

IV.C.13 High-Capacity Hydrogen Storage Systems via Mechanochemistry

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Overall Objectives

The overarching goal of the project is to discover and develop hydrogen storage materials that are constituted largely from earth abundant, benign and low cost elements, such as silicon and boron. Specifically, the goal is to identify computationally and synthesize hitherto unknown high H-capacity Si-based borohydrides (Si-BHs) with useable gravimetric density of over 10 wt% H₂, and decomposition enthalpies in range of 25–35 kJ/mol-H₂, such that H₂ desorption occurs at the operating temperature (~80–100°C) of the proton exchange membrane fuel cells.

Fiscal Year (FY) 2017 Objectives

- Establish composition and structure of a new Si-BH hypersalt discovered in the LiBH₄-SiS₂ system, and demonstrate H₂ reversibility in this system.
- Explore synthesis of analogous Si-BH compounds in related systems including NaBH₄-SiS₂, KBH₄-SiS₂ and Mg(BH₄)₂-SiS₂ using mechanochemical processes, and characterize their structure, composition, and hydrogen sorption properties. Demonstrate feasibility of synthesis of Si-BHs from elemental and pre-reacted components via mechanochemistry under high H₂ pressure (delayed due to equipment availability).

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section (3.3) of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan.

- (A) System Weight and Volume
- (B) System Cost
- (D) Durability/Operability
- (O) Lack of Understanding of Hydrogen Physisorption and Chemisorption

Technical Targets

The project addresses lack of suitable materials impeding implementation of materials-based onboard H-storage systems. Successful completion would provide an H-storage material with high gravimetric and volumetric capacity, and kinetics and thermodynamics suitable to supply high-purity hydrogen to a proton exchange membrane fuel cell. The new materials identified and synthesized as an outcome of this project will achieve or exceed the DOE targets, see Table 1.

TABLE 1. H-Storage Parameters of Si-based Borohydrides in Comparison with the DOE Targets

Storage Parameters	DOE Technical Targets*	Our Targets**
Gravimetric capacity (kg H ₂ /kg)	0.065	>0.100
Volumetric capacity (kg H ₂ /L)	0.050	>0.130

*Ultimate system level targets, **material basis

FY 2017 Accomplishments

- A detailed structural characterization of the novel Si-BH compound synthesized in the LiBH₄-SiS₂ system was achieved by solid-state nuclear magnetic resonance (SSNMR) and Fourier transform infrared (FT-IR) analyses, establishing the role of sulfide anions in formation of mixed silicon borohydrides.
- A thorough investigation of other M_x(BH₄)_y-SiS₂ systems (M = Na, K, Mg) shows formation of Si-BHs likely analogous to the LiBH₄-SiS₂ system. Among the systems investigated, hydrogen cycling in Mg(BH₄)₂-SiS₂ was found to be the most promising.
- Decomposition onset temperatures and amounts of H₂ released from the new Si-BHs meet the DOE targets; high purity H₂ (>99.8%) is released and diborane release, if any, is below the detection limits.

- In conjunction with experimental results in the $\text{LiBH}_4\text{-SiBr}_4$ system, the multi-gas canonical linear programming (MGCLP) calculations [1], revealed that halogenated silanes have relatively low formation energies among silicon-borohydride species, leading to the possibility to engineer the reaction pathway for stabilizing Si-BHs.
- Experimental evidence indicates that complexes such as $\{\text{PhSiCl}_{3-x}(\text{BH}_4)_x\}$ (Ph = phenyl) are likely to form during the reaction between LiBH_4 and PhSiCl_3 . Suitable substituents at the Si atom can (de)stabilize Si-BHs structures and alter their chemical behavior.
- A series of “4Li:Si:xB” compounds prepared mechanochemically shows promising hydrogen sorption behavior, and could potentially meet DOE targets.



