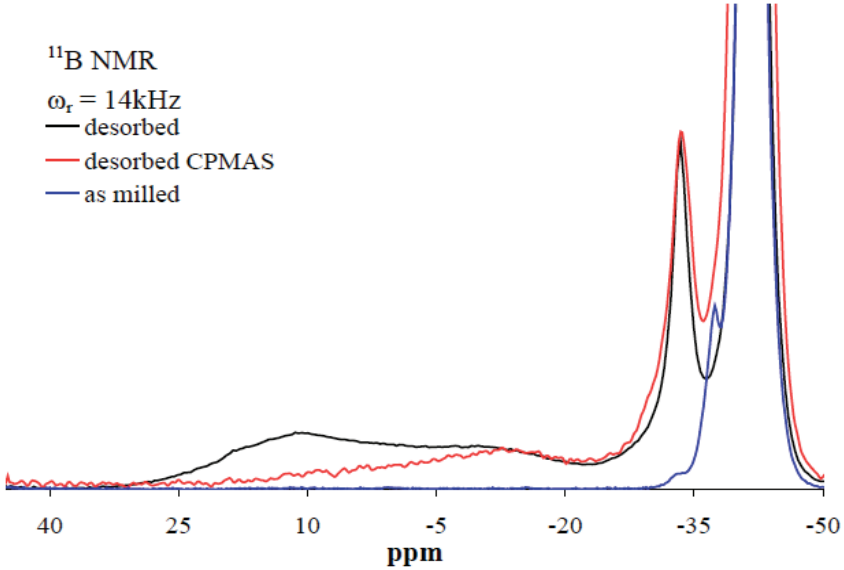
Technical Accomplishments and Progress: The CaH_2+6$LiBH_4$ → CaB_6 + 6LiH + 10H_2 Analogues cont'd -- ^{1}H and ^{11}B NMR of the SrH_2 system



^{1}H MAS NMR shows a small peak at ~7.5 ppm, shifted from the $LiBH_4$ peak at ~0. This change to positive shifts is consistent with higher molecular weight borohydrides, including calcium borohydride.

^{11}B MAS NMR also shows a similar peak off of the shoulder of the borohydride peak at -35 ppm. This is evidence for the formation of a strontium-containing borohydride during the milling process. This peak disappears after the desorption, and is replaced by another peak at -30 ppm that also appears in CPMAS. This indicates the formation of a third borohydride species in the system. More work is needed to determine the identities of these new borohydrides.





Technical Accomplishments and Progress: The Li-Sc-B-H system

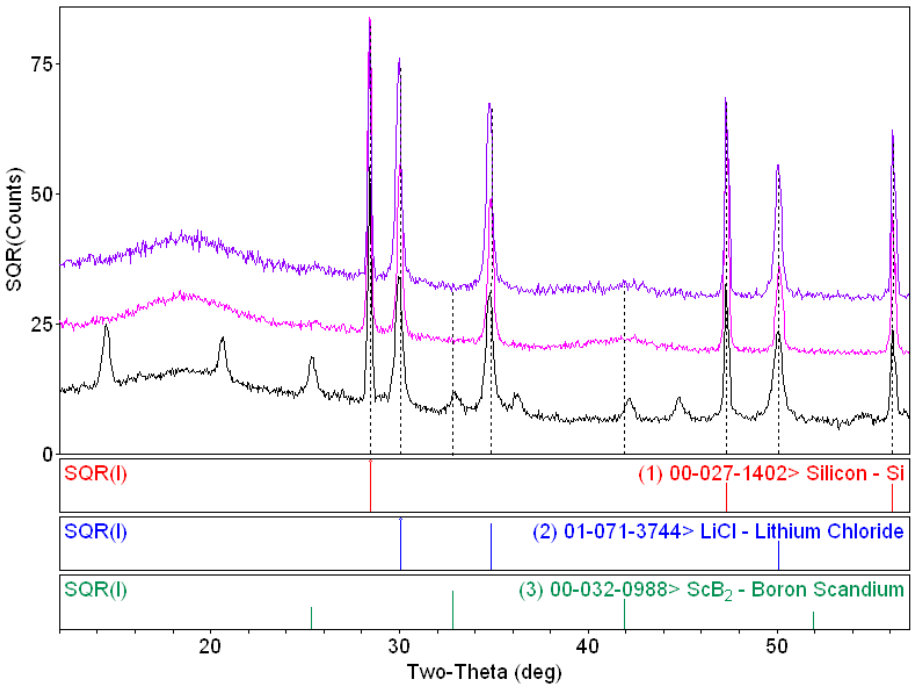
- Previously we have shown[a] that the $ScH_2 + 2LiBH_4 \rightarrow ScB_2 + 2LiH + 5/2H_2$ system that had a zero point energy corrected reaction enthalpy of 34 kJ/mole[b] had a high kinetic barrier and could not react up to temperatures of 450°C.
- We have followed up this work with the $LiSc(BH_4)_4$ system in order to assess reaction pathways that result in:
  - Mixed double cation system
  - Favorable ΔH values[c] (see table at right with calculated enthalpies by Majzoub & Ozolins)
- Powder XRD detects only LiCl and ScB_2 crystalline phases in desorption product, suggesting that reaction #1 and #2 might have proceeded.
- MAS NMR shows some ScB_2 and the closo-borane $Li_2B_{12}H_{12}$. Recovery of $LiSc(BH_4)_4$ was not achieved in this case.

