Overview

Timeline
• Start Date: July 1, 2015
  – Phase 1: June 30, 2016*
*Project continuation and direction determined annually by DOE
• End Date: June 30, 2018
• % Complete: N/A; New project

Barriers
• Barriers addressed
  - Lack of fully functional high-H₂ capacity solids for PEMFC
  - High cost of synthesis and raw materials
  - High (>250 °C) discharge temperature
  - Poor reversibility at low H₂ pressure

Budget
• Total Project budget: $1.225 million
  – Total Recipient Share: $0.025 million
  – Total Federal Share: $ 1.2 million
  – Total DOE Funds Spent (to date): $ 0
• Planned Funding in FY15: $100,000
• Subcontract UMSL: $58,000 (Phase I)

Partner(s)
• UMSL: Eric Majzoub
  (Computational effort)
Relevance

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 a combination of:

(1) **Si-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 for desorption into the 20–30 kJ/mol H₂ 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 two approaches will be unified using an efficient and scalable mechanochemical approach to the synthesis of functional hydrogen storage materials.
Relevance

• The project addresses lack of suitable materials impeding implementation of materials-based onboard H-storage systems.

• Successful completion would provide a H-storage material with high gravimetric and volumetric capacity, and

• Kinetics and thermodynamics suitable to supply high-purity hydrogen to a PEM fuel cell.

<table>
<thead>
<tr>
<th>Storage parameters</th>
<th>DOE Technical Targets*</th>
<th>Our Targets**</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gravimetric capacity (KgH₂/Kg)</td>
<td>0.075</td>
<td>&gt;0.100</td>
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<tr>
<td>Volumetric capacity (Kg H₂/l)</td>
<td>0.070</td>
<td>&gt;0.130</td>
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</tbody>
</table>

*Ultimate (2020) system level targets, **material basis
1. 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
- Over 20 peer reviewed publications using PEGS
Examples: PEGS Finds High-symmetry Structures for Si(BH$_4$)$_4$ and NaSi(BH$_4$)$_5$

Si(BH$_4$)$_4$ $I\bar{4}2m$ (#121)  
NaSi(BH$_4$)$_5$ $I\bar{4}$ (#82)

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

**Down selection:** Hypersalt Structures Increasingly More Stable Against Decomposition

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formation Energy $\Delta E_f^\circ$ [kJ/mol]</th>
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</thead>
<tbody>
<tr>
<td>Si(BH$_4$)$_4$</td>
<td></td>
</tr>
<tr>
<td>LiSi(BH$_4$)$_5$</td>
<td></td>
</tr>
<tr>
<td>NaSi(BH$_4$)$_5$</td>
<td></td>
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<tr>
<td>KSi(BH$_4$)$_5$</td>
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</tr>
</tbody>
</table>

Increasing Stability

Preliminary computational results:

- Formation energy calculated via density functional theory (DFT), including zero point energy
- Structures are unstable with respect to disproportionation into borides and alkali hydrides or borohydrides at Si:M ratio of 1:1 for M={Li,Na,K}
**Thermodynamic Stability and Reaction Pathway Computations:** *Multiple Gas Canonical Linear Programming (MGCLP)*

\[ G(N, V, T) = PV + \sum_{i} x_i F_i (N, V, T) \]

\[ P = \sum_{g} P_g \]

Includes partial pressures of all possible gas phases

- Canonical ensemble free energy minimization that handles multiple gas phases naturally
- Borohydride/graphene composites stability will be investigated for decomposition into possible gas-phase by-products including B\(_2\)H\(_6\), SiH\(_4\), CH\(_4\), NH\(_3\), and H\(_2\)
2a. Synthesis of borohydrides: Mechanochemistry