INTRODUCTION

Because of the practical barriers and safety concerns associated with the H-storage in liquid and gaseous forms, hydrogen storage in solids continues to be a promising alternative storage technology for fuel cell applications. A material that can fully satisfy demands must store a large amount of hydrogen in a light and compact form, can be rapidly refueled, and be affordable for safe, easy and inexpensive production in large quantities. Despite the discovery and synthesis of numerous hydrogen rich compounds, their utility for H-storage and delivery remains limited by unfavorable thermodynamics or/and kinetics of hydrogen release and uptake [2]. The U.S. Department of Energy, in collaboration with the automotive industry defined the criteria for onboard H-system, which requires 1–10 bar H_2 equilibrium pressure at the working temperature of a proton exchange membrane fuel cell. Only a few candidates hold promise to achieve this with required gravimetric density and enthalpies of dehydrogenation in the range of -25 to -30 kJ/mol- H_2 .

Guided by validated computational tools, this project seeks to discover hitherto unknown silicon-based borohydrides (Si-BHs) and optimize their low cost synthesis in powder form. Materials will be experimentally accessed via mechanochemistry, a sustainable, green, energy-efficient process that potentially offers a cost-effective solution for large-scale production of functional materials.

APPROACH

Guided by computations and known chemistry of metal borohydride solids, numerous systems covering a broad compositional landscape of potential Si-BH hypersalts have been identified. After a preliminary screening, an exploratory, primarily mechanochemical,

synthesis is conducted in the most promising systems. The computational crystal structure search is performed by the prototype electrostatic ground state approach [3] followed by structure relaxation using density functional theory. Thermodynamic properties and reaction pathways involving gas-phase precursors are determined using the MGCLP method. Structure and phase characterization is performed using powder X-ray diffraction, FT-IR, and SSNMR spectroscopies, and hydrogen de/absorption properties are evaluated using volumetric methods.

RESULTS

Silicon-based borohydrides via hypersalt stabilization:

Mechanochemical synthesis targeting Si-BHs in the $\text{LiBH}_4\text{-SiBr}_4$ system led to the formation of a mixed anion borohydride compound and release of gaseous SiH_4 and B_2H_6 as shown in Equation 1.



These results are in line with MGCLP calculations that indicate that Si-BHs are unstable toward decomposition to SiH_4 and B_2H_6 . Trends in MGCLP-derived reaction energies, however, indicate that the formation of SiH_4 and B_2H_6 may be prevented in reactions under elevated pressure.

In another approach to stabilize Si-BHs, large electron-withdrawing groups were introduced in place of similarly electronegative halide anions. For example, trichloro(phenyl)silane (PhSiCl_3) was used instead of SiHal_4 (Hal = Cl or Br) to carry out the exchange reaction with LiBH_4 . Thermogravimetric analysis-differential scanning calorimetry, FT-IR and ^1H nuclear magnetic resonance (NMR) data indicate possible formation of $\{\text{PhSiCl}_{3-x}(\text{BH}_4)_x\}$ -like complex(s) in the $\text{PhSiCl}_3\text{-LiBH}_4$ system. In contrast to PhSiCl_3 , PhSiH_2Cl reacts with LiBH_4 yielding PhSiH_3 , B_2H_6 , and H_2 . Although the reasons for the difference in products from PhSiH_2Cl and PhSiCl_3 is yet unclear, it is likely that an appropriate choice of substituents at the silicon center can stabilize/destabilize Si-BH-like structures and alter chemical behavior of silicon derivatives. This conclusion is indirectly supported by results obtained in the $\text{LiBH}_4\text{-SiS}_2$ system.

