High-capacity Hydrogen Storage Systems via Mechanochemistry

PI :Vitalij K. Pecharsky

Co-PIs: Duane Johnson, Marek Pruski, Shalabh Gupta, and Viktor Balema (Ames Laboratory)

and Eric Majzoub (UMSL)

2018 Annual Merit Review

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Overview

Timeline

- Start Date: July 1, 2015
  - Phase 1: September 30, 2016
  - Phase 2: October 1, 2016 - September 30, 2017
  - Phase 3: October 1, 2017 - September 30, 2018
- End Date: September 30, 2018
- % Complete: ~90

Barriers addressed

(A) System Weight and Volume
(B) System Cost
(O) Lack of Understanding of hydrogen Chemisorption

Budget

- Total Project budget: $1.225 M
  - Total Recipient Share: $0.025 M
  - Total Federal Share: $ 1.2 M
- Total funds received: $200K (FY15), $500K (FY16), $300K (FY17), $0K (FY18)
- Total DOE Funds Spent (to date): $899,774K as of March 31, 2018
- Subcontract UMSL: $58K (Phase I)

Partner(s)

- UMSL: Eric Majzoub (Computational effort)

UMSL

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Relevance/Objectives

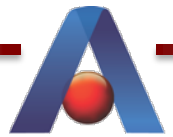
<u>Main Focus</u>: Development of Novel High H-capacity Si-based borohydrides (Si-BH) and composites

<u>Objectives:</u> Development of low-cost, high-performance hydrogen storage materials based on:

1. Silicon-based complex borohydrides

- Projected to have borderline thermodynamic stability.
- Stabilization strategies based on hypersalt/adduct formation; cation and anion engineering.

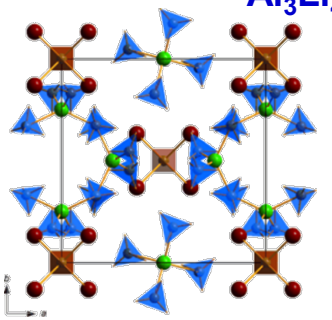
2. ***Borohydride/graphene composites***
(Discontinued as per PM guidance)



Relevance/Objectives

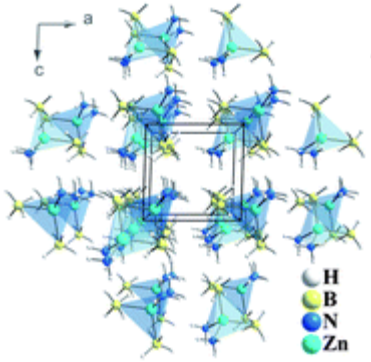
- Borohydrides have largest gravimetric density among all known metal hydrides: $LiBH_4$, $Mg(BH_4)_2$, $Al(BH_4)_3$,..
- Like nearly all other complex hydrides they suffer from poor kinetics and limited reversibility
- Structurally diverse: provide numerous opportunities for tuning
- May be stabilized by forming hypersalts and/or adducts
- No Si-based borohydrides reported in the past; Si and B are abundant and inexpensive

$Al_3Li_4(BH)_{13}$



Int. J. Hydr. En., 2013, **38**, 2790

$Zn(BH_4)_2 \cdot 2NH_3$



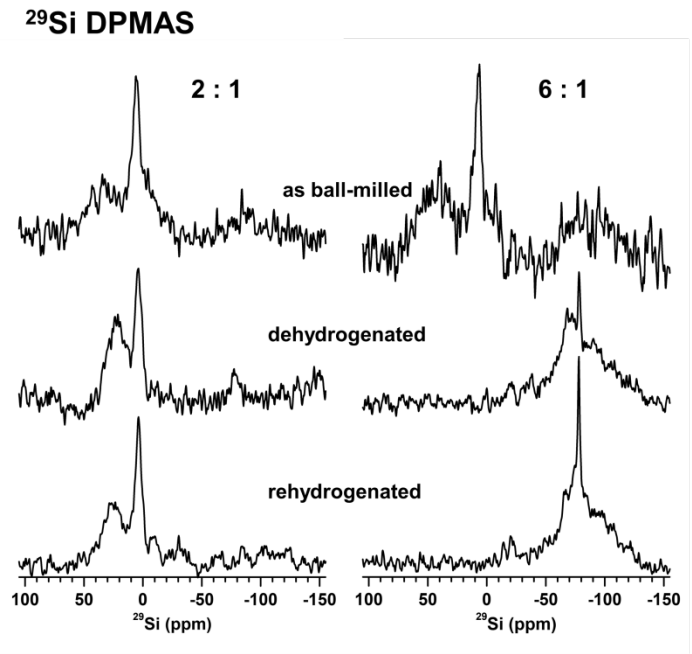
Energy Environ. Sci., 2012,**5**, 7590

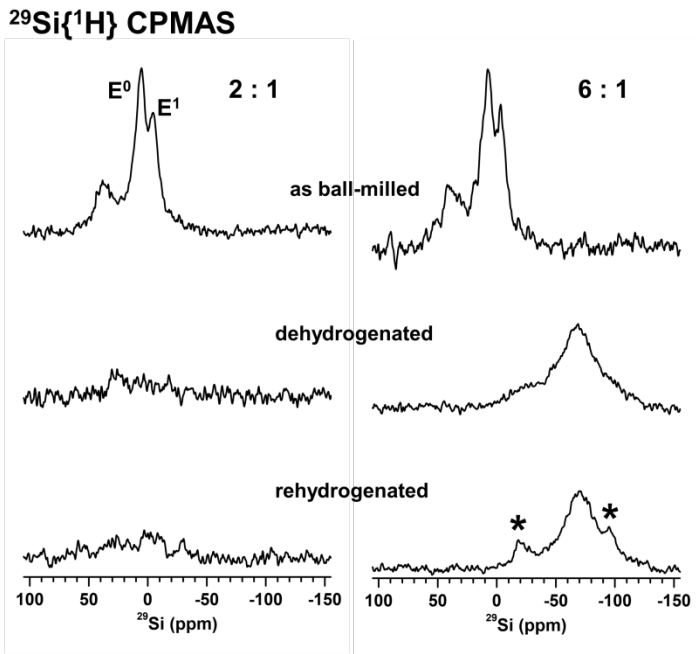
Accomplishments: *$LiBH_4$ – SiS_2 system*