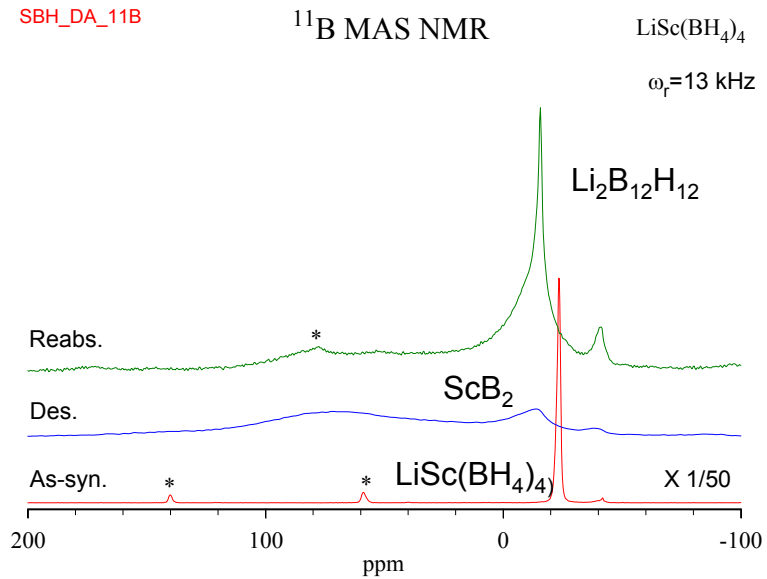
Predicted thermodynamically favored reversible hydrogen storage reactions in the Li-Sc-B-H system.

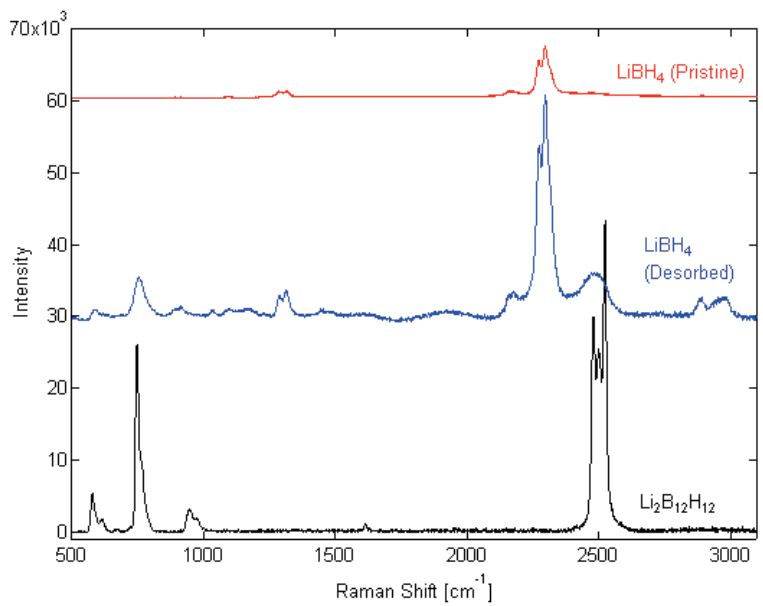
No.	Reactions	Wt. % H_2	$\Delta H_{T=0\,K}$
1.	$10LiSc(BH_4)_4 \rightarrow 4LiBH_4 + 3Li_2B_{12}H_{12} + 10ScH_2 + 44H_2$	8.0	2.8
2.	$Li_2B_{12}H_{12} + 5ScH_2 \rightarrow 2LiBH_4 + 5ScB_2 + 7H_2$	3.6	9.5
3.	$2LiBH_4 + ScH_2 \rightarrow 2LiH + ScB_2 + 4H_2$	8.9	29.2
4.	$12LiBH_4 \rightarrow Li_2B_{12}H_{12} + 10LiH + 13H_2$	10.0	39.9
5.	$5Li_2B_{12}H_{12} + 6ScB_2 \rightarrow 10LiH + 6ScB_{12} + 25H_2$	4.3	101.4
6.	$Li_2B_{12}H_{12} \rightarrow 2LiH + 12B + 5H_2$	6.5	108.5