Mechanochemical reactions in the $\text{LiBH}_4\text{-SiS}_2$ system were studied at length by FT-IR and SSNMR. Based on the observed build-up curves in the cross-polarization experiments, Si atoms are within ~4 Å of H atoms and most likely belong to the same compound (Figure 1a). This Si-H distance is consistent with the formation of $\text{Si-S}^{(-)}\text{-Li}^{(+)}$ motifs [4], where $[\text{BH}_4]^-$ coordinates the Li atoms as shown in Figure 1b. The increased E^1 intensity in the cross polarization magic angle spinning (CPMAS) spectra suggests that more E^1 sites have $\text{Si-S}^{(-)}\text{-Li}^{(+)}$ structure than the others. The ^{11}B direct polarization magic angle spinning (DPMAS) spectra of the ball milled samples showed the presence of BH_4^- anion in both 2:1 and 6:1 compositions. The following mechanism

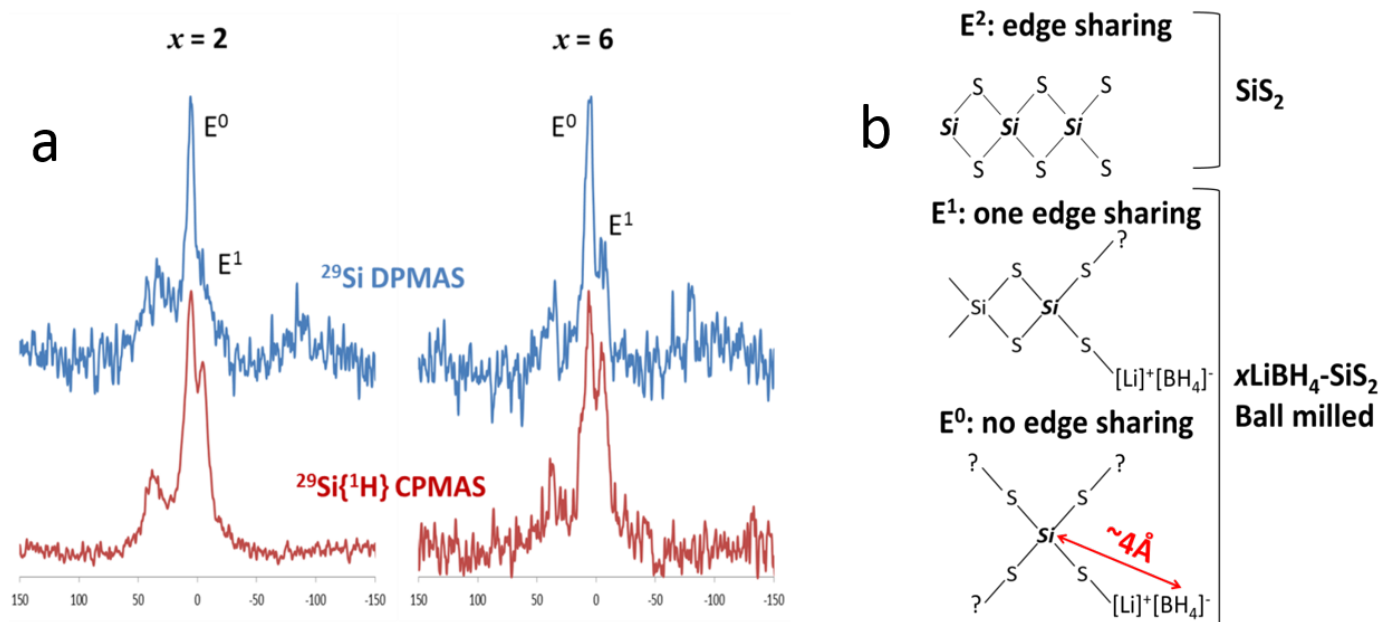


FIGURE 1. (a) ^{29}Si DP/CP MAS NMR spectra of ball milled $x\text{LiBH}_4\text{-SiS}_2$ ($x = 2, 6$) mixtures and (b) proposed peak assignments to Si-coordinations in the complex (question marks represent bonds of S to Si or Li)

(sequence of events) leading to the Si-BH complex may be proposed:

- Edge-shared SiS_2 (E^2) transforms into a mixture of one (E^1) and no-edge shared (E^0) forms.
- The formation E^1 and E^0 proceeds through appearance of “free bonds” with S $^-$ in the structure.
- The proximity of a positively charged Li^+ leads to S^--Li^+ bonds. The Li atoms expectedly remains coordinated to the BH_4^- anion.