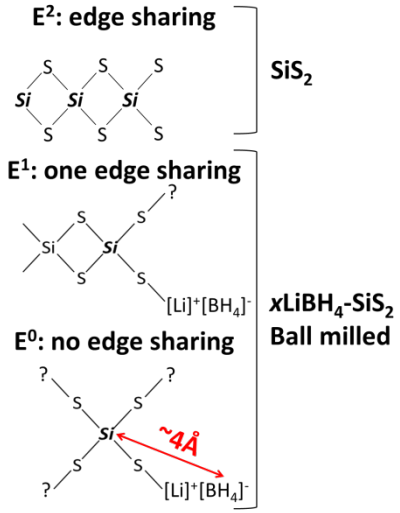
$xLiBH_4(c) + SiS_2(c) = \text{“}Li_xSiS_2(BH_4)_x\text{”}(a)$ (x = 2–6)

SSNMR: Observed $^{29}Si\{^1H\}$ CP signal
Clear evidence of new motifs – Si and H present within bonding distance, both in as-milled and rehydrogenated samples

- **Max. capacity 8.2 wt.% at x = 6**
- **30 – 35 % reversible capacity**



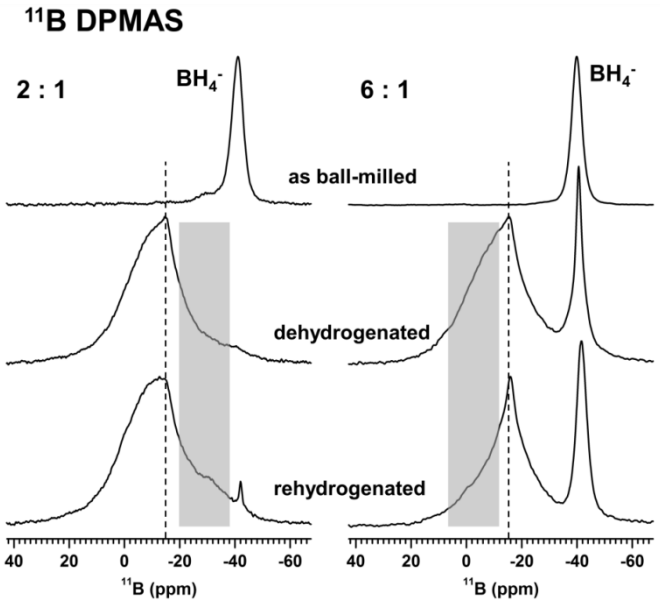




Accomplishments: *$LiBH_4$ – SiS_2 system*

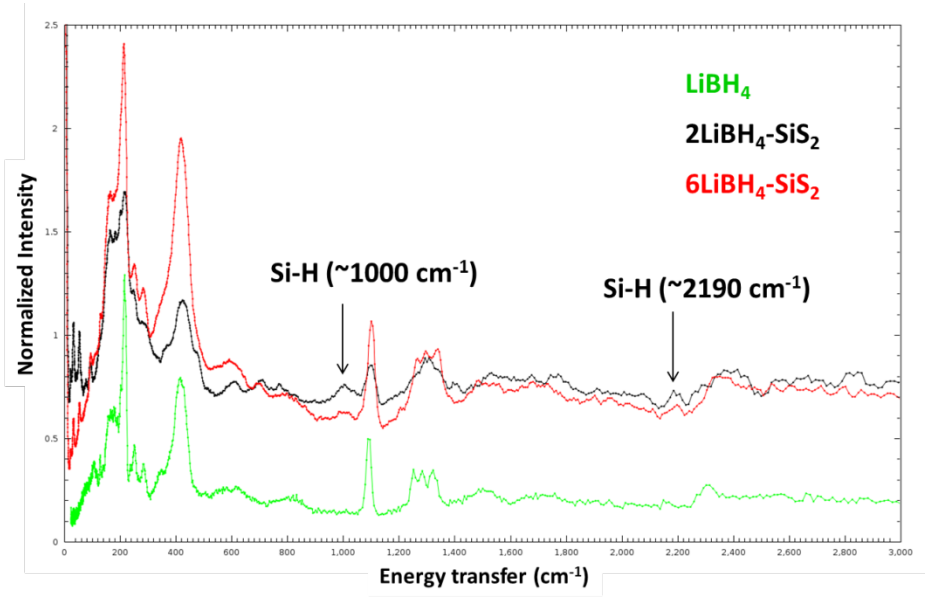
SSNMR:

- BH_4^- anion in all as-milled samples
- $[BH_x]$ units form upon decomposition
- Rehydrogenation leads to:
  - Reemergence of BH_4^- signal in 2:1 mixture
  - Protonation of $[BH_x]$ units in 6:1 mixture

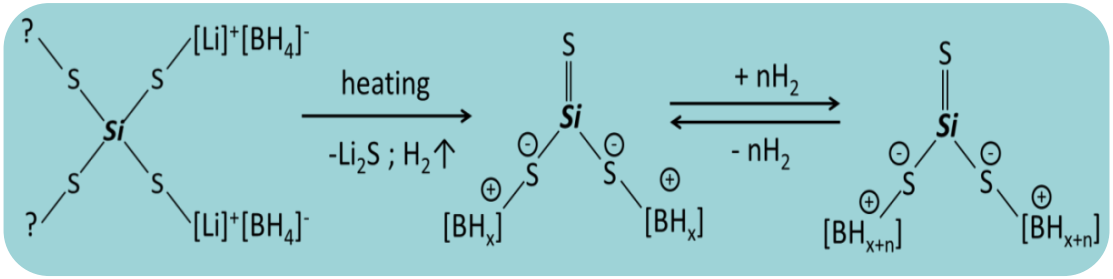


INS:

