High-capacity Hydrogen Storage Systems via Mechanochemistry

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Annual Merit Review, 2016

Project ID # ST119

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Overview

Timeline

- Start Date: July 1, 2015
  - Phase 1: August 31, 2016*
- End Date: June 30, 2018
- % Complete: 30 %

*Project continuation and direction determined annually by DOE

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), $400K (FY16)
    - Total DOE Funds Spent (to date): $225K
    - Subcontract UMSL: $58,000 (Phase I)

Partner(s)

• UMSL: Eric Majzoub (Computational effort)

UMSL

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Relevance/Objectives

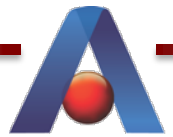
Main Focus: Development of Novel High H-capacity *Si-based borohydrides and composites*

Objectives: Development of low-cost, high-performance hydrogen storage materials based on :

(1) *Silicon-borohydride hypersalts* - Si-based borohydride materials are predicted to have borderline thermodynamic stability. We will use stabilization strategies based on hypersalt formation using alkali and alkaline-earth cation additions to bring the enthalpy of desorption into the 20–30 kJ/mol H_2 range.

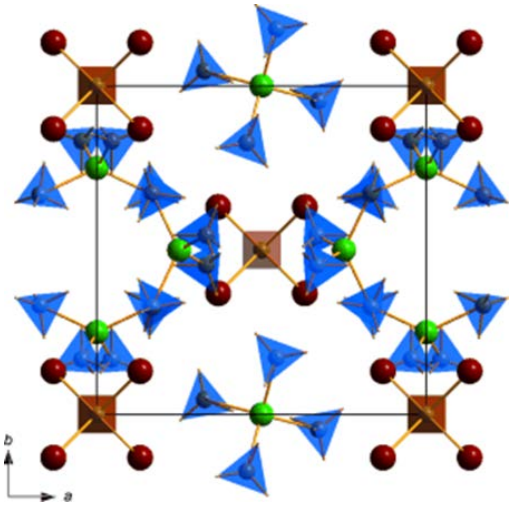
(2) *Borohydride/graphene composites* - We will develop hydride/graphene nano-composites that utilize the high thermal conductivity and unique properties of graphene such as high surface area and excellent thermal and chemical stability.

The common thread is an efficient and scalable mechanochemical approach to the synthesis of functional hydrogen storage materials.



Relevance/Objectives

- Borohydrides have largest gravimetric density (GD) among all known 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
- Offer opportunity for stabilization via hypersalts and adduct formation
- No Si-based borohydrides reported; Si and B are abundant and inexpensive



$Al_3Li_4(BH_4)_{13}$ T_d=~90 °C

Lindemann et al. IJHE, 2013

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

Phase 1 approach and goals:

- Determine the preferred oxidation state for Si in $Si(BH_4)_n$ for n={1,2,3,4} using nominal Si oxidation state in PEGS
- Determine relative stability of $Si(BH_4)_n$ phases
- Use information from $Si(BH_4)_n$ phases in hypersalt candidate PEGS+DFT calculations
- Determine relative stability of alkali and alkaline earth hypersalts and search for stable compounds

Approach - Synthesis and Characterization; Subtasks 1.1–1.3

1. Synthesis:

- Mechanochemistry

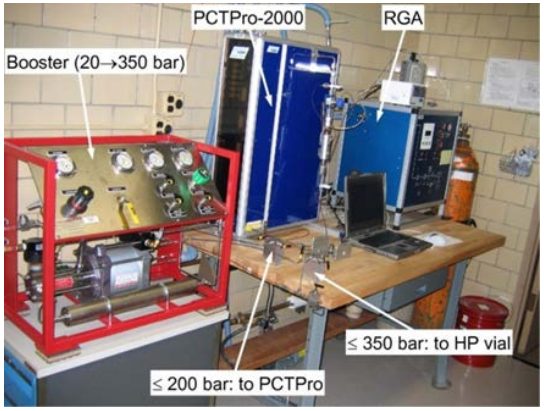
(Dry and liquid-assisted)

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



Accomplishments - Computational Screening

Preferred Oxidation State is Si^{2+} for PEGS-generated $Si(BH_4)_n$ Structures

DFT- calculated Born effective charges and formation enthalpies for borohydride structures in the Si-B-H system. PEGS structures generated assuming silicon charge states from +1 to +4. Charges are in units of the electron charge *e*, and enthalpies in kJ/mol.

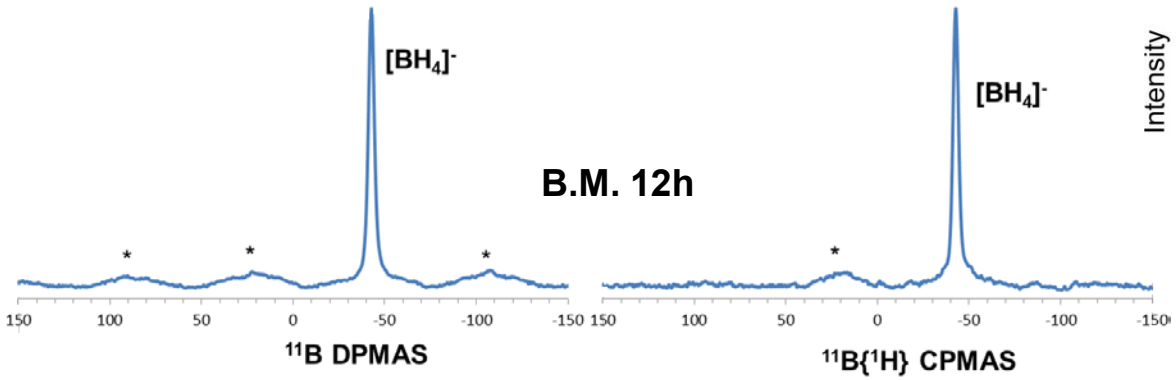
Structure	Z_B^{eff}	Z_H^{eff}	Z_{Si}^{eff}	ΔH_f^0/atom
$Si(BH_4)$	+0.59	-0.49	+2.31	-282
$Si(BH_4)_2$	+0.20	-0.18	+1.95	-287
$Si(BH_4)_3$	+0.15	-0.14	+2.36	-276
$Si(BH_4)_4$	+0.13	-0.17	+2.25	-275