[a]J. Purewal, S.-J. Hwang, R. C. Bowman, Jr., E. Rönnebro, B. Fultz and C.C. Ahn, "Hydrogen Sorption Behavior of the ScH_2-$LiBH_4$ System: Experimental Assesment of Chemical Destabilization Effects," *J. Phys. Chem. C* **2008**, *112*, 8481.
[b]Calculated by Center partner David Sholl and published as Alapati, S. V.; Johnson, J. K.; Sholl, D. S., J. Alloys Compd. 2007, 446–447, 23
[c]Calculated by Center partner Eric Majzoub with collaboration with V. Ozolins "Kim, C. et al. "$LiSc(BH_4)_4$ as a Hydrogen Storage Material: Multinuclear High Resolution Solid State NMR and First-Principles Density Functional Theory Studies" submitted to J. Phys. Chem. C. (Feb 2009).

Technical accomplishments: Li-Sc-B-H system cont'd







JPL

For above figure, powder XRD profiles of as ball-milled $4LiBH_4$+ $ScCl_3$ mixture (bottom); after a 400ºC desorption that removed about 6.4 w% of the initial hydrogen content (middle); and following a 400ºC desorption and a subsequent hydrogen absorption under ~70 bar H_2 gas and cooling to room temperature (top).

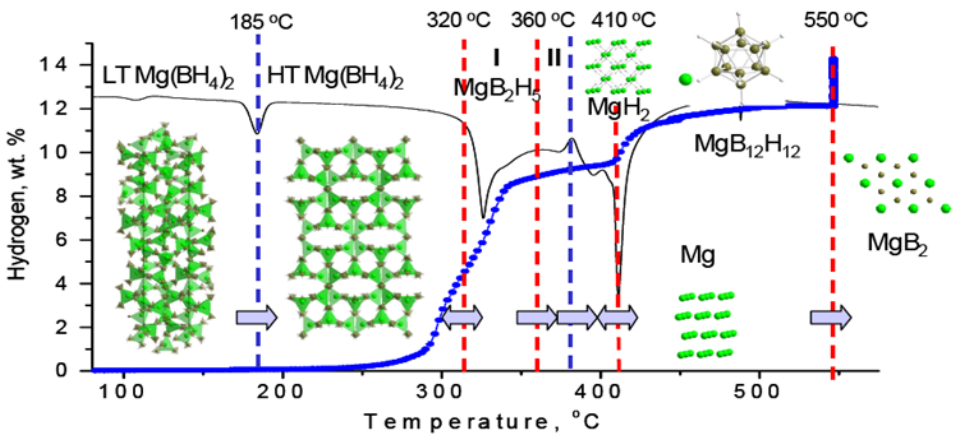
For upper right figure, ^{11}B MAS NMR spectra of (a) as-synthesized (lower trace), (b) desorbed (middle trace), and (c) reabsorbed $4LiBH_4$ + $ScCl_3$ (upper trace). The asterisks indicate spinning side bands.

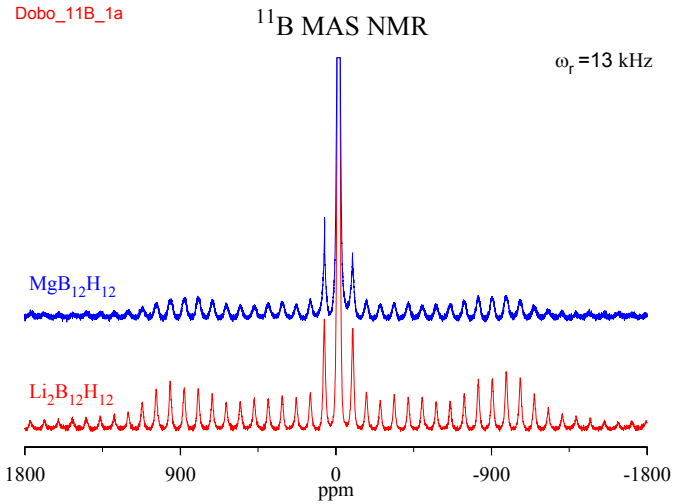
Note the formation of $Li_2B_{12}H_{12}$ in high concentration after absorption, indicating the characteristic stability of this phase against hydrogenation and showing a high kinetic barrier to BH_4 conversion.