- Si-H stretching modes observed

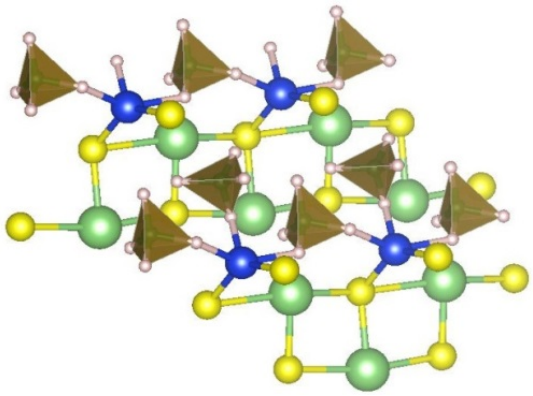


Suggested cycling mechanism

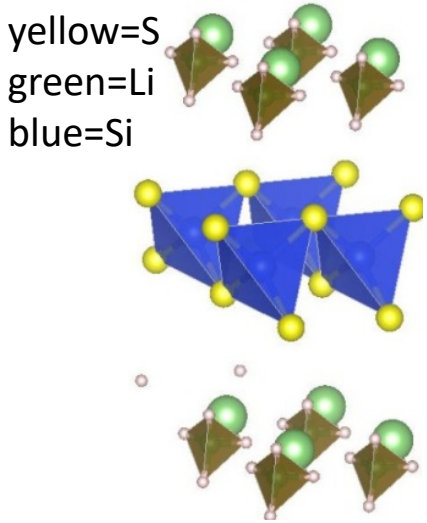


Accomplishments: *$LiBH_4$ – SiS_2 system*

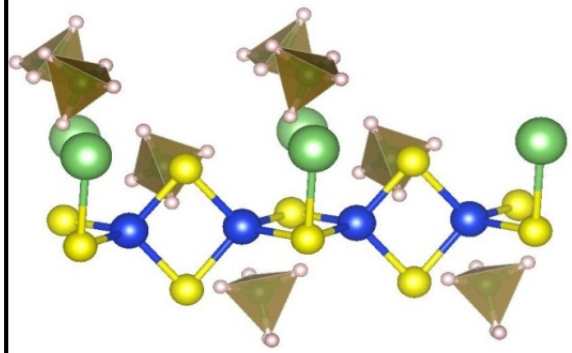
PEGS structure search: $Li_2SiS_2(BH_4)_2$



Si-H direct bonding



Corner-shared SiS_4 (E^0)
No direct S-H bonding
Si-H distance > 4 Å



Edge-shared SiS_4 (E^2)
No direct S-H bonding
Si-H distance > 3 Å

$Li_xSiS_2(BH_4)_x$ – PEGS shows several relatively low energy (metastable) structures in this composition space is possible

Accomplishments: $Mg(BH_4)_2$ – SiS_2 system

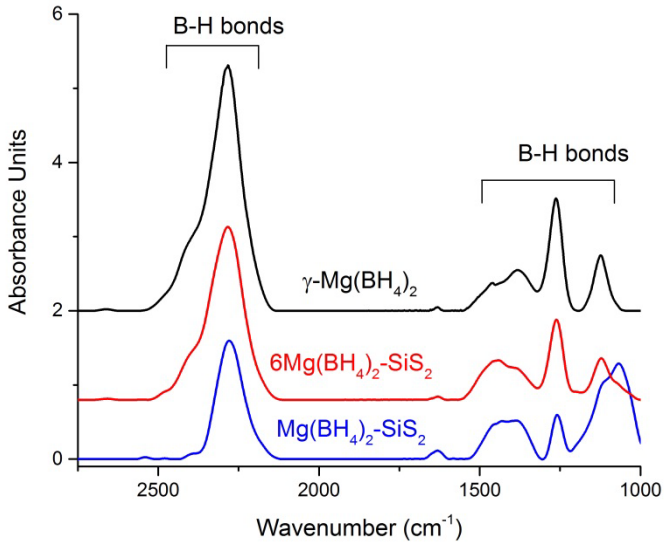
$xMg(BH_4)_2(c) + SiS_2(c) = "Mg_xSiS_2(BH_4)_{2x}"(a)$ (x = 1–6)

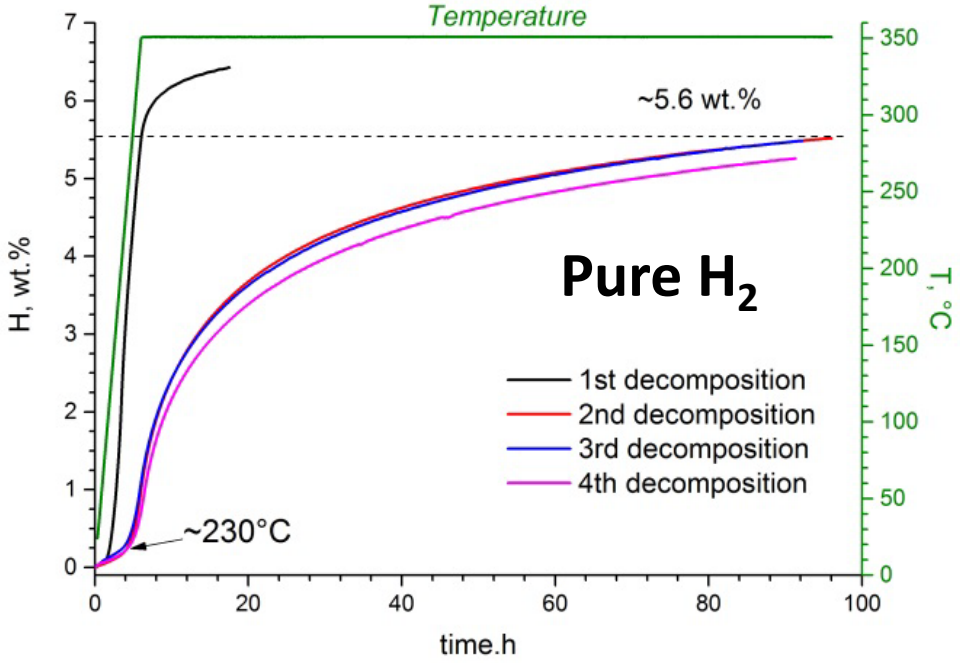
XRD:

- As-milled products: Amorphous

FT-IR

- Newly formed complex has similar structural motif as in γ-$Mg(BH_4)_2$.