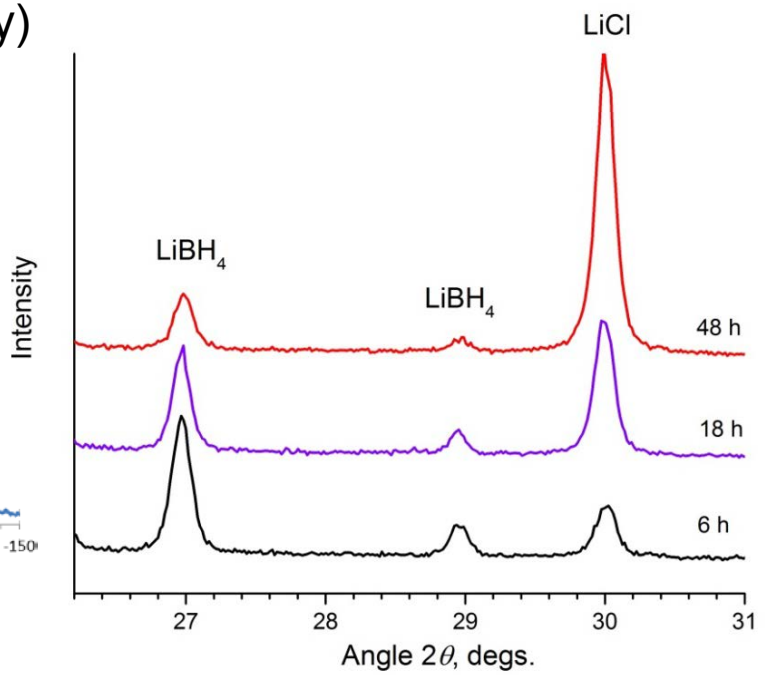
- There is no stationary point for the change in Gibbs free energy for the hypothetical reactions given by $Si(BH_4)_n \rightarrow Si + n\ B + 2n\ H_2$. No enthalpy change can be calculated.
- Compare relative stability using energy (ΔE) and Helmholtz free energy (ΔF = ΔE – T ΔS) at T=300 K.
- Least stable to most stable: **$Si^{+1}(BH_4) < Si^{+3}(BH_4)_3 < Si^{+4}(BH_4)_4 < Si^{+2}(BH_4)_2$**

Accomplishments - $Si(BH_4)_4$ (Theo. 18.4 wt. % H_2)

$$4LiBH_4 + SiCl_4 \rightarrow 4LiCl + Si(BH_4)_4\uparrow$$

1. Reaction proceeds, only LiCl observed on XRD
2. No Si seen on SSNMR: $Si(BH_4)_4$ or SiH_4 escapes as gas? (analysis of gases planned when new vials ready)
3. Distortion of $[BH_4]^-$ group
4. **T_d decrease**





System	Decomp. Temp. Onset, °C
$LiBH_4$	320
$4LiBH_4+SiCl_4$ (B.M. 3h)	240

Accomplishments - Computational Screening

Alkali and Alkaline Earth Hypersalts Show Metastability Within DFT Errors

Total DFT energy (static + dynamic) and Helmholtz free energy changes for the decomposition reactions of metastable hypersalts of $MSi(BH_4)_3$ compounds for M={Li,Na,K} for decomposition into elemental Si, B, H_2 (gas), and either M or MH at 300 K. Units are kJ/mol H_2.

Compound	M, ΔE	M, ΔF	MH, ΔE	MH, ΔF
$LiSi(BH_4)_3$	13	-26	0	-39
$NaSi(BH_4)_3$	14	-25	7	-32
$KSi(BH_4)_3$	22	-15	16	-21
$LiNaSi(BH_4)_4$	31	-7	17	-20
$LiKSi(BH_4)_4$	36	-1	24	-14
$NaKSi(BH_4)_4$	36	-1	29	-9
Compounds with divalent alkaline earth metals				
$MgSi(BH_4)_4$	4	-31	-4	-37
$CaSi(BH_4)_4$	29	-10	8	-29
$LiMgSi(BH_4)_5$	25	-13	13	-24
$NaMgSi(BH_4)_5$	18	-19	10	-26

- Nominal Si^{2+} yields most stable candidates (checked against Li, Na hypersalts)
- ΔE > 0 for all hypersalts with ΔF showing possible stability within DFT error (+/- 10 kJ/mol)
- Best candidates include $LiKSi(BH_4)_4$ and $NaK(BH_4)_4$

Accomplishments - Systems Investigated

Target compound	H_2, wt. % (Theo.)	Reactions examined
$Si(BH_4)_4$	18.4	$SiCl_4 + 4LiBH_4$*
$LiSi(BH_4)_5$	18.4	a) $4LiBH_4+TBABH_4+SiCl_4$ b)(a) + $Li[Al\{OC(CF_3)_3\}_4$ $SiS_2 + 5LiBH_4$
$(NH_4)Si(BH_4)_5$	20.0/16.7	$NH_4Cl+5LiBH_4+SiCl_4$
$MgSi(BH_4)_6$	17.1	$MgSiF_6+6LiBH_4$; $MgSiF_6+6NaBH_4$ $MgCl_2+6LiBH_4+ SiCl_4$ $MgCl_2+6NaBH_4+ SiCl_4$ $Mg(BH_4)_2+4NaBH_4+ SiBr_4$
$AlSi(BH_4)_7$	17.8	$AlCl_3+3LiBH_4+SiCl_4$ $AlBr_3+3LiBH_4+SiBr_4$ $AlCl_3+7LiBH_4+SiCl_4$ $AlBr_3+7LiBH_4+SiBr_4$ $AlCl_3+7NaBH_4+SiCl_4$ $AlCl_3+3NaBH_4+SiCl_4$ $AlBr_3+7NaBH_4+SiBr_4$

* Promising reactions discussed in this presentation are shown in yellow.

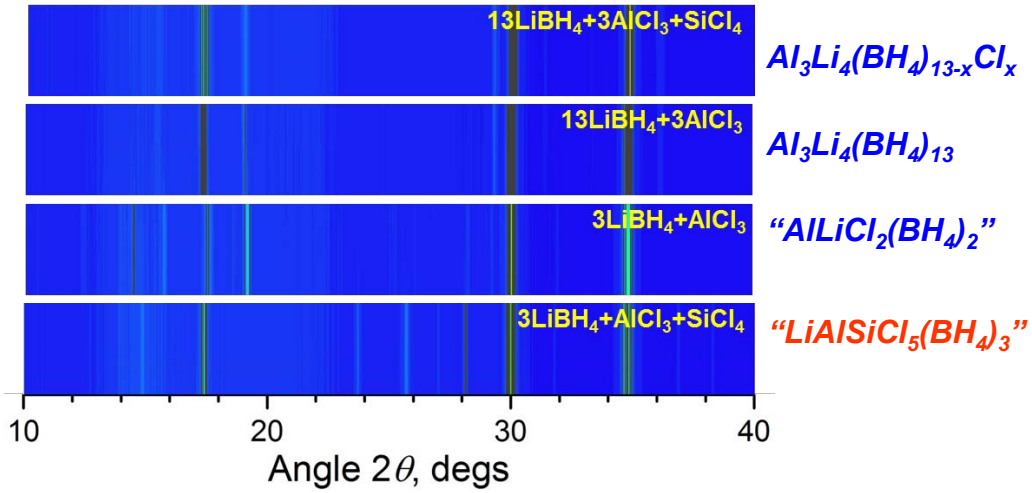
Accomplishments - $AlSi(BH_4)_7$ (Theo. 17.5 wt. %)

