

IV.C.4 High-Capacity Hydrogen Storage Systems via Mechanochemistry

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Overall Objectives

The proposed research seeks to discover and develop hydrogen storage materials that are constituted largely from highly abundant and low cost elements, such as silicon and boron. The specific objectives of this project are two-fold.

- Identify computationally and synthesize hitherto unknown high-capacity Si-based borohydrides (Si-BHs) possessing gravimetric hydrogen density of 12–14 wt%, and decomposition enthalpies of 25–35 kJ/mol-H₂, such that hydrogen desorption occurs at the operating temperature (~80–100°C) of the proton exchange membrane (PEM) fuel cell
- Develop simple and scalable strategies to form two-dimensional (2D) graphene/hydride composites that will directly address the (re)-dehydrogenation kinetic issues that often plague the performance of high capacity borohydrides and other known complex metal hydrides

The successful completion of this project would provide a hydrogen storage material with kinetic and thermodynamic properties tailored appropriately to supply high-purity hydrogen to a PEM fuel cell, satisfying one of the most important goals of the DOE and the Fuel Cell Technologies Office and the Hydrogen Storage Program.

Fiscal Year (FY) 2015 Objectives

- We will initiate studies on computational identification of novel hypersalts of Si-based borohydrides of the type (A/AE)_xSi_y(BH₄)_z, in which A and AE represent light/early alkali and alkaline earth metals, respectively. Validated computational methods such as prototype electrostatic ground states (PEGS) [1] will be used to guide synthesis and save experimental time by avoiding attempted synthesis of clearly unstable compounds. The focus will be to identify candidates for hypersalts of silicon borohydride that provide finite-temperature enthalpies within 27 ± 10 kJ/mol-H₂. The new Si-based borohydrides will possess hydrogen contents of at least 11 wt% and volumetric capacity in excess of 130 g H₂/L. For example, in the simplest case of x = y = 1, the composition will be (A/AE)Si(BH₄)_{5/6}.
- During FY 2015 we will also initiate experiments to synthesize the most promising Si-based borohydrides identified computationally. Mechanochemical reactions involving metathesis will be performed on those systems that have positive enthalpies for desorption. Preliminary characterization of the newly synthesized borohydrides will be performed by X-ray diffraction and gas-volumetric 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 provide a hydrogen storage material with high gravimetric and volumetric capacity, and kinetics and thermodynamics suitable to supply high-purity hydrogen to a PEM fuel cell. The new materials identified and synthesized as an outcome of this project will achieve or exceed the DOE targets as presented in Table 1.

TABLE 1. Hydrogen Storage Parameters of Novel Si-Based Borohydrides Targeted in This Project and Comparison with DOE Ultimate 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



INTRODUCTION

Hydrogen has unequivocally been identified as a sustainable fuel for the next generation energy needs that offers tremendous potential to reduce our dependence on fossil fuels, and thereby mitigates our carbon footprint caused by their use. However, since hydrogen is an energy carrier and not the primary energy source, energy must first be invested to produce it. Moreover, the produced hydrogen must be stored and distributed to the point of end use in an efficient and safe manner. This has proved to be a major roadblock in the implementation of hydrogen fuel cell technologies, and a challenging technological caveat to overcome.

For most energy applications, hydrogen has been traditionally stored and transported as a compressed or liquefied gas. The potential safety risks and economical drawbacks associated with these forms of hydrogen storage (H-storage) are well recognized. In this regard, materials-based H-storage, in which hydrogen is either physically or chemically bound in a light weight solid, has emerged as the cutting-edge solution to the H-storage problem. Although a large number of such hydrogen rich compounds have been discovered and synthesized over the last decade, their utility for H-storage and delivery is limited either by their unfavorable thermodynamics or/and poor kinetics of hydrogen release and subsequent uptake [2]. The H-storage problem is compounded by the fact that only a few candidate hydrides with useful gravimetric density have enthalpies of dehydrogenation in the range of -25 kJ/mol-H₂ to -30 kJ/mol-H₂ that is required to achieve 1–10 bar H₂ equilibrium pressure at the working temperature of a PEM fuel cell. Discovery of novel functional solids that combine high gravimetric hydrogen content (>11 wt%) and the desired thermodynamic properties is thus challenging. A commercially viable material must also be inexpensive and easily produced on a mass scale. This project adopts a comprehensive and rational approach based on experiments guided by theory for (1) design and synthesis of hitherto unknown silicon (Si)-based borohydrides and (2) formulation of carbon/hydride nano-composites based on graphene-derived, 2D carbon allotropes. Both of these classes of materials will be experimentally accessed via a highly

versatile and sustainable, green, and energy-efficient mechanochemical process that potentially offers a cost effective solution for large scale production of advanced functional materials.

APPROACH

A combined theoretical and experimental approach will be adopted for rapid down-selection of stable candidates in the novel multi-cation Si-borohydride hypersalt and/or ammoniated systems of the type Alkaline/Alkaline earth-Si-(BH₄) followed by their synthesis and performance evaluation. Highly efficient and validated computer codes based on density functional theory (DFT) and crystal structure searching methods will lead to quick and precise identification of promising Si-borohydrides based on their calculated thermodynamic properties. These short-listed candidate Si-borohydrides will then be synthesized via a mechanochemical route by utilizing well known double-exchange or metathesis reactions, followed by their comprehensive characterization and hydrogen sorption properties. The as-synthesized Si-borohydrides will be further processed mechanochemically to obtain graphene/borohydride nano-composites with the aim of improving/tuning the hydrogen desorption kinetics and reversibility. The fabrication of graphene/hydride composites will also be extended to other high hydrogen capacity hydrides, such as LiAlH₄, LiBH₄ and Mg(BH₄)₂ that are currently being actively investigated.