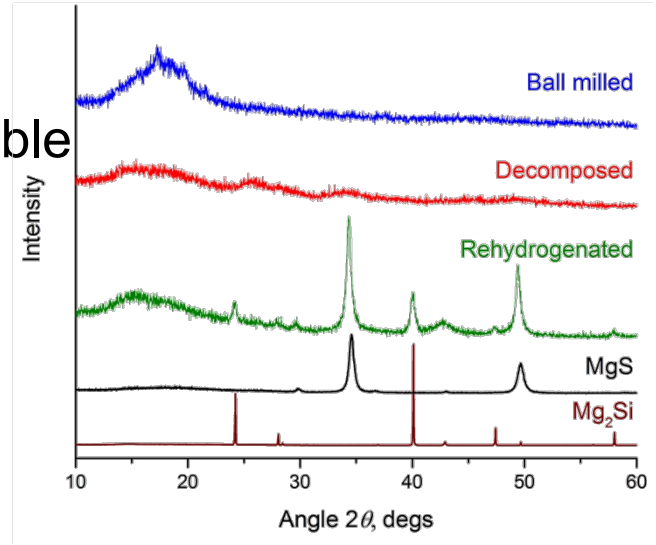
- Reversible capacity of 5 wt. % (at 350°C) achieved at x = 6: meets FY17 target
- >90% capacity retention after 4th cycle

Accomplishments: $Mg(BH_4)_2$ – SiS_2 system

$6Mg(BH_4)_2(\alpha)$-SiS_2 system

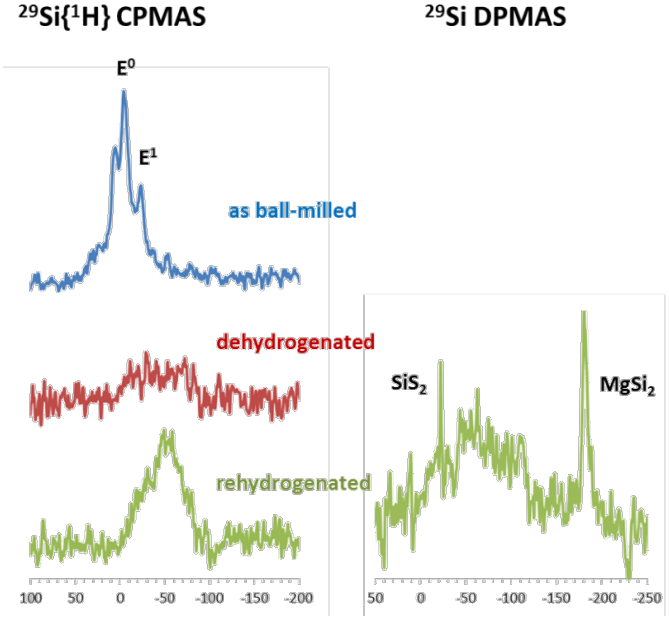
XRD:

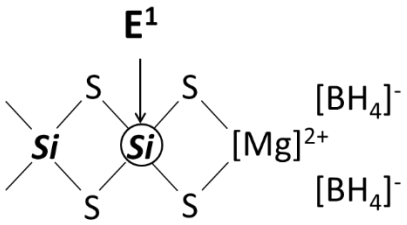
- 1st dehydrogenation: Amorphous products
- 2nd dehydrogenation: MgS and Mg_2Si detectable

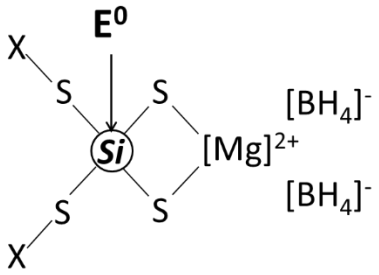


^{29}Si SSNMR:

- ^{29}Si{^{1}H} CPMAS signals in the as-milled and rehydrogenated samples







X=Si or Mg

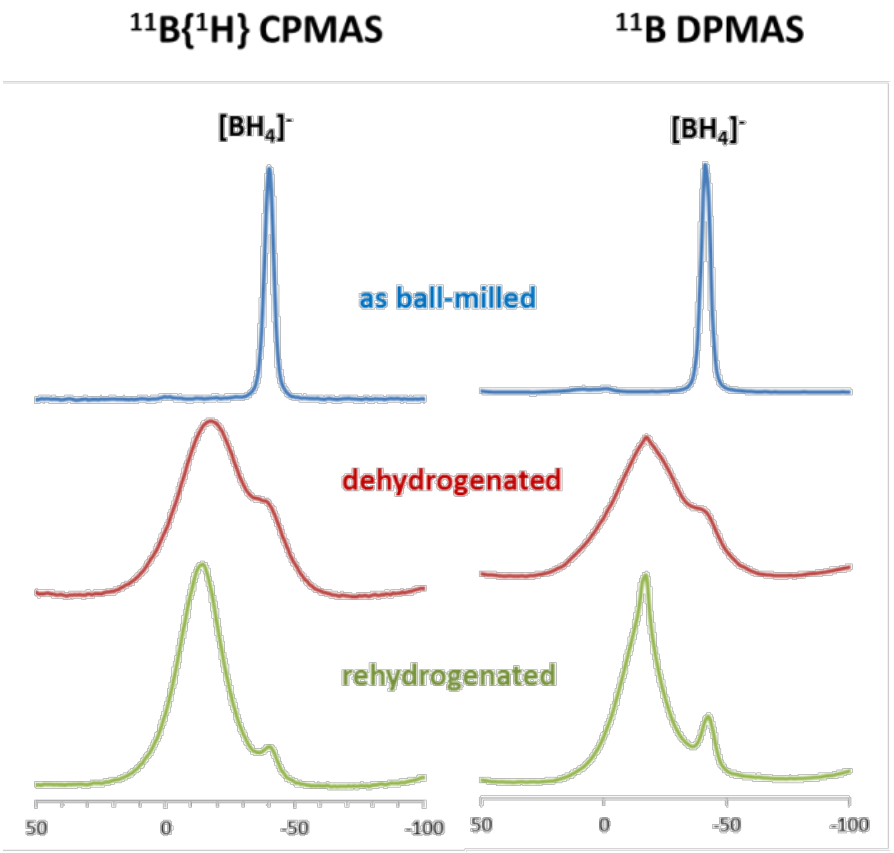
Coexistence of Si and H in the material; likely in single phase