$LiBH_4$ - $AlHal_3$ - $SiHal_4$ systems (Hal=Cl, Br)

XRD:

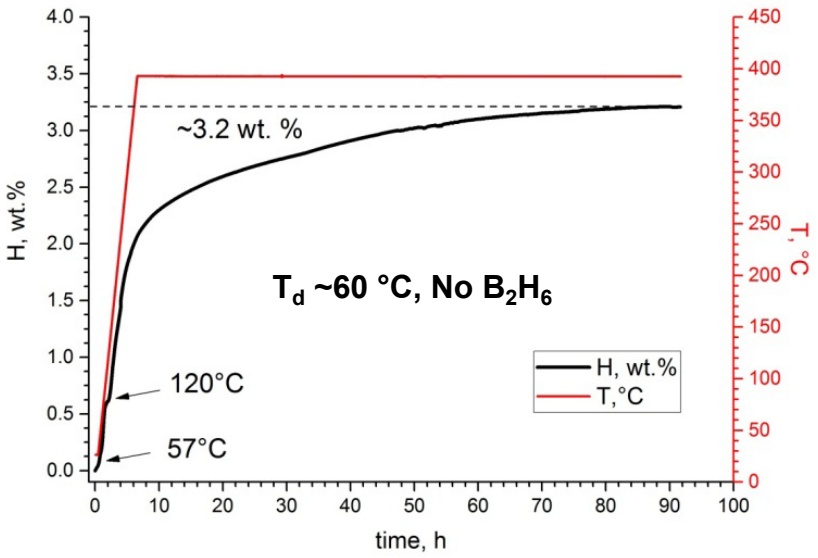
"$LiAlSiCl_5(BH_4)_3$" (Sp. gr. Ccca) 4.2 wt % H_2

"$LiAlSiBr_5(BH_4)_3$" (Sp. gr. Ccca) 2.4 wt % H_2



NMR:

- Presence of $SiCl_4$
- 5-coordinated Al
- BH_4^- group in the resulting compounds



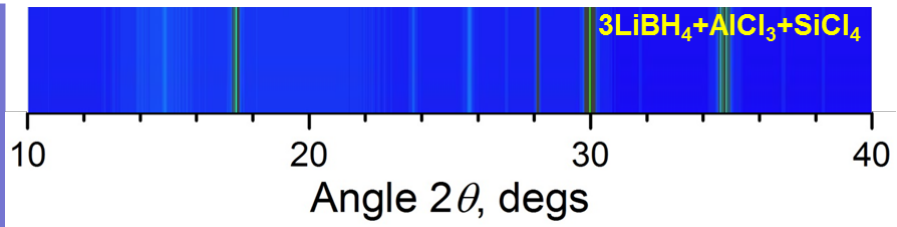
$3LiBH_4 + AlCl_3 + SiCl_4 \rightarrow 2LiCl + \text{"}LiAlSiCl_5(BH_4)_3\text{"}$

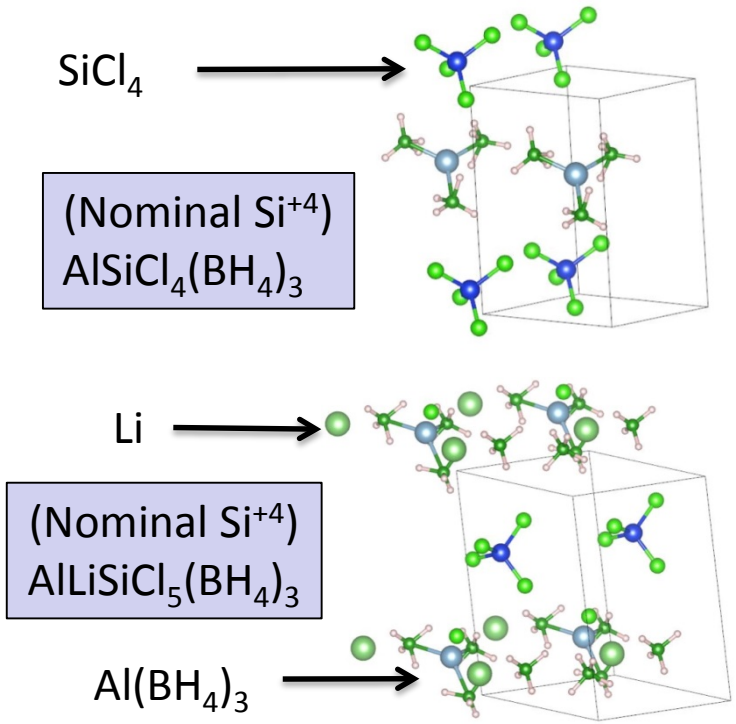
H_2 3.3 wt. %

Accomplishments - $AlSi(BH_4)_7$ (Theo. 17.5 wt. %)

Candidates for Hypersalts With Al Require Nominal $Si^{+3,+4}$ for Stable $(BH_4)^-$ Anions

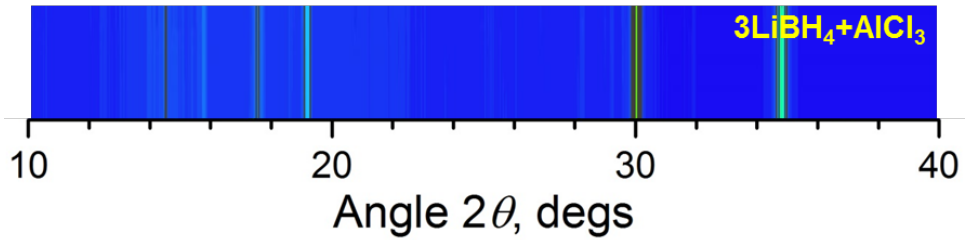
- PEGS prototypes generated for $AlSiCl_n(BH_4)_3$ for n={1,2,3,4} and for $AlSiLiCl_n(BH_4)_3$ with n={2,3,4,5} to investigate charge states of Si.
- Nominal charge
- **Si^{+1}**: DFT-relaxed structures result in **unstable BH_4 anions**, splitting into BH_3+H with Si-H coordination of the disconnected hydrogen.
- **Si^{+2}**: **unstable BH_4 anions** or stable but highly distorted BH_4
- **Si^{+3}**: stable BH_4 anions, layered structure with {$SiCl_4$, BH_4} and {Al, Cl, Li, BH_4}
- **Si^{+4}**: stable BH_4 anions, layered structure containing planar $Al(BH_4)_3$ with a bidentate orientation of the BH_4 to Al, and $SiCl_4$ tetrahedra





Accomplishments - *AlSi(BH$_4$)$_7$* (Theo. 17.5 wt. %)