Hence, complex structures containing both Si^{4+} and BH_4^- are possible through their coordination with S (for Si^{4+}) and Li (for BH_4^-).

Amorphous products of mechanochemical transformations in the $\text{Mg}(\text{BH}_4)_2\text{-SiS}_2$ system were characterized by FT-IR. Broad peaks corresponding to B-H stretching in $\text{Mg}(\text{BH}_4)_2$ indicate that BH_4^- anions in the product remain in configurations similar to pristine $\text{Mg}(\text{BH}_4)_2$.

Considering similarities in the chemistry of LiBH_4 and $\text{Mg}(\text{BH}_4)_2$, it is likely that the Mg-analogue is closely related to that described for $\text{LiBH}_4\text{-SiS}_2$ system. SSNMR experiments to establish the local structures of the amorphous products in this system are in progress.

Reversibility of sulfur stabilized Si-BHs: Hydrogen (de)absorption properties of $\text{M}_x(\text{BH}_4)_y\text{-SiS}_2$ systems ($M = \text{Li, Na, K and Mg}$) are summarized in Table 2. As also shown in Figure 2, nearly 4 wt% of H_2 is released during the second

TABLE 2. TPD Results of $\text{M}_x(\text{BH}_4)_y\text{-SiS}_2$ Systems ($M = \text{Li, Na, K and Mg}$). Numbers in parentheses represent data from the second desorption cycle after hydrogen absorption.

System, ratio	wt% H_2	T_{ons}^* , °C	wt% of total H_2
$\text{LiBH}_4\text{-SiS}_2$			
2:1	4.3(1.5)	88(230)	73(35)
4:1	7.1	113	81
5:1	7.5	116	76
6:1	8.2(2.4)	92(199)	77(30)
8:1	6.2	96	52
LiBH_4 (B.M. 3h)	2.9	276	16
$\text{NaBH}_4\text{-SiS}_2$			
2:1	3.3(1.0)	124(270)	69(30)
5:1	2.1	134	29.6
6:1	2.4	159	32
$\text{Mg}(\text{BH}_4)_2\text{-SiS}_2$			
2:1	5.6	101	70
3:1	5.9(1.8)	99(246)	62.8(30.5)
6:1	8.94	104	77.7
6:1 (B.M.)	10.12(4.0)	117(249)	88(40)
10:1	8.5(3.77)	112(243)	67.5(44.3)
$\text{Mg}(\text{BH}_4)_2$ (pure)	10.7	150	72.3
$\text{KBH}_4\text{-SiS}_2$			
6:1 (B.M. 3h)	1.3	165	17.6

