

IV.C.6 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 and low cost elements, such as silicon and boron. The specific objectives of this project are:

- 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 of 25–35 kJ/mol-H₂, such that H₂ desorption occurs at the operating temperature (~80–100°C) of the proton exchange membrane (PEM) fuel cells.
- Develop simple and scalable strategies to form two-dimensional graphene/hydride composites that will directly address the (re)-dehydrogenation kinetics issues plaguing the performance of high capacity borohydrides and other known complex metal hydrides.
- The successful completion of this project would afford a H-storage material with kinetic and thermodynamic properties tailored appropriately to supply high-purity hydrogen to PEM fuel cells, satisfying one of the most important goals of the DOE and the Fuel Cell Technologies Office and the Hydrogen Storage program.

Fiscal Year (FY) 2016 Objectives

- Use prototype electrostatic ground states (PEGS) [1] and multi-gas canonical linear programming (MGCLP) [2] tools to screen for stable hypersalts of Si-based borohydrides of the type (A/AE)_xSi_y(BH₄)_z, in which A and AE are light alkali and alkaline earth metals, respectively. Identify candidates that provide finite-temperature enthalpies within 27 ± 10 kJ/mol-H₂. The new Si-BHs are expected to have H-contents of at least 10 wt% and volumetric capacity in excess of 130 g H₂/L.
- Synthesize the most promising Si-BHs identified computationally using mechanochemical processes involving metathesis (exchange) reactions, and characterize the newly synthesized borohydrides by X-ray diffraction (XRD), solid state nuclear magnetic resonance (SSNMR), and gas volumetric pressure-composition-temperature techniques.

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 hydrogen storage systems. Successful completion would lead to hydrogen storage materials with high gravimetric and volumetric capacity, and kinetics and thermodynamics suitable to supply high-purity H₂ to a PEM fuel cell. The new materials identified and synthesized as an outcome of this project will achieve or exceed the DOE targets listed in 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)	0.075	>0.100
Volumetric capacity (kg H ₂ /L)	0.070	>0.130

*Ultimate (2020) system level targets, **material basis

FY 2016 Accomplishments

- More than 10,000 structures were examined by PEGS and density functional theory (DFT), and the most thermodynamically stable candidates were considered for synthesis; silicon, when present in an environment coordinated by $[\text{BH}_4]^-$ tetrahedra, prefers a 2+ state. The bi-alkali hypersalts are more stable than the mono-alkali hypersalts.
- Nearly 20 exchange or metathesis reaction systems were studied mechanochemically. There are clear indications that Si-BHs can be stabilized mechanochemically.
- The presence of halogen or sulfur in the structure stabilizes silicon borohydrides.
- Decomposition temperatures and amount of H_2 released from hypersalts meet the DOE targets; high purity H_2 was obtained from the mixed Si-BHs with no diborane release.



INTRODUCTION

A safe and efficient hydrogen storage method suitable for powering hydrogen fuel cell cars and supporting other H-based technologies remains an outstanding technological and scientific challenge. Because of the practical barriers associated with the H-storage in liquid and gaseous forms, hydrogen storage in solid materials continues to be the most promising alternative and an emerging technology. The target materials should store a large amount of hydrogen in a light, compact form and be amenable to rapid recharging, safe, and affordable. Despite the discovery and synthesis of a large number of hydrogen rich compounds, their utility for H-storage and delivery remains limited by unfavorable thermodynamics or/and poor kinetics of H_2 release and uptake [3]. The U.S. Department of Energy (DOE), 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 PEM fuel cell. Only a few known hydrides can satisfy these conditions and have a useful gravimetric density with enthalpies of dehydrogenation in the range of -25 kJ/mol- H_2 to -30 kJ/mol- H_2 .

Guided by robust and validated computational tools, this project seeks to (1) discover a hitherto unknown silicon (Si)-based borohydrides and optimize processes for their low cost synthesis in high purity powder form, and (2) develop mechanochemical processes to formulate nano-composites based on graphene-derived, two-dimensional carbon allotropes. Both classes of materials will be experimentally accessed via a versatile and sustainable, green, and energy-efficient mechanochemical process, offering a cost effective solution for large scale production.

APPROACH

A combination of computational screening and shortlisting followed by synthesis of the most promising candidates is adopted to cover a wide range of compositional landscape available for multi-cation Si-BH hypersalts. The computational search is performed using PEGS followed by structure relaxation using DFT. Thermodynamic properties of selected decomposition pathways are determined using MGCLP. Promising reaction systems are tested mechanochemically by utilizing double-exchange or metathesis reactions. Comprehensive structure and phase characterization is performed using powder XRD and SSNMR and the hydrogen de-absorption and absorption properties are evaluated using volumetric methods.