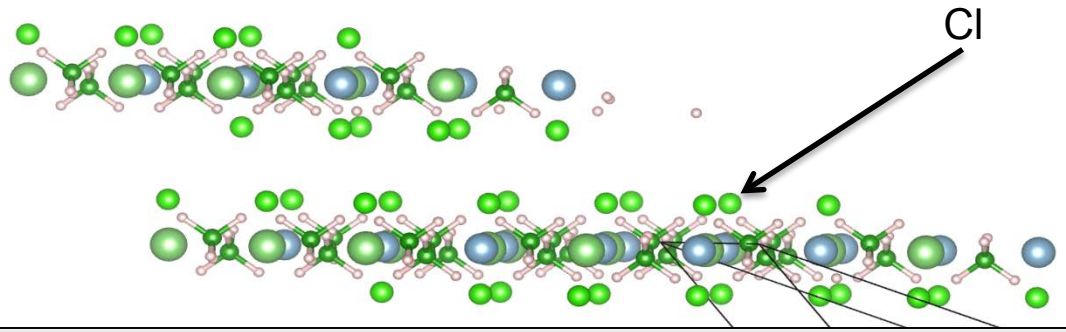
MGCLP Calculations for Li-Al-Cl-(BH$_4$) System



$$AlLiCl_2(BH_4)_2 \rightarrow Al + 2B + \frac{1}{2}Cl_2(g) + LiCl + 4H_2$$

- ΔH = 75 kJ/mol H_2
- T_c = 330 °C

$AlLiCl_2(BH_4)_2$



$$AlLiCl_2(BH_4)_2 + LiBH_4 \rightarrow Al + 3B + 2LiCl + 6H_2$$

- ΔH = 17 kJ/mol H_2
- T_c = -113 °C

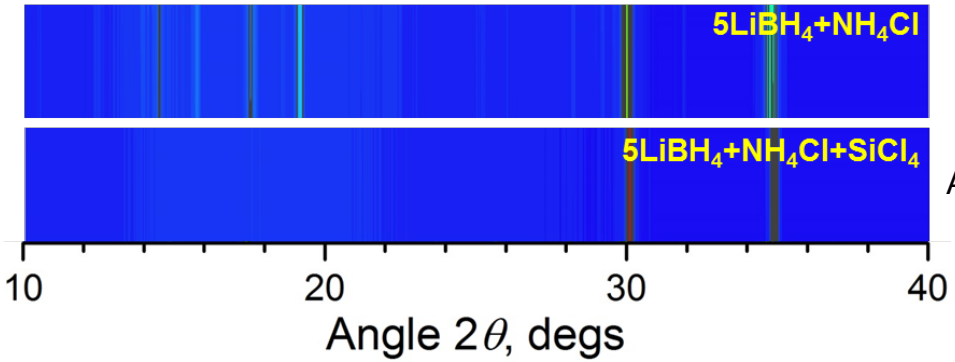
Destabilized reaction with excess $LiBH_4$

Accomplishments - $NH_4Si(BH_4)_5$ (Theo. 20.0 wt. %)

Anticipated: $5LiBH_4 + NH_4Cl + SiCl_4 \rightarrow 5LiCl + NH_4Si(BH_4)_5$

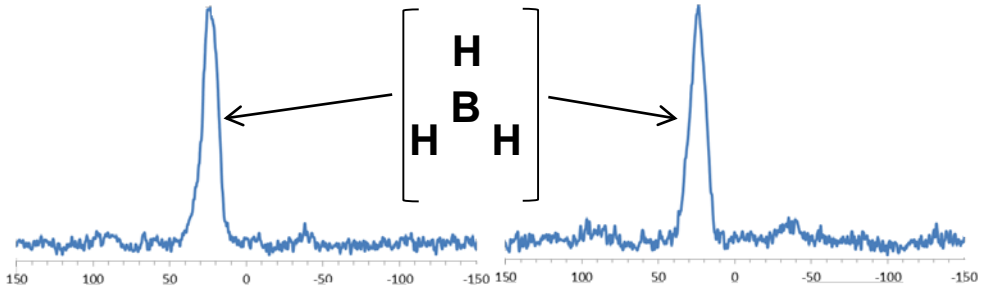
H_2 9.2 wt. %

Observed:
- Fast reaction
- Formation of LiCl and amorphous products
- Loss of H_2 upon ball milling (may be reduced or eliminated by cryo-milling - planned)
- Si in a vicinity of a proton
- B-H bonds



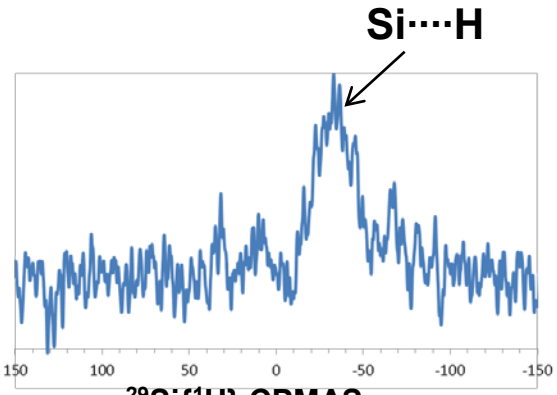
$LiBH_4$/$LiBH_4$-AB

Amorph.

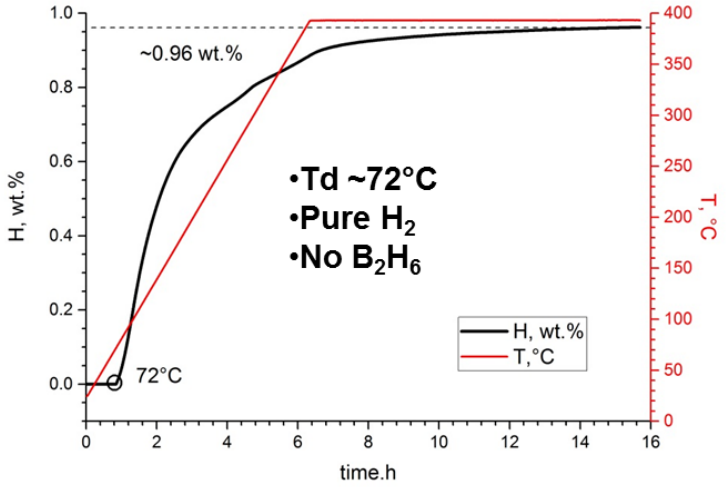


^{11}B DPMAS

^{11}B{^{1}H} CPMAS



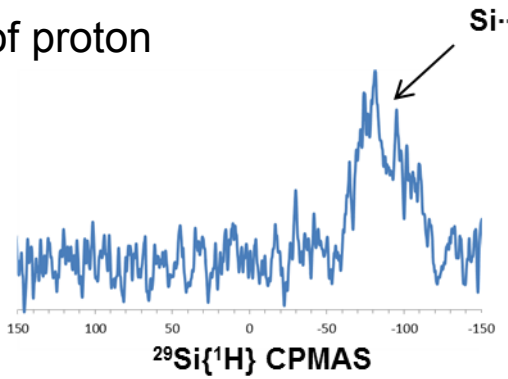
^{29}Si{^{1}H} CPMAS



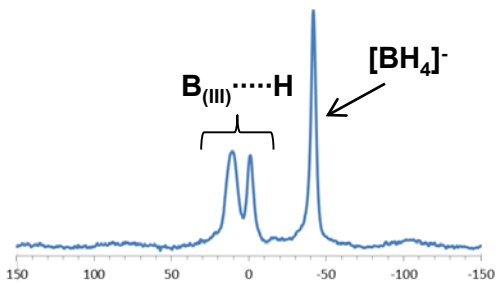
Accomplishments - $MgSi(BH_4)_6$ (Theo.16.9 wt. %)

$$4LiBH_4 + MgSiF_6 \rightarrow \underbrace{5LiF + MgSiF_2(BH_4)_4}_{H_2\ 6.4\ wt.\ \%}$$