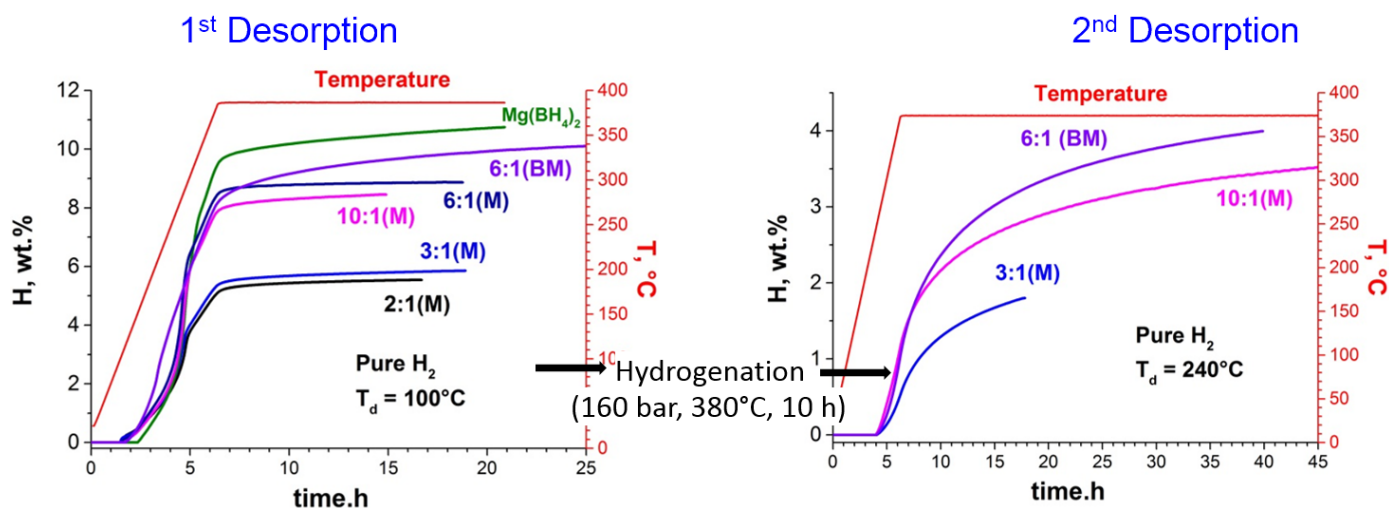


FIGURE 2. Temperature programmed desorption plots of the pristine mixtures (M) and ball-milled samples (BM) of the $\text{Mg}(\text{BH}_4)_2\text{-Si}_2$ system taken in different molar ratios, (left) first decomposition and (right) decomposition after rehydrogenation

desorption cycle in the $6\text{Mg}(\text{BH}_4)_2\text{-Si}_2$ mixture, accounting for ~40% reversible gravimetric capacity. This system has the potential to achieve Phase 2 targets, i.e., 2.5 wt% (at 200°C) and 5 wt% (at 300°C).

Si-BHs by high-pressure ball-milling: Density functional theory calculations carried out during Phase 1 revealed higher relative stabilities for Si^{2+} in Si-based borohydrides. Notwithstanding these findings, no stable compounds with Si^{2+} are known that may serve as a suitable precursor. To get around the problem, elemental Si was combined/alloyed with B and other alkali and alkaline earth metals, e.g. as in $\text{M}_x\text{Si}_y\text{B}_z$ ($\text{M} = \text{Li}, \text{Na}, \text{Mg}, \text{Ca}$) that were further reacted with hydrogen to yield borohydrides of the type $\text{M}_x\text{Si}_y(\text{BH}_4)_z$. Hydrogenation of such metal borosilicides can be performed either by milling under pressurized H_2 similar to conversion of MgB_2 to $\text{Mg}(\text{BH}_4)_2$ [5] or by high temperature hydrogenation [6].

Hydrogenation of one such system based on Li-Si-B was found to be very promising. A compound with composition Li_4Si and structure similar to $\text{Li}_{4.25}\text{Si}$ (also known as $\text{Li}_{17}\text{Si}_4$), forms upon liquid-assisted ball milling of the 4:1 molar mixture of Li and Si in heptane. Addition of elemental B into the reaction mixture leads to products with nominal compositions of “4Li:Si:xB” ($x = 1 - 4$) and structures, where boron is incorporated into the Li_4Si structure. Preliminary hydrogenation study of the “4Li:Si:2B” sample shows ~1.2 wt% reversible H_2 storage with T_{onset} at 146°C (Figure 3). It was also observed that T_{onset} of hydrogen release from hydrogenated samples is lowered when boron is present in the mixture compared to pure Li_4Si . More importantly, the amount of reversible hydrogen nearly doubles (to 2.4 wt%) when the composition is changed from “4Li:Si:2B” to “4Li:Si:4B”. The FT-IR analysis of the hydrogenated products shows absorption bands with frequencies that correspond to