Accomplishments: *$Mg(BH_4)_2$ – SiS_2 system*

$6Mg(BH_4)_2(\alpha)$-SiS_2 system

^{11}B SSNMR:

- BH_4^- anion in as-milled sample
- $[BH_x]$ units form upon decomposition
- Protonation of $[BH_x]$ to $[BH_{x+\delta}]$ upon rehydrogenation



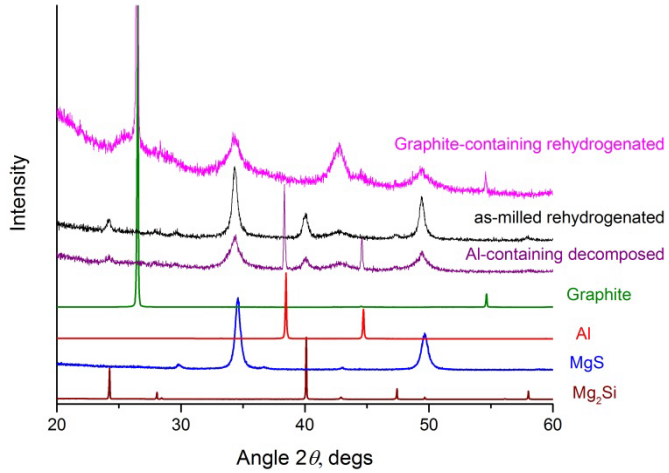
Formation of novel borohydride complex with nominal composition of $Mg_xSiS_2(BH_4)_{2x}$ (x=1–6) is likely

Accomplishments: $Mg(BH_4)_2 – SiS_2$ system

$6Mg(BH_4)_2(\alpha)$-SiS_2 : Improved kinetics and reversibility

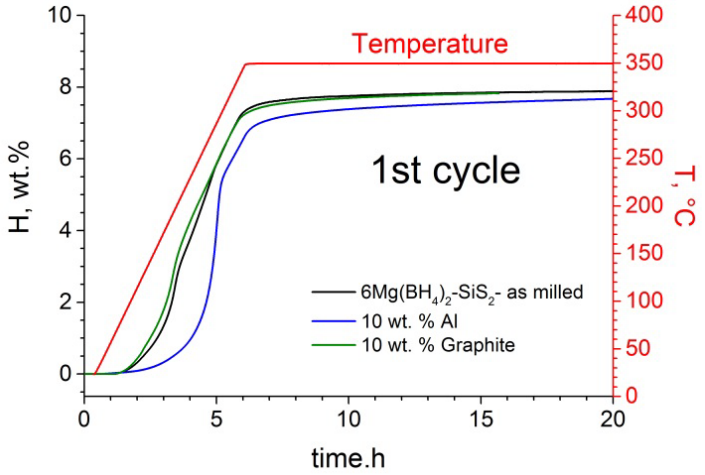
Improved H_2 de/absorption kinetics and reversibility via enhanced thermal conductivity.

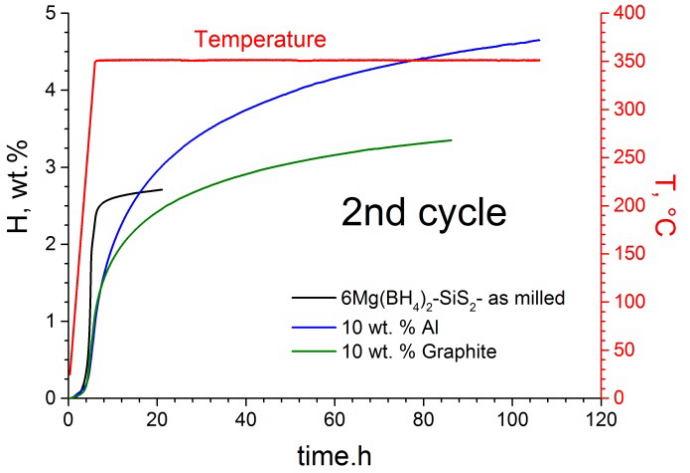
- Addition of 10 wt. % of Al
- Addition of 10 wt. % Graphite