RESULTS

Screening candidate Si^{n+} hypersalt compounds using PEGS: Silicon borohydride, $\text{Si}(\text{BH}_4)_n$, $n = \{1,2,3,4\}$, candidate structures with Si oxidation states from +1 to +4 were generated using the PEGS algorithm and relaxed using DFT and conjugate gradient method. The calculated Born effective charge for Si ($Z_{\text{Si}}^{\text{eff}}$) in each structure, irrespective of its coordination, indicates that Si prefers a nominal 2+ state when surrounded by the $[\text{BH}_4]^-$ tetrahedra. Free energy minimization at $T = 300$ K via the MGCLP method showed that $\text{Si}(\text{BH}_4)_2$ is relatively more stable than the others towards decomposition to elements.

Alkali (A) and alkaline earth (AE) metal based hypersalts of Si-BHs were examined next for stability against decomposition into the elements in their standard states, and into the associated A, AH, AE, or AEH_2 . The calculated total energy (static + dynamic) and Helmholtz free energy changes for the decomposition reactions indicate that mono-A hypersalts are less stable than the bi-A hypersalts. In particular, $\text{LiKSi}(\text{BH}_4)_4$ and $\text{NaKSi}(\text{BH}_4)_4$ were found to be the most stable compositions and good candidates for experimental screening.

Screening, synthesis, and characterization of novel Si-BHs via hypersalt stabilization: Targeted synthesis of multi-cation borohydrides in multiple systems is based on mechanochemical exchange reactions, some examples are listed in Table 2. A few systems, such as $\text{LiBH}_4\text{-AlHal}_3\text{-SiHal}_4$ and $\text{ABH}_4\text{-SiS}_2$, etc. (where Hal = Cl or Br) have shown potential for the hypersalt stabilization and promising hydrogen desorption and absorption properties, and are discussed in details. A few other systems that will continue to have attention are also presented in Table 2.

$\text{LiBH}_4\text{-AlCl}_3\text{-SiCl}_4$ system: In an attempt to prepare aluminum stabilized Si-BHs, LiBH_4 , AlCl_3 and SiCl_4 were mechanochemically reacted in varying proportions. The reference reactions carried without SiCl_4 yielded potentially new phases for 13:3 and 3:1 molar ratio of LiBH_4 and AlCl_3

TABLE 2. Systems Currently under Investigation to Synthesize Si-Based Borohydride Hypersalts

Target compound	H ₂ , wt%*	Reactions examined
LiSi(BH ₄) ₅	18.4	4LiBH ₄ +TBABH ₄ +SiCl ₄ ; b)+Li[Al{OC(CF ₃) ₃] ₄
		SiS ₂ + nABH ₄ (n = 2-8; A = Li, Na)
		Si(CH ₃ COO) ₄ + 5LiBH ₄
K ₂ Si(BH ₄) ₆	12.4	K ₂ SiF ₆ +6ABH ₄ (A = Li, Na)
(NH ₄)Si(BH ₄) ₅	20.0/16.7	NH ₄ Cl+5LiBH ₄ +SiCl ₄
MgSi(BH ₄) ₆	17.1	MgSiF ₆ +6ABH ₄ (A = Li, Na)
		Mg(BH ₄) ₂ +4NaBH ₄ +SiBr ₄
CaSi(BH ₄) ₆	15.4	CaCl ₂ +6LiBH ₄ +SiCl ₄
AlSi(BH ₄) ₇	17.8	AlHal ₃ +nABH ₄ +SiCl ₄ (n=3, 7; Hal = Cl, Br; A = Li, Na)
LiSi(BH ₄) ₃	15.0	Li + 3ABH ₄ + SiCl ₄ (A = Li, Na)
CaSi(BH ₄) ₄	12.5	Ca + 4ABH ₄ + SiCl ₄ (A = Li, Na)

* Total gravimetric capacity of the pure compound as written; for the ammonium salt, second number is H-content excluding NH₄.

and full phase analysis and structure determination is in progress. Excess SiCl₄ during these reactions yields only LiCl and a known compound, Al₃Li₄(BH₄)₁₃ [4] in the 13:3 reaction. SiCl₄ has a more pronounced effect on the 3:1 reaction. Apart from LiCl, a new compound with yet unidentified structure appears. Based on XRD and hydrogen desorption analysis the product is expected to have a composition close to “LiAlSiCl₅(BH₄)₃”, see Equation 1 below:

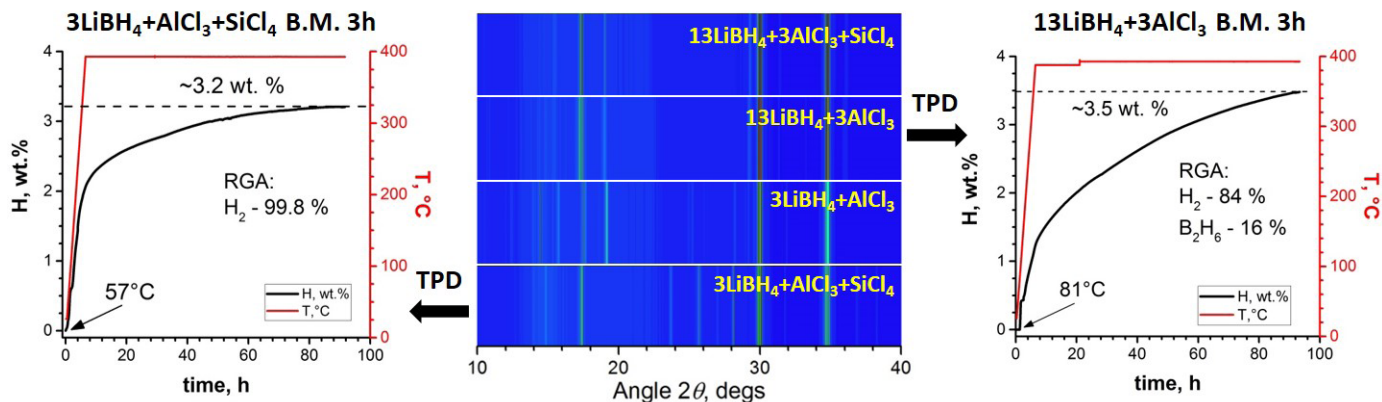


Consistent with Equation 1, the product yields 3.2 wt% of pure H₂ with onset at ~57°C (Figure 1).

Based on XRD, the isostructural Br analogue LiAlSiBr₅(BH₄)₃ forms with SiBr₄. These isostructural compounds are orthorhombic with *Ccca* space group. The presence of BH₄ group has been confirmed by ¹¹B SSNMR measurements. ²⁷Al SSNMR shows 5-coordinated Al in both

compounds, which is not present in the starting materials. Consistent with PEGS, ²⁹Si Direct Polarization Magic Angle Spinning NMR showed signal attributed to SiCl₄ in the structure. PEGS points to stable structures with Si⁴⁺ in AlSiCl_n(BH₄)₃ and AlSiLiCl_n(BH₄)₃, n = {1,2,3,4} composition spaces (Figure 2). Stable structures in both systems feature layers of SiCl₄ tetrahedra with planar and non-planar Al(BH₄)₃ units in AlSiCl₄(BH₄)₃ and AlSiLiCl₅(BH₄)₃, respectively.

LiBH₄-SiS₂ system: The mechanochemical reaction of LiBH₄ and SiS₂ in 2:1 molar ratio shows formation of an amorphous product that is currently under investigation. Thermodynamic calculations based on MGCLP have identified possible existence of a sulfur-stabilized hypersalt with the composition Li₂SiS₂(BH₄)₂. Nearly 5.1 wt% of H₂ is released from the products, which is close to the theoretical



TPD – Temperature programmed desorption; RGA – Residual gas analysis

FIGURE 1. The XRD patterns and temperature programmed decomposition plots of the LiBH₄ - AlCl₃ mixtures in the presence and absence of SiCl₄, ball milled for 3 h