In lower right figure are baseline Raman data used for our analysis.

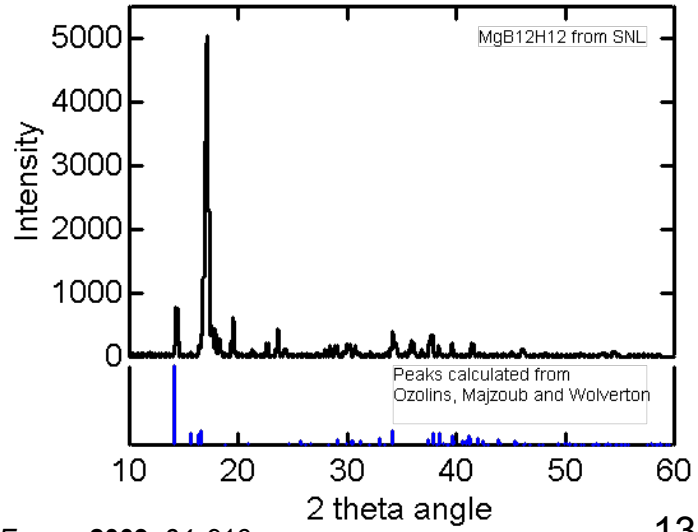
Technical accomplishments: $MgB_{12}H_{12}$ characterization and reaction pathway assessment of $Mg(BH_4)_2$ decomposition

- $Mg(B_{12}H_{12})_2$ found to be an important reaction intermediate[a]



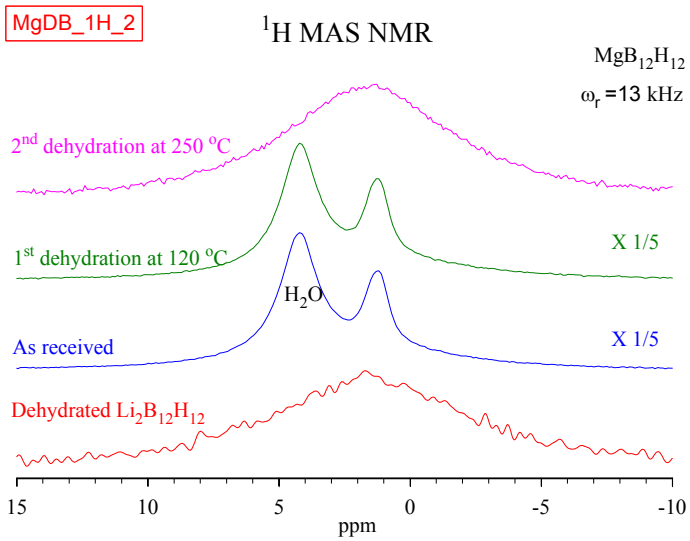


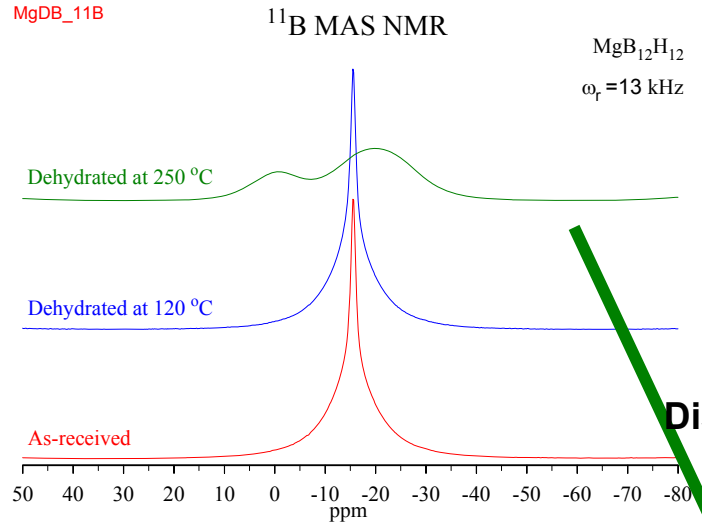
- Independent assessment of $Mg(B_{12}H_{12})_2$ reactivity needed. Its structure and thermodynamics were theoretically predicted[b].
- Sample prepared by Satish Jalisatgi (U. Missouri-Columbia), and center partner Vitalie Stavila (SNL), J.-C. Zhao (OSU).
- Spectroscopic baseline characterization: NMR (shown in upper right), XRD (shown in lower right), Neutron Scattering (with Center partner J. Hur, T. Udovic (NIST))