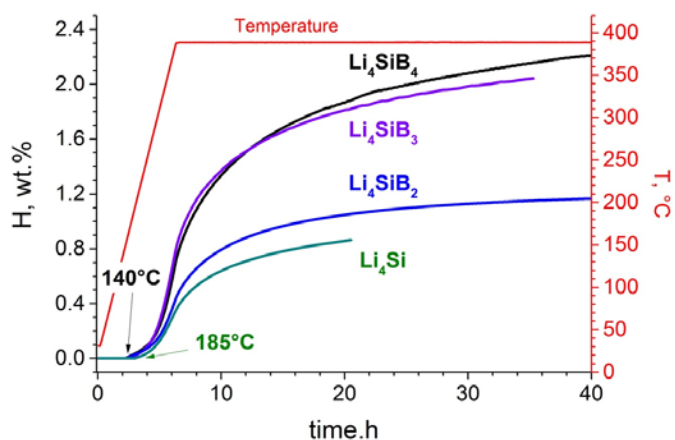


FIGURE 3. Temperature programmed desorption plots of the Li-Si-B mixtures prepared by high-energy ball milling of different compositions followed by their hydrogenation

B–H bonds; their intensity is highest for the hydrogenated “4Li:Si:4B”. The coordination of Si and Li in this compound will be subject of future investigation by SSNMR. The formation of B-H bonds upon hydrogenation of the Li-Si-B system under hydrogen pressure provides support for possibility of increased hydrogen uptake during milling under hydrogen pressure.

CONCLUSIONS AND UPCOMING ACTIVITIES

As evidenced by experimental results in the $\text{LiBH}_4\text{-Si}_2$ system, mechanochemical reactions are suitable for stabilization of Si-based borohydride complexes, particularly with sulfur. The newly synthesized complex shows low

desorption onset temperatures that meets DOE requirements and releases pure hydrogen. Therefore, studies on this system will continue to further improve the cycling properties. Such investigations will be extended to other metals and mixed metal borohydrides $M_xM'_y(BH_4)_z-SiS_2$ (M or M' = Li, Na, K, Al, Ca, Mg). The project will also continue to focus on other sulfur based systems using precursors like Al_2S_3 and B_2S_3 .

The Si-BH complex(es) may be stabilized by relatively bulky electron-withdrawing phenyl groups, therefore investigation of different $RSiX_3$ carbosilanes (X = F, Cl, Br) with increased hydrogen content is considered.

Based on the computational results it was concluded that elevated pressure may stabilize Si-BHs. Therefore, synthesis of Si-BHs via ball milling under high pressures and in a cryo-mill is planned in the next phase. The M-Si-B systems (M = Li, Na, Ca, Mg), prepared mechanochemically from metals shows promising preliminary results, and opens up a possibility of formation Si-BH complexes by hydrogenation at elevated temperatures or mechanical milling under high pressure. The high-pressure milling capabilities are expected to be fully functional by the end of September 2017, and the latter investigations will be given highest priority.

FY 2017 PUBLICATIONS/PRESENTATIONS

1. T. Kobayashi, O. Dolotko, S. Gupta, V.K. Pecharsky, M. Pruski, "Insights into the role of composition for purity of released hydrogen from the $LiBH_4-AlCl_3$ system," *manuscript in preparation*.
2. O. Dolotko, T. Kobayashi, S. Gupta, M. Pruski, E. Majzoub, V.K. Pecharsky, "Novel hydride and destabilization of the lithium borohydride by SiS_2 ," *manuscript in preparation*.
3. T. Kobayashi, O. Dolotko, S. Gupta, Y. Fillinchuk, V.K. Pecharsky, M. Pruski, "Solid-State NMR studies of hydrogen storage materials; mechanochemically induced reaction of $LiBH_4$ and $AlCl_3$," 58th ENC, Asilomar, USA, March 26–31, 2017.
4. O. Dolotko, S. Gupta, T. Kobayashi, E. Majzoub, V.P. Balema, M. Pruski, V.K. Pecharsky, "Novel hydrides and destabilization of the alkali-metal borohydrides by SiS_2 ," GRC Hydrogen-Metals Interactions: Making the Hydrogen Economy Work - New Developments and Recent Applications, Stonehill College, Easton, MA, July 16–21, 2017.

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