Much improved H_2 cycling capacity in presence of elemental Al

Hydrogen desorption

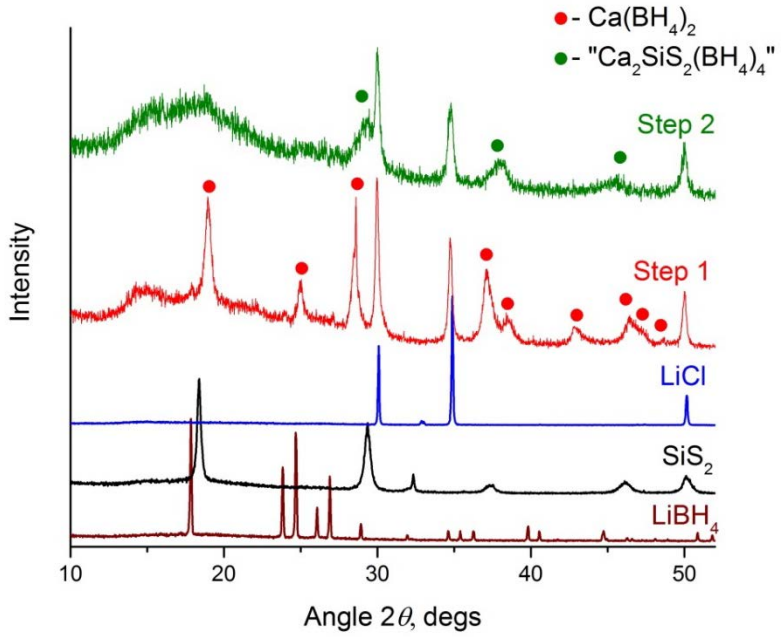




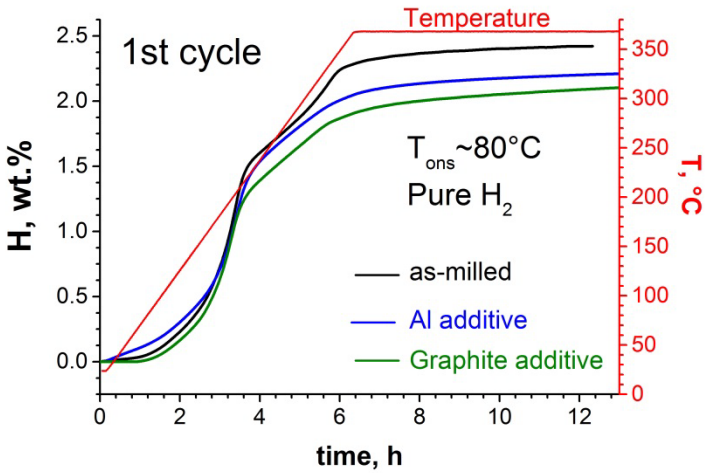
Accomplishments: $Ca(BH_4)_2 - SiS_2$ system

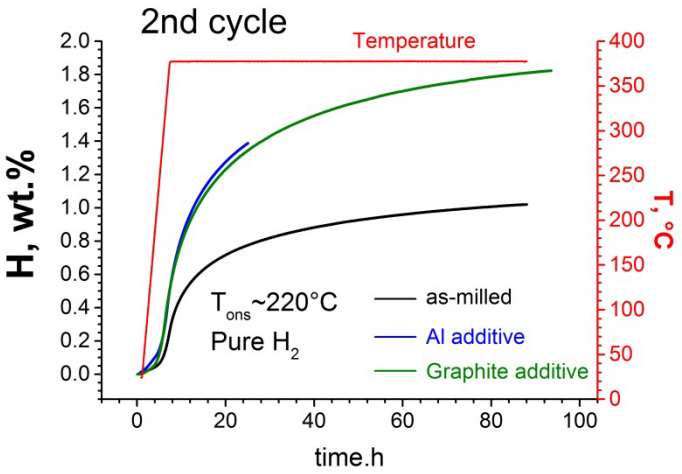
Synthesis and H_2 cycling the $Ca(BH_4)_2$-SiS_2 complex

1) $2LiBH_4 + CaCl_2 \rightarrow Ca(BH_4)_2 + 2LiCl$
2) $2Ca(BH_4)_2 + SiS_2 \rightarrow$ "$Ca_2SiS_2(BH_4)_4$"



Hydrogen desorption





- Borohydride complex- $Ca_xSiS_2(BH_4)_{2x}$ similar to Mg analogue is plausible.
- Much enhanced kinetics and reversible capacity in presence of Al and C(g).

Accomplishments: *Li-Si-B-H system*

A potential for low formal Si-valence in Si-BHs

Path forward:

$xLi^0 + Si^0 + yB^0 \rightarrow Li_xSiB_y \rightarrow Li_xSi(BH_n)_y$

XRD:

- Formation of Li_4SiB_x (x=1–4) upon milling
- Nanocrystalline Si and LiH are detectable after de/hydrogenation

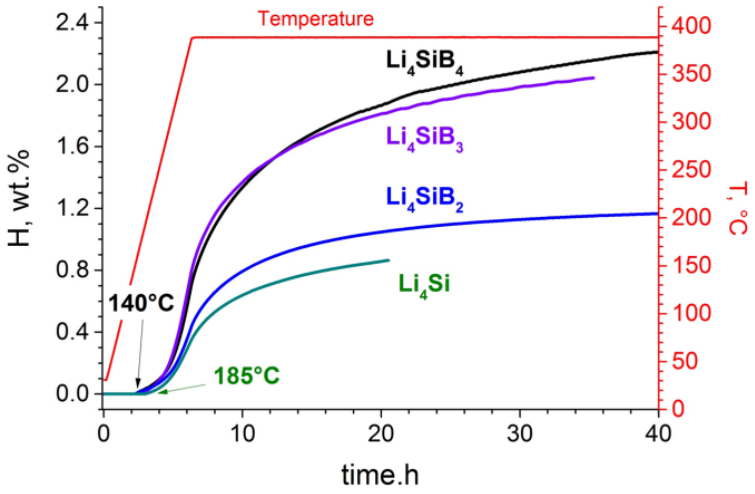
FT-IR:

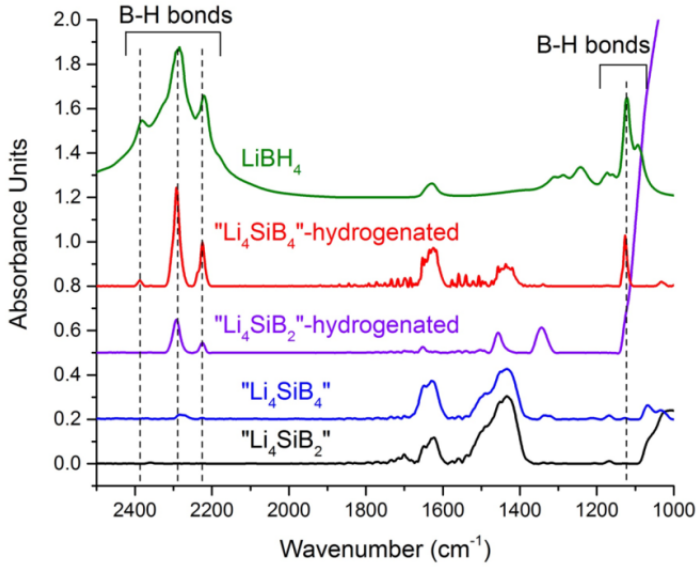
- Formation of B-H bonds upon hydrogenation under static H_2 pressure (160 bar, 380°C)
- Concentration of $[BH_4]$ units is maximum at x=4

TPD:

- Maximum hydrogen ab/desorption in Li_4SiB_4 material

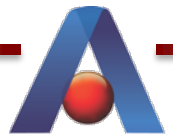
Formation of Si-BH under hydrostatic H_2 pressure is likely.