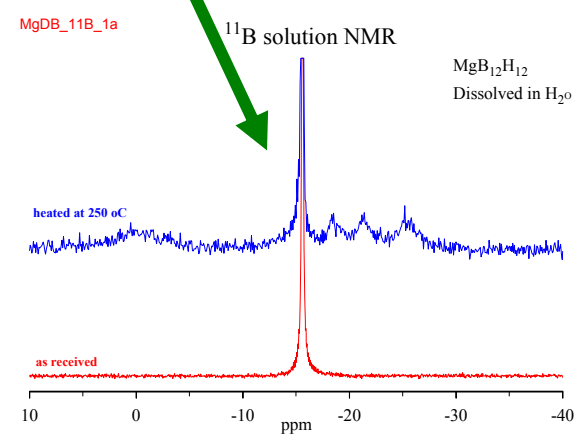
[a]schematic from center partner J.-C. Zhou and in Soloveichik, G. L. et al. Int. *J. Hydrogen Energy* **2009**, *34*, 916.
[b]Ozolins, V.; Majzoub, E. H.; Wolverton, C. *JACS,* **2009**, *131*, 230.

Technical accomplishments: $MgB_{12}H_{12}$ (cont'd)





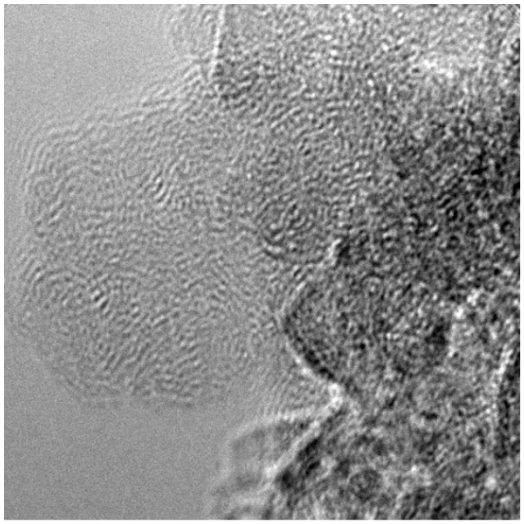
Dissolution into water



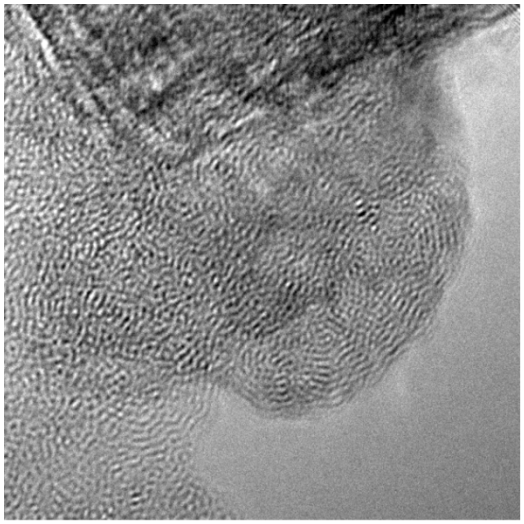
- $Mg(B_{12}H_{12})_2$ appears stable with water molecules in the crystallites.
- Vacuum dehydration at 120ºC for overnight causes no change in both ^{1}H and ^{11}B MAS NMR spectra as shown in upper left plot. $Li_2B_{12}H_{12}$ data in upper left plot is shown as a reference.
- Water dehydration over 250ºC shows absence of water in crystal as determined from ^{1}H MAS NMR, however ^{11}B MAS NMR indicates significant change in the icosahedron cage. XRD shows nearly no crystalline peak (amorphous). The same sample was dissolved into water for ^{11}B solution NMR. Numerous small peaks around -20 to -30 ppm and around 0 ppm, all indicate formation of B-OH bonds as a result of possible formation of $[B_{12}H_{12-n}(OH)_n]^{2-}$.
- The same NMR results are obtained even after the heat treatment up to 250 ºC under H_2 pressure.