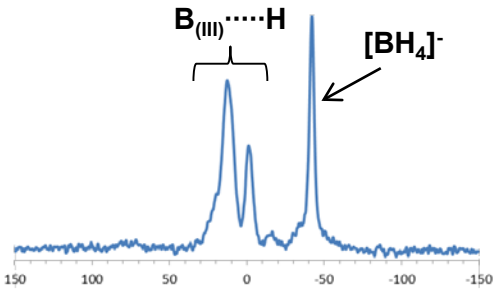
- In 6:1 ratio $LiBH_4$ remains in excess
- Fast kinetics in 4:1 ratio of $LiBH_4$ and $MgSiF_6$
- Si in vicinity of proton
- B-H bonds



$^{29}Si\{^1H\}$ CPMAS

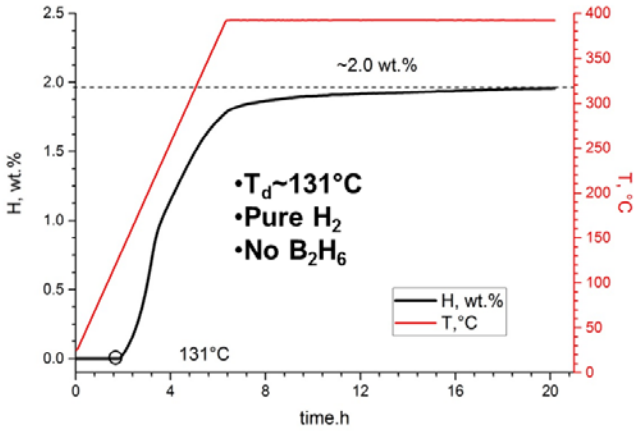


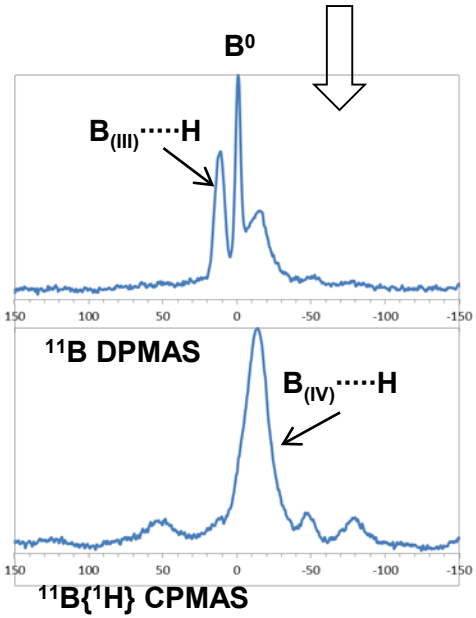
^{11}B DPMAS



$^{11}B\{^1H\}$ CPMAS

Desorption

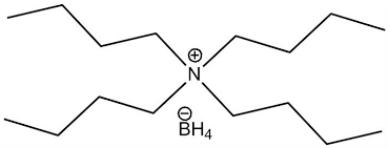




$^{11}B\{^1H\}$ CPMAS

Accomplishments - *LiSi(BH$_4$)$_5$* (Theo. 18.4 wt. % H$_2$)

Step 1 (*Mechanochemical or solution synthesis*):

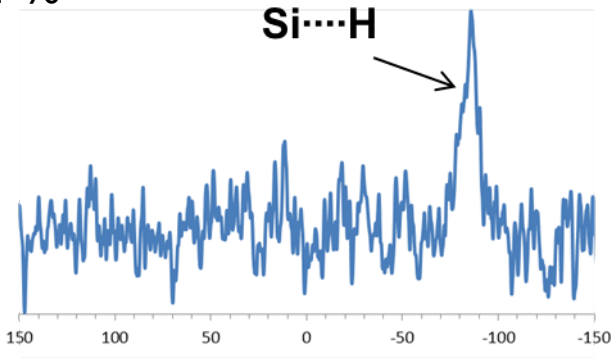


4LiBH$_4$ + TBABH$_4$ + SiCl$_4$ → 4LiCl↓ + *TBASi(BH$_4$)$_5$*

Step 2 (*Reaction in organic solvent - planned*):

TBASi(BH$_4$)$_5$ + Li[Al{OC(CF$_3$)$_3$}$_4$ → ***LiSi(BH$_4$)$_5$*** ↓+ TBA[Al{OC(CF$_3$)$_3$}$_4$

- Fast reaction; completed even by mixing of the components in a SiCl$_4$ solution
- T$_d$ (*TBASi(BH$_4$)$_5$*) ~128°C
- Gas release (vol.%): H$_2$ (~86), CH$_4$ (~1), C$_4$H$_{10}$ (~12), C$_2$NH$_7$ (~1), **no B$_2$H$_6$**
- Overall H$_2$ release ~1.3 wt. %