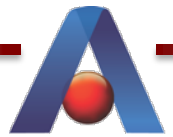
Summary

- Tasks 3.1-3. *Novel Silicon-based Borohydrides via Hypersalt Stabilization*
  - Sulfide anion can stabilize silicon borohydrides in Li, Mg and Ca containing systems
  - T_d onsets of as-prepared hypersalts meet the DOE targets
  - Cycling of H_2 in MBH_4-SiS_2 systems (M=Li, Ca, Mg) can reach 40-90 % of the initial hydrogen capacity
  - Observed controlled suppression of $B_2H_6 \rightarrow$ improved potential for reversibility
  - Cycling kinetics can be significantly improved by thermal conductive additives
- Task 3.4. *High-Pressure Mechanochemistry*
  - "Li_4SiB_x" (x=1-4) prepared mechanochemically may open a field toward low-valence-silicon Si-BHs



Remaining Challenges and Barriers

- Separation of as-synthesized Si-BHs from by-products
- Crystal structure determination due to amorphization upon synthesis
- Identifying Si-H bonds/interactions in newly synthesized Si-BHs
- High H_2 pressure mechanochemistry activity reinstatement is slower than anticipated



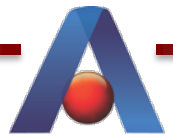
Future plans

- Detailed study of as-synthesized, decomposed and rehydrogenated Si-BHs (X-, N- diffraction, FT-IR, NMR, DSC) in systems with additives
- Improvement reversibility of H_2 in promising systems by using different thermally conductive additives
- Stabilization of derivatives of $Si(BH_4)_4$ by using high pressures and low temperatures
- Hypersalt synthesis via ball milling at high hydrogen pressures using M-Si-B solids where M=Li, Na, Mg, Ca, Al
- Hypersalt synthesis at ultra high hydrogen pressures in collaboration with HyMARC using M-Si-B solids where M=Li, Na, Mg, Ca, Al

Any proposed future work is subject to change based on funding level

High-capacity Hydrogen Storage Systems via Mechanochemistry

Technical Backup Slides



Approach - Synthesis and Characterization; Subtasks 2.1–2.4

1. Synthesis:

- Mechanochemistry (both at cryogenic and RT)

2. Characterization:

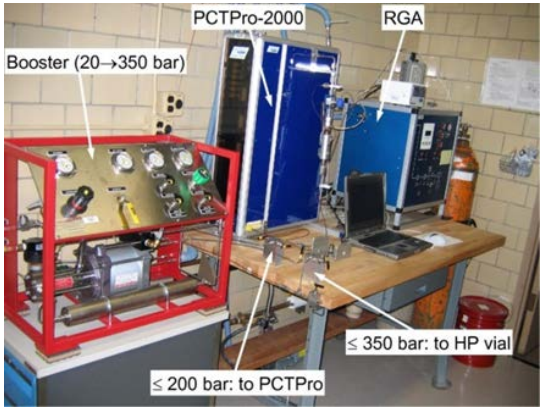
- Powder X-ray diffraction

- Gas sorption analysis - PCTPro-2000 integrated with gas analyzer.

-1D and 2D Solid-state NMR of spin-$^{1}/_{2}$ (^{1}H, ^{29}Si) and quadrupolar (^{7}Li, ^{11}B, ^{23}Na) nuclei, including highly sensitive DNP SSNMR

- Fourier transform infrared spectroscopy (FT-IR)

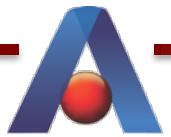
- Thermogravimetric analysis combined with differential scanning calorimetry (TGA-DSC).



Approach - Theory and Computation Subtasks 1.4, 3.3: PEGS+DFT Hypersalt Stability Screening

Computational Methods:

- Crystal structure candidates generated using the prototype electrostatic ground states (**PEGS**) method [PRB, 77, 104115 (2008)]
- Thermodynamic properties and decomposition pathways predicted using multi-gas canonical linear programming (**MGCLP**) [J. Phys. Chem. C., 118, 14759 (2014)]
- Density functional theory (**DFT**) using the VASP code