Technical Accomplishments: Microstructural analysis of MgH_2 incorporated into carbon aerogel

• In collaboration with Center partners U. Hawaii and HRL Laboratories[a], we conducted, transmission electron microscopy analysis of a dibutyl Mg precursor incorporated into a carbon aerogel that was subsequently hydrogenated to form MgH_2. TEM was used in order to determine the distribution of Mg in the aerogel scaffold.
• Two samples with different Mg loadings (shown below) were analyzed in this work, that showed that nanoscale or nanoconfinement in a carbon aerogel is an effective way to promote fast dehydrogenation kinetics, which remain unchanged with cycling up to 4 times. Our initial analysis of results that were conducted on an FEI TF20 using energy dispersive x-ray analysis gave Mg loadings that varied from ~1.5 to 4.5 wt%. The apparent variation in Mg values might be due to our use of the thinnest areas for micro-analysis where the thin-film approximation holds, and that this might yield data that is different from Mg-bulk aerogel values.



Specimen : ZS-1-55-1
Operator : MIL
Voltage : 200 kV
Microscope Name : Tecnai F20
Total Magnification : X6790000
5 nm
Acquisition Date : 6/13/2008
Acquisition Time : 2:37:50 PM

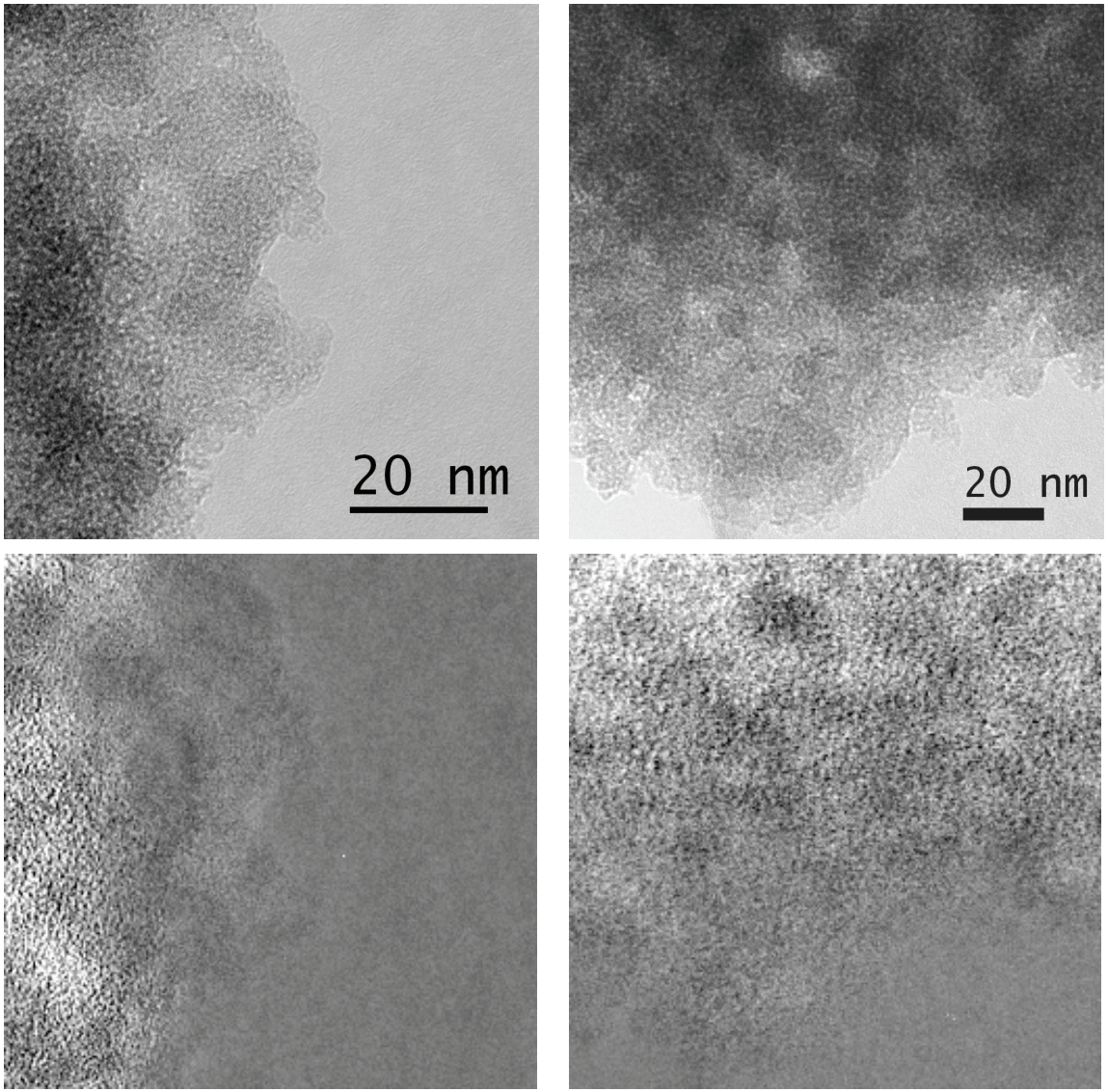


Specimen : ZS-1-55-1
Operator : MIL
Voltage : 200 kV
Microscope Name : Tecnai F20
Total Magnification : X6790000
5 nm
Acquisition Date : 6/13/2008
Acquisition Time : 3:49:25 PM

•Surprisingly, normal imaging techniques were incapable of resolving specific MgH_2 features on the aerogel, in spite of the Mg X-ray signals were clearly discernable in all regions of the microstructure.

[a]Shu Zhang, Adam F Gross, Sky L Van Atta, Maribel Lopez, Ping Liu, Channing C Ahn, John J Vajo and Craig M Jensen, "Synthesis and hydrogen storage properties of MgH_2 incorporated carbon aerogel scaffold," to appear in Nanotechnology, 2009

Technical Accomplishments: Microstructural analysis of MgH_2 incorporated into carbon aerogel, cont'd



In order to try to better spatially resolve and detect for the presence of MgH_2 on aerogel, we have employed energy filtered imaging[a], using an energy filter located on our TF20 transmission electron microscope and using the Mg $L_{2,3}$ edge as an image source.