RESULTS

Preliminary computational studies using prototype electrostatic ground state methods have identified high symmetry structures for Si(BH₄)₄ and NaSi(BH₄)₅. Both, Si(BH₄)₄ and NaSi(BH₄)₅ are found to crystallize with tetragonal structures in the space group (121) and (82), respectively. The ground state structures of these two compounds are presented in Figures 1a and 1b.

Furthermore, formation energies were calculated for several hypothetical hypersalt structures using the density functional theory including zero point energy. The calculated hypersalt structures were found to be increasingly stable with the size of the cation as presented in Table 2.

CONCLUSIONS AND FUTURE DIRECTIONS

Because decomposition temperature of borohydrides scale well with the cation Pauling electronegativity (χ_p), it is estimated that for metal borohydrides to be potentially suitable for H-storage applications, the cation χ_p must fall within the range of 1.2–1.5 [3]. Notwithstanding such a prediction, silicon has χ_p of 1.9, which is higher than the prescribed window. Nevertheless, preliminary calculations

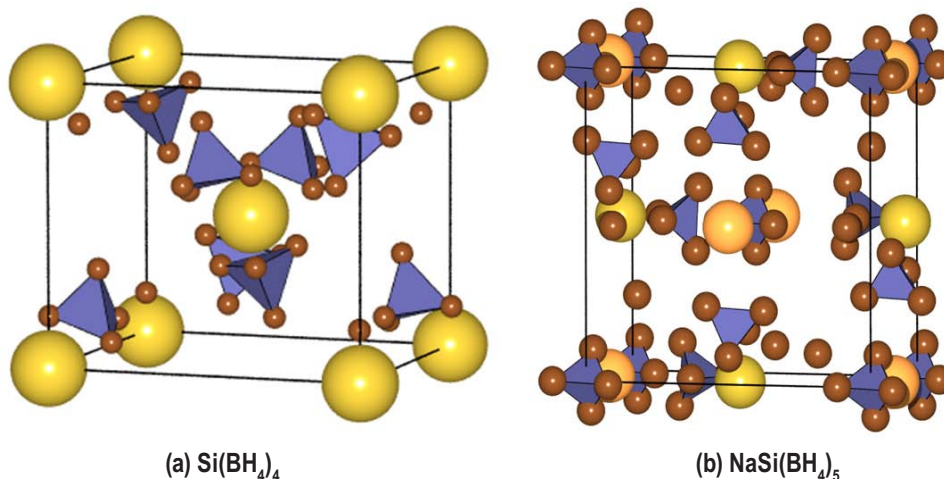


FIGURE 1. Ground state structures of (a) $\text{Si}(\text{BH}_4)_4$ and (b) $\text{NaSi}(\text{BH}_4)_5$ calculated by prototype electrostatic ground state method. The yellow, orange, and brown spheres represent silicon, sodium, and hydrogen, respectively. The hydrogen tetrahedras (lilac) are centered by boron atoms.

TABLE 2. Formation Energies of Si-Based Hypersalt Structures Calculated via DFT Indicate That Stability Increases with Increasing Cation Size

Compound	Formation Energy ΔE_f° [kJ/mol]
$\text{Si}(\text{BH}_4)_4$	
$\text{LiSi}(\text{BH}_4)_5$	
$\text{NaSi}(\text{BH}_4)_5$	
$\text{KSi}(\text{BH}_4)_5$	

indicate that silicon-borohydrides hypersalts are increasingly stabilized with increasing the size of the cation.

Future work will focus of identifying stable borohydride hypersalts, and the synthetic attempts will target hypersalts that shows negative formation enthalpies. In the upcoming Phases 1–3 of this project the following tasks will be undertaken.

- Computational screening and synthesis of novel silicon-based borohydrides via hypersalt stabilization
- Screening candidate Si^{4+} and Si^{2+} hypersalt compounds using PEGS
- Synthesis of Si-based borohydrides with monovalent, double-cation monovalent alkali metals or divalent alkaline earth metals
- First principles thermodynamics calculations for graphene/hydride composites
- Synthesis and physiochemical characterization of $\text{LiAlH}_4/\text{Mg}(\text{BH}_4)_2$ / Si-borohydrides-graphene composites

- Nuclear magnetic resonance characterization of Si-based borohydrides and graphene-hydride composites
- Thermal and mechanochemical reversibility of Si-borohydride salts
- Purification and characterization of newly synthesized Si-borohydride salts
- Optimization of kinetics in the Si-borohydride hypersalts synthesized and characterized in Phases 1 and 2
- Computational optimization of kinetics in Si-based borohydride hypersalts
- Optimization of kinetics in graphene/hydride composites

FY 2015 PUBLICATIONS/PRESENTATIONS

1. A poster entitled “High-capacity Hydrogen Storage Materials via Mechanochemistry,” was presented during the kick-off meeting at the Annual Merit Review meeting, 2015 in Crystal City, VA.

REFERENCES

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