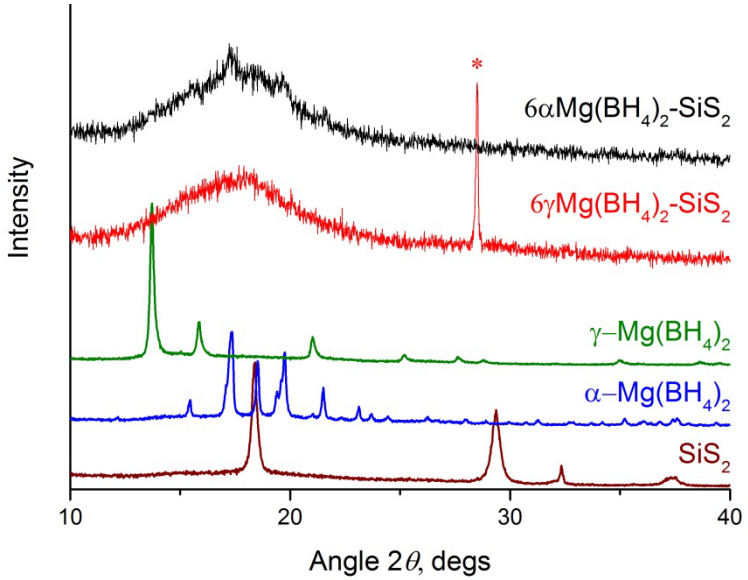


Accomplishments: $Mg(BH_4)_2 – SiS_2$ system

γ-$Mg(BH_4)_2$ vs α- $Mg(BH_4)_2$ modification in the $6Mg(BH_4)_2$-SiS_2 system

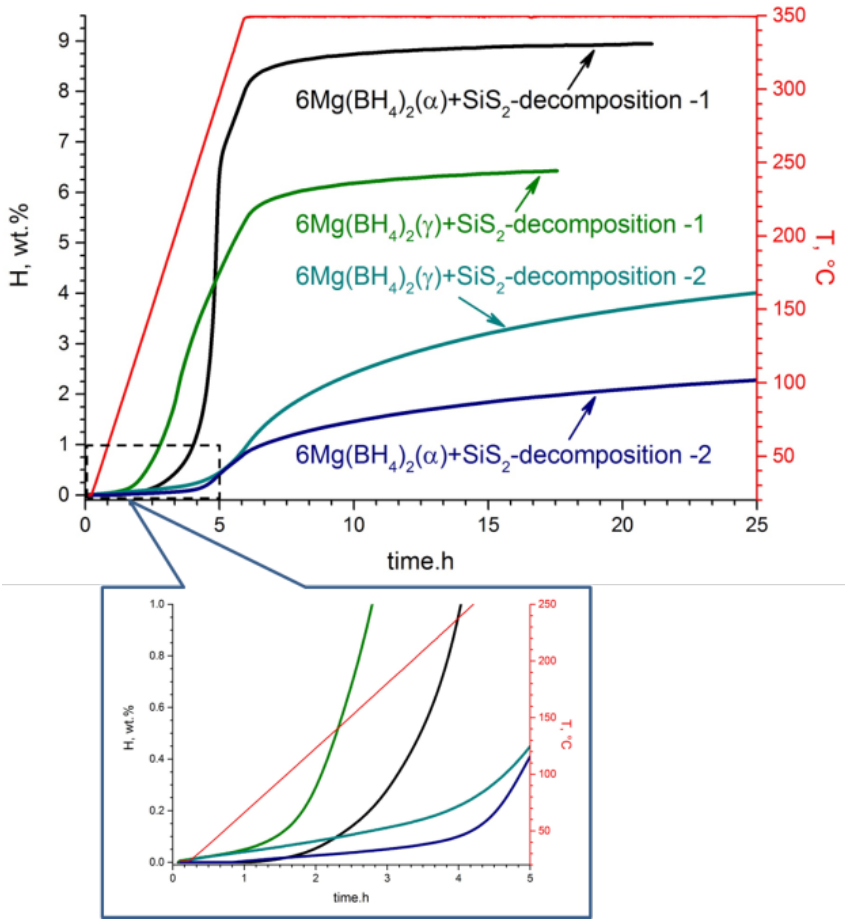
XRD:

- Similar products on XRD pattern



*impurities from precursor

TPD:



Higher H_2 release in the 1st cycle and lower in the 2nd cycle by the $6Mg(BH_4)_2(α)$-SiS_2 mixture

Reviewers Comments

FY2017 Reviewers Comment	FY2017 Response to Comments
Concern with mechanochemistry is that the energy formed during the ball milling decomposes the unstable Si-BH species. It would be desirable to attempt to perform this under gentle conditions, like low-temperature solution approaches.	Intuitively, we agree with the reviewer. However, there are multiple examples of formation of borohydrides with borderline stability via mechanochemistry. For example $Al_3Li_4(BH_4)_{13}$ is synthesized by ball milling, and has T_{onset} = 44.5°C.
Scalability of ball milling for large-scale application might be limited.	There has been tremendous technological progress in scaling-up of mechanochemical process and we do not see any future roadblocks in this direction, e.g., see Kaupp, J. Chem. Eng. Process. Technol. 2017, 8 DOI: 10.4172/2157-7048.1000335
While the efforts to date have generated some very interesting new phases, the Si-containing phases remain poorly characterized. None of the Si phases have been found to have an adequate hydrogen cycling capacity, and all of these phases are plagued by some level of B_2H_6 elimination during discharge.	Our latest results, particularly in the $Mg(BH_4)_2$-SiS_2 system, show promising H_2 reversibility, and retain up to 90 % capacity after 3 cycles. Kinetics, however remains poor and needs additional work. Extensive SSNMR studies have highlighted local coordination of Si and B in the new complex. B_2H_6 was not observed.
It is surprising that no other synthetic approaches have been attempted to isolate obtained species. The authors should explore alternative synthetic approaches in instances when mechanochemistry fails to yield the desired product.	It is plausible that more conventional approaches may be beneficial. However, the strength of this project is in solvent-free synthesis at room-temperature and ability to incorporate precursor that may be off-limits to other approaches.
The authors should explore more avenues for collaboration with HyMARC and HySCORE.	The proposed high pressure experiments in the SiH_4-B_2H_6 system is not yet possible within the HyMARC complex. A preliminary spectroscopic measurements in $LiBH_4$-SiS_2 system were performed at the SNS, Oak Ridge National Laboratory.
It is recommended to look more closely at the RGA assessments for the formation of critical gaseous impurities (e.g., B_2H_6, SiH_4, and H_2S). Detection of these reactive species can be extremely elusive because of their decomposition or reactions prior to entering the RGA sampling chamber.	The Residual Gas Analysis system (RGA-100) was evaluated for its detection capabilities for B_2H_6. For systems, that are known to release B_2H_6, the gas was detected without any issues.
There is good proposed work, but there are questions about moving to Li-based systems because of cost issues. The reason for starting with Li is understandable, but moving to Na, Ca, etc. is suggested.	We agree. And therefore the Ca-, Na, Mg- containing systems have also been studied. Results are presented in the review slides.
The synthetic conditions and the composition space should be expanded to increase the chance of isolating the desired Si-BH_4 species.	Please see the comment above. In addition we have made attempts to improve kinetics in order to achieve greater conversions in reasonable time.