^{29}Si{^{1}H} CPMAS

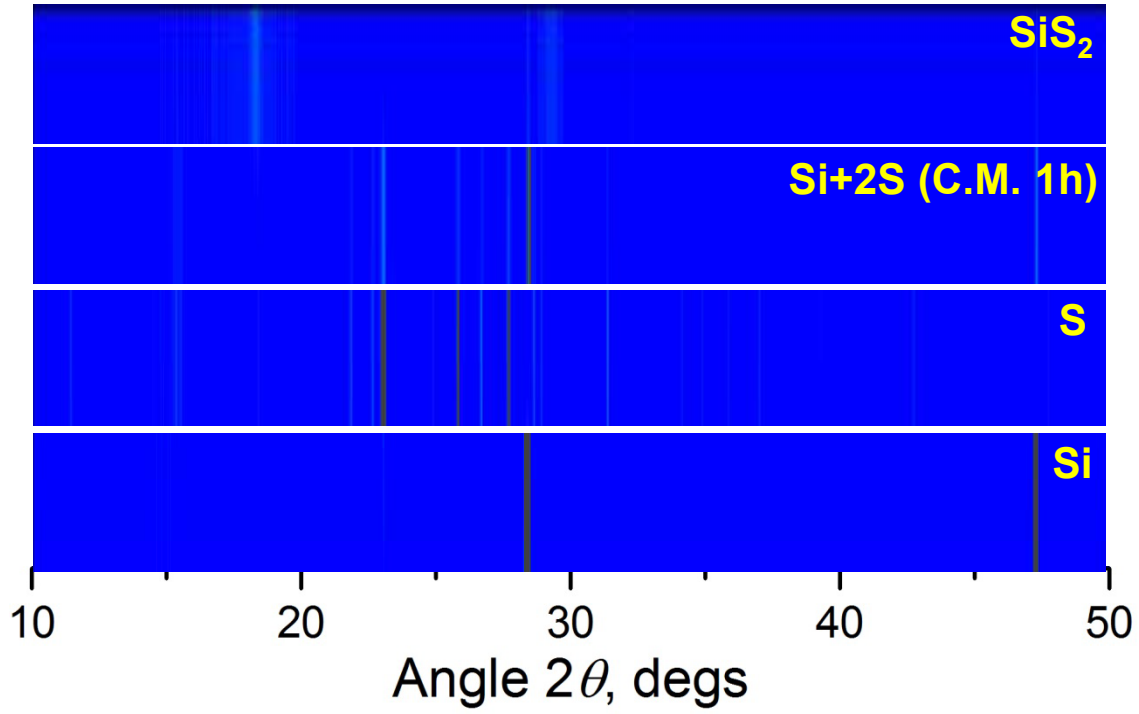
Synthesis of – SiS_2

Step 1 (*Cryo-milling in N_2 atmosphere*):

Si + 2S → homogeneous mixture

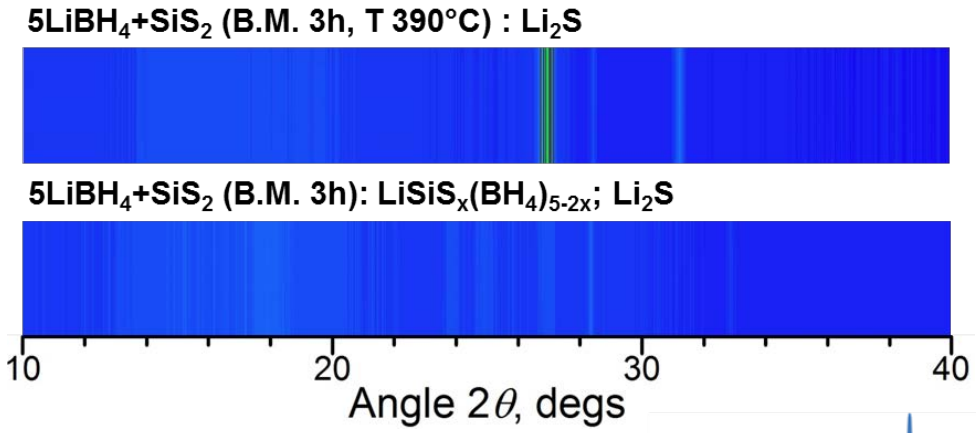
Step 2 (*Hold at T=390°C for 12 hours, S in excess*):

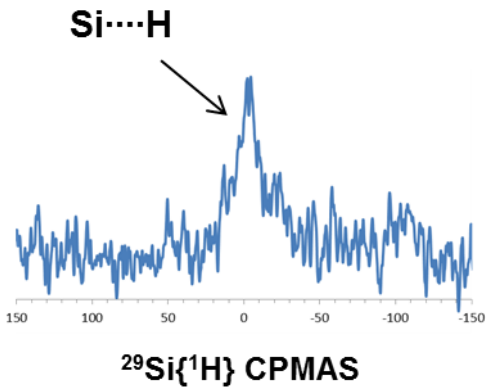
Si + 2S → SiS_2

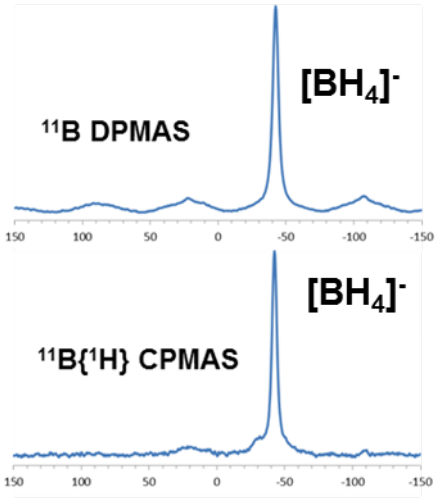


Accomplishments - $LiSi(BH_4)_5$ (Theo. 18.2 wt. % H_2)

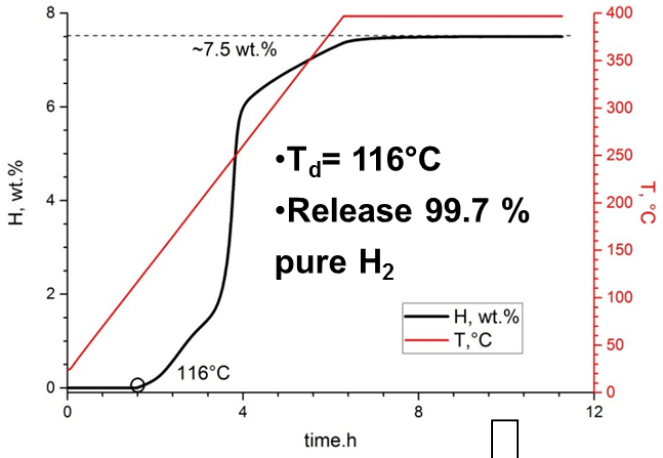
$$5LiBH_4 + SiS_2 \rightarrow 2Li_2S_{amorph.} + \text{“}LiSi(BH_4)_5\text{”}$$

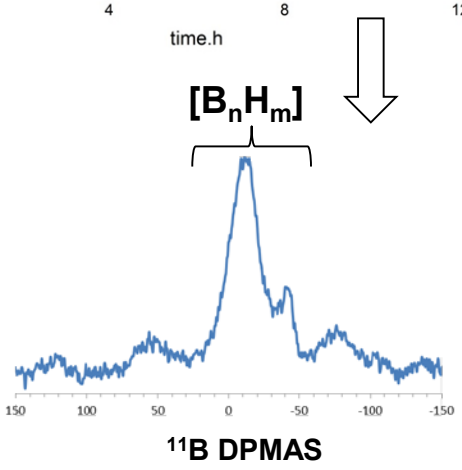






Desorption





- No signal in $^{29}Si\{^1H\}$ CPMAS.

$$2Li_2S_{amorph.} + \text{“}LiSi(BH_4)_5\text{”} \xrightarrow{T=390\ °C} 2Li_2S_{cryst.} + \text{“}LiSiB_5H_4\text{”} + 8H_2\uparrow$$