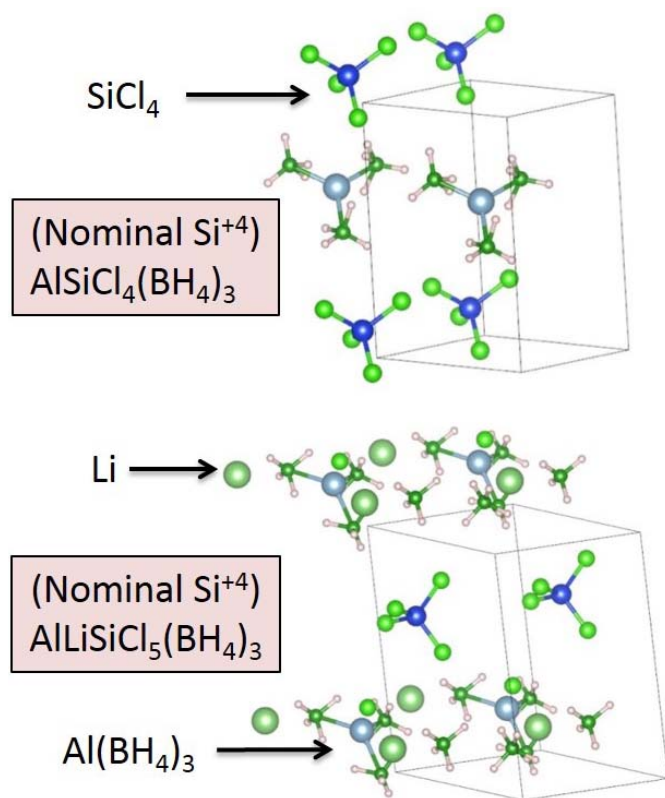


FIGURE 2. DFT-relaxed PEGS prototypes of $\text{AlSiCl}_4(\text{BH}_4)_3$ and $\text{AlLiSiCl}_5(\text{BH}_4)_3$ structures

value of 5.9 wt% for $2\text{LiBH}_4 + \text{SiS}_2$. Further, $6\text{LiBH}_4\text{-SiS}_2$ composition releases the highest amount of hydrogen (~8.2 wt%) on heating to 385°C with 92°C onset (Figure 3). Based on pressure-composition-temperature and XRD data, the possible reaction can be described as follows in Equation 2:



Additional SSNMR, hydrogen de/absorption experiments of fully and partially (de)hydrogenated samples are in progress to determine the local structures of the amorphous product.

CONCLUSIONS AND FUTURE DIRECTIONS

Analysis of numerous multi-cation systems using available computational and experimental tools shows that Si-BH hypersalts can be stabilized, and synthesized mechanochemically. Although most Si-BH hypersalts have borderline stability, evidence suggests that they can be stabilized by sulfur or halogen ions in the structure. These new materials have low desorption onset temperatures and release uncontaminated hydrogen. There is a strong likelihood of formation of sulfur stabilized Si-BHs in the $\text{LiBH}_4\text{-SiS}_2$ system. We will continue to focus on this and

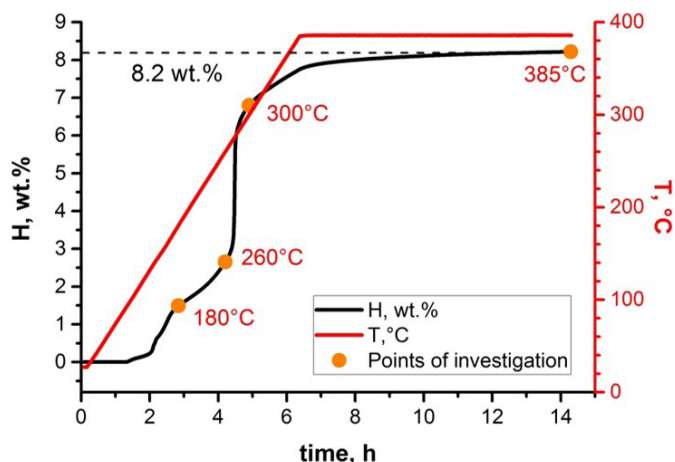


FIGURE 3. The temperature-programmed decomposition of the $6\text{LiBH}_4\text{-SiS}_2$ mixture and points of investigations at different temperatures

other sulfur-based systems using precursors like Al_2S_3 and B_2S_3 . The high pressure milling is expected to be recommissioned and fully functional by the end of August, at which point most mechanochemical reactions shown in Table 1 and other will be performed under ~350 bar H_2 pressure. Milling at cryogenic temperatures will also remain in focus.

Preliminary experiments on graphene-hydride composites have shown significant reduction in desorption onset temperature of LiBH_4 , along with considerable improvement in kinetics. Future work will aim at optimizing milling parameters, characterizing the composites and introduction of other borohydrides. Computational studies will be initiated to evaluate relative stabilities of Si-borohydrides and their hypersalts on graphene surface.

FY 2016 PUBLICATIONS/PRESENTATIONS

1. T. Kobayashi, O. Dolotko, S. Gupta, M. Pruski, E. Majzoub, V.K. Pecharsky “Insights into the role of composition for purity of released hydrogen from the $\text{LiBH}_4\text{-AlCl}_3$ system” *manuscript in preparation*.
2. O. Dolotko, T. Kobayashi, S. Gupta, M. Pruski, E. Majzoub, V.K. Pecharsky “Hydrogen generation from the $\text{LiBH}_4\text{-SiS}_2$ system.” *manuscript in preparation*.
3. O. Dolotko, S. Gupta, T. Kobayashi, M. Pruski, V.K. Pecharsky “Improved method of hydrogen generation from borohydrides by introducing sulfide materials” *IPDR in preparation*.

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