Zero loss images of the microstructure are shown in the upper set and the corresponding Mg images are shown in the lower set. The Mg images (bright features) suggest that Mg is fairly uniformly distributed in the aerogel structure. There is though, possibility that the image information is dominated by thickness effects. In the future we plan avoid this by the use plasmon imaging to better resolve the differences in electron density of the hydride phase (14 eV) and that are distinct from the metal (10 eV), oxide (22 eV) and carbon (25 eV) signatures.

[a]"Transmission Electron Energy Loss Spectrometry in Materials Science and the EELS Atlas," ed. C. C. Ahn, Wiley 2004.

Collaborations

John Vajo, HRL Laboratories, LLC (industrial lab partner), scaffold microstructural analysis and wetting studies of destabilization systems.

Vitalie Stavila, Sandia Natl. Lab. (national lab partner), synthesis of closo-borane systems for NMR analysis and destabilization studies.

Karl Johnson, Univ. Pittsburgh (University partner), computational screening of destabilization systems.

David Sholl, Georgia Inst. Tech. (University partner), computational screening of destabilization systems.

J.C. Zhao, GE/Ohio State Univ. (University partner), $Mg(BH_4)_2$ system studies.

Terry Udovic, NIST (national lab partner), Neutron scattering studies of borohydride based systems.

Joseph Reiter, JPL (national lab partner), Sieverts analysis for gravimetric studies, destabilization reaction studies, residual gas analysis assessment, kinetic studies of dehydrogenation reactions.

Craig Jensen, U. Hawaii (University partner), Mg incorporation into aerogel for nano MgH_2 kinetic enhancement studies.

FY 2009-10 plans

- Wetting and aerogel pore size enthalpy dependent studies.
- Continued NMR studies to identify reaction species that lack definitive crystallographic features.
- Further exploration of approaches to destabilize closo-boranes
- Further microstructural analysis of hydride size morphology in scaffolds.
- Coordination with T. Baumann (LLNL) in synthesis of aerogels with pore size range down to 1 to 2 nm. Surface/interface effects will play a dominant role in reaction kinetics at these size dimensions.
- Use of surface treatments/additives to enhance wetting/reactivity of hydrides in aerogel pores.
- Confirmation of lowered enthalpies and diffusion paths in hydrides encapsulated within aerogel pores.