IP disclosure filed

Accomplishments - $Li_2SiS_2(BH_4)_2$ (Theo. 6.2 wt. % H_2)

MGCLP Calculations for Li-Si-S-(BH_4) System
Indicate Stable Phase in $Li_2SiS_2(BH_4)_2$ with ΔH = 32 kJ/mol H_2

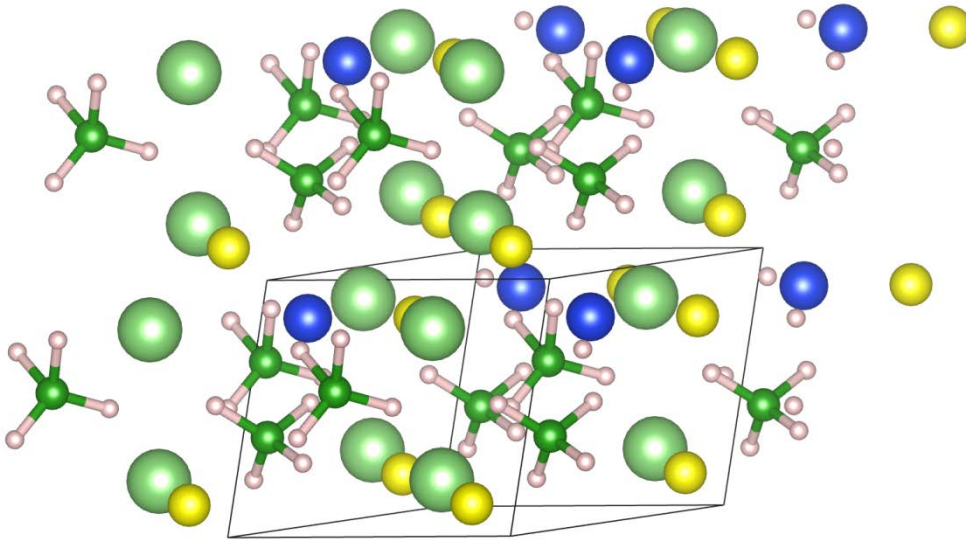
$$Li_2SiS_2(BH_4)_2 \rightarrow 2B + Li_2S + \tfrac{1}{2}\,Si + \tfrac{1}{2}\,SiS_2 + 4H_2$$

- **ΔH = 32 kJ/mol H_2**
- T_c = -33 °C

6.2 wt.% H_2

$Li_2SiS_2(BH_4)_2$

yellow=S
green=Li
blue=Si



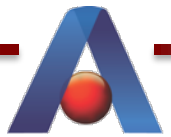
Summary

Task 1; Subtasks 1.1-1.3- ***Synthesis and characterization of Novel Silicon-based Borohydrides via Hypersalt Stabilization***

- ❑ Mechanochemical reactions in 20+ systems studied
- ❑ Si/Cat/B/H hypersalts can be prepared mechanochemically
- ❑ Hal/S can stabilize silicon borohydrides
- ❑ T_d of hypersalts meet the DOE targets
- ❑ **No B_2H_6**

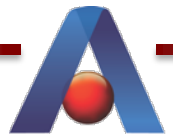
Tasks 1 and 3; Subtasks 1.4-3.3- ***Screening candidate Si^{4+} and Si^{2+} hypersalt compounds using PEGS***

- ❑ 10,000+ structure candidates examined by PEGS and DFT



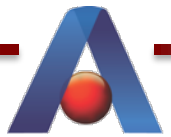
Remaining Challenges and Barriers

- Confirmation of product identity- composition and structure
- Purification of as-synthesized borohydride salts
- Volatility of $SiHal_4$ (hard to control stoichiometry)
- Pool of Si precursors is limited
- No precursors with Si^{2+}

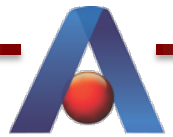


Future plans

- Confirmation of identity of obtained mixed silicon borohydrides
  - Purification from byproducts
  - Ab-initio solution of available powder diffraction data aided by PEGS/DFT
  - Synthesis of single crystals
- Determine reversibility of hydrogen in observed systems
- Synthesis of hypersalts by using the M-Si-Hal materials as a source of Si (M is metal or NH_4^+).
- Mechanochemistry at liquid nitrogen temperature (cryo-milling)
- DP method will be applied for quantitative analysis of synthesized hypersalts
- Computational and preliminary synthetic attempts will be made to evaluate stability of Si-borohydrides on graphene surface.



Backup Slides



Backup slides-Full list of systems Investigated

Target compound	H_2, wt. %	Reactions examined
$Si(BH_4)_4$	18.4	$SiCl_4 + 4LiBH_4$
$LiSi(BH_4)_5$	18.4	a) $4LiBH_4+TBABH_4+SiCl_4$; b) + $Li[Al\{OC(CF_3)_3\}_4$ $SiS_2 + 5LiBH_4$
$Li_2Si(BH_4)_5$	17.3	$Li_2SiF_6+6LiBH_4$; $Li_2SiF_6+6NaBH_4$
$Na_2Si(BH_4)_6$	14.8	$Na_2SiF_6+6LiBH_4$; $Na_2SiF_6+6NaBH_4$
$K_2Si(BH_4)_6$	12.4	$K_2SiF_6+6LiBH_4$; $K_2SiF_6+6NaBH_4$
$(NH_4)_2Si(BH_4)_6$	20.9/15.7	$(NH_4)_2SiF_6+6LiBH_4$; $(NH_4)_2SiF_6+6NaBH_4$
$(NH_4)Si(BH_4)_5$	20.0/16.7	$NH_4Cl+5LiBH_4+SiCl_4$
$MnSi(BH_4)_6$	14.1	$MnCl_2+6LiBH_4+SiCl_4$
$MgSi(BH_4)_6$	17.1	$MgSiF_6+6LiBH_4$; $MgSiF_6+6NaBH_4$; $MgCl_2+6LiBH_4+SiCl_4$; $MgCl_2+6NaBH_4+SiCl_4$; $Mg(BH_4)_2+4NaBH_4+SiBr_4$
$FeSi(BH_4)_6$	14.0	$FeCl_2+6LiBH_4+SiCl_4$; $FeCl_2+6NaBH_4+SiCl_4$
$CaSi(BH_4)_6$	15.4	$CaCl_2+6LiBH_4+SiCl_4$
$AlSi(BH_4)_7$	17.8	$AlCl_3+7LiBH_4+SiCl_4$; $AlCl_3+3LiBH_4+SiCl_4$; $AlBr_3+7LiBH_4+SiBr_4$; $AlBr_3+3LiBH_4+SiBr_4$; $AlCl_3+7NaBH_4+SiCl_4$; $AlCl_3+3NaBH_4+SiCl_4$; $AlBr_3+7NaBH_4+SiBr_4$

Approach

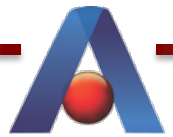
Computational Screening:

Prototype Electrostatic Ground State Crystal Structure Prediction (PEGS)

- Energy functional:

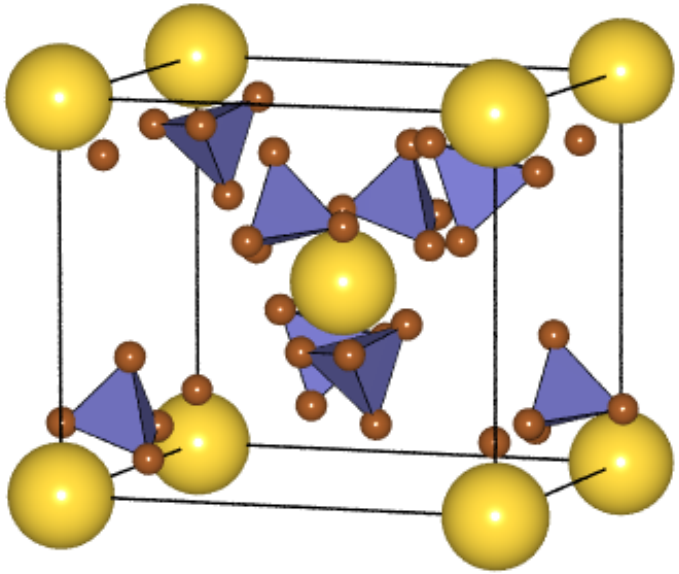
$$\sum_{i<j}\left(\frac{Z_i Z_j}{r_{ij}}+\frac{1}{r_{ij}^{12}}\right)$$

- Simulated annealing Monte Carlo energy minimization
- Generally obtains ground state and polymorph structures for complex ionic hydrides
- **Majzoub & Ozolins, Phys. Rev. B, 77, 104115, (2008)**

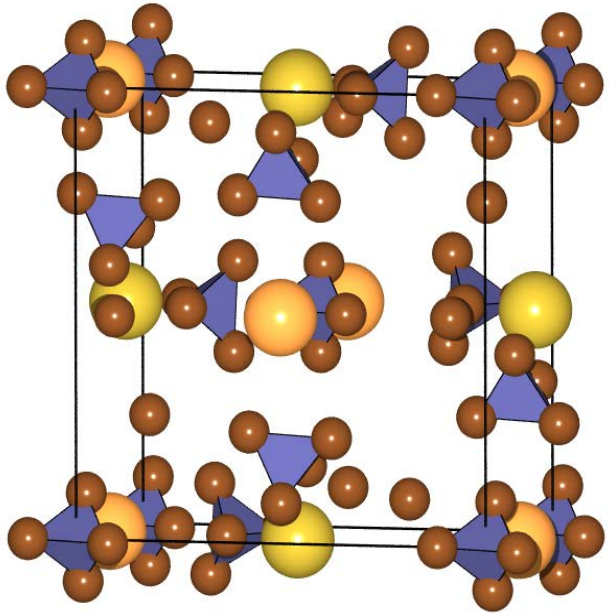


PEGS Structures

Examples: PEGS Finds High-symmetry Structures for $Si(BH_4)_4$ and $NaSi(BH_4)_5$



$Si(BH_4)_4$ I-42m (#121)



$NaSi(BH_4)_5$ I-4 (#82)

Atom legend - Yellow: silicon; Brown: hydrogen; Orange: sodium

Milestones and Performance

Milestones and Go/No Go Decision

Task	Task or Subtask Title	Milestone # (Go/No-Go Decision Point #	Milestone Description (Go/No-Go Decision Criteria)	Anticipated Date (Months)
Phase 1 (0–12 month)				
1	Screening, Synthesis and characterization of Novel Silicon-based Borohydrides via Hypersalt Stabilization	M1.1	Calculate thermodynamic stability of Si^{4+}-borohydride hypersalts with either alkali or alkaline earth cation additions	3
		M1.2	Demonstration of Si-borohydride formation through metathesis reaction	6
		M1.3	Computational identification of candidate Si-borohydride hypersalts for synthesis	9
2	Graphene/hydride composite-based storage of metal hydrides	M1.4	Preparation of graphene/hydride composites with $LiBH_4$ via mechanochemistry	12
		D1	Demonstrate that novel hypersalt Si-borohydrides can be stabilized and may be tailored to exhibit desorption temperatures below 200 °C with a minimum desorption capacity of 5 wt.% below 200 °C and 10 wt % wt. % below 350 °C	12
Phase 2 (12–24 month)				
3	Novel Silicon-based Borohydrides via Hypersalt Stabilization	M2.1	Demonstrate reversibility of a Si-borohydride hypersalt candidate	15
4	Graphene/hydride composite-based storage of complex metal hydrides	M2.2	Demonstrate reversibility of a graphene/hydride composite	18
		M2.3	Characterize graphene/hydride interactions using DNP SSNMR	21
		M2.4	Calculate thermodynamic stability of graphene/hydride composites to minimize composite degradation	24
		D2	Demonstrate at least one Si-borohydride prepared in phase 1 and/or at least one graphene/hydride composite with no less than 5 wt. % reversible capacity between room temperature and 300 °C and reversibility of 50 % or more of the initial H_2 content.	24
Phase 3 (24–36 month)				
5	Novel Silicon-based Borohydrides via Hypersalt Stabilization	M3.1	Optimize kinetics of Si-borohydrides through addition of transition metal dopants	27
6	Graphene/hydride composite-based storage of complex metal hydrides	M3.2	Optimize the kinetics and thermodynamics of composites using NMR characterization of the interactions	30
		M3.3	Demonstrate reversibility of Si-BH hypersalt with 11+ wt. % capacity and optimize thermodynamics	33
		M3.4	Demonstrate reversibility of graphene/hydride composite with 10+ wt. % capacity and optimize thermodynamics	36

Milestones and Performance

Task	Task or Subtask Title	Milestone # (Go/No-Go Decision Point #	Milestone Description (Go/No-Go Decision Criteria)	Anticipated Date (Months)	% complete
Phase 1 (0–12 month)					
1	Screening, Synthesis and characterization of Novel Silicon-based Borohydrides via Hypersalt Stabilization	M1.1	Calculate thermodynamic stability of Si^{4+}-borohydride hypersalts with either alkali or alkaline earth cation additions	3	100
		M1.2	Demonstration of Si-borohydride formation through metathesis reaction	6	100
		M1.3	Computational identification of candidate Si-borohydride hypersalts for synthesis	9	100
2	Graphene/hydride composite-based storage of metal hydrides	M1.4	Preparation of graphene/hydride composites with $LiBH_4$ via mechanochemistry	12	40
		D1	Demonstrate that novel hypersalt Si-borohydrides can be stabilized and may be tailored to exhibit desorption temperatures below 200 °C with a minimum desorption capacity of 5 wt.% below 200 °C and 10 wt % wt. % below 350 °C	12	100