- Metathesis or double-exchange reactions will be principally utilized to stabilize the proposed Si-BHs via:
  - Formation of hypersalts with alkali or alkaline earth cations (e.g. $A/AE(Si(BH_4))_{5/6}$, $A=Li-K$, $AE=Mg-Sr$)
  - Formation of hypersalts with double cation (e.g. $Na_xK_{(n-x)}Si_y(BH_4)_z$)
- Alternatively silicon borohydrides will be stabilized by formation of ammoniates e.g. $Si(BH_4)_4.nNH_3$
2b. Synthesis of hydride/graphene composites: Mechanochemistry

- **Graphene** - A two-dimensional (single to a few stacked layers) crystalline allotrope of carbon provides (a) durable light-weight scaffolding for hydrides, (b) extremely high specific surface area (>2500 m²g⁻¹) (c) high thermal conductivity for better thermal management.

- High-throughput mechanochemical exfoliation of graphite will be performed by ball-milling according to the established procedures [Jeon, I. –Y. et al., *PNAS*, 2012 109, 5588].

- The edge-selectively functionalized graphene nano-sheets (with amine, CO₂, SO₃ etc.) will be further processed along with various high capacity hydrides (including alanates and borohydrides) using high-energy ball milling.
2c. Characterization:

- Newly synthesized borohydrides and hydride/graphene composites will be characterized by:
  - X-ray and neutron (NIST, ORNL) diffraction
  - 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)
  - Gas sorption analysis by Sievert’s type apparatus (PCTPro-2000) integrated with gas analyzer.
  - Surface area analysis using BET for graphene and graphene/hydride composites.
## Approach

### Milestones and Go/No Go Decision

<table>
<thead>
<tr>
<th>Task</th>
<th>Task or Subtask Title</th>
<th>Milestone # (Go/No-Go Decision Point #)</th>
<th>Milestone Description (Go/No-Go Decision Criteria)</th>
<th>Anticipated Date (Months)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Screening, Synthesis and characterization of Novel Silicon-based Borohydrides via Hypersalt Stabilization</td>
<td>M1.1</td>
<td>Calculate thermodynamic stability of Si4+-borohydride hypersalts with either alkali or alkaline earth cation additions</td>
<td>3</td>
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<tr>
<td></td>
<td></td>
<td>M1.2</td>
<td>Demonstration of Si-borohydride formation through metathesis reaction</td>
<td>6</td>
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<tr>
<td></td>
<td></td>
<td>M1.3</td>
<td>Computational identification of candidate Si-borohydride hypersalts for synthesis</td>
<td>9</td>
</tr>
<tr>
<td>2</td>
<td>Graphene/hydride composite-based storage of metal hydrides</td>
<td>M1.4</td>
<td>Preparation of graphene/hydride composites with LiBH4 via mechanochemistry</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td></td>
<td>D1</td>
<td>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</td>
<td>12</td>
</tr>
<tr>
<td>3</td>
<td>Novel Silicon-based Borohydrides via Hypersalt Stabilization</td>
<td>M2.1</td>
<td>Demonstrate reversibility of a Si-borohydride hypersalt candidate</td>
<td>15</td>
</tr>
<tr>
<td>4</td>
<td>Graphene/hydride composite-based storage of complex metal hydrides</td>
<td>M2.2</td>
<td>Demonstrate reversibility of a graphene/hydride composite</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td></td>
<td>M2.3</td>
<td>Characterize graphene/hydride interactions using DNP SSNMR</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td></td>
<td>M2.4</td>
<td>Calculate thermodynamic stability of graphene/hydride composites to minimize composite degradation</td>
<td>24</td>
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<tr>
<td></td>
<td></td>
<td>D2</td>
<td>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 H₂ content.</td>
<td>24</td>
</tr>
<tr>
<td>5</td>
<td>Novel Silicon-based Borohydrides via Hypersalt Stabilization</td>
<td>M3.1</td>
<td>Optimize kinetics of Si-borohydrides through addition of transition metal dopants</td>
<td>27</td>
</tr>
<tr>
<td>6</td>
<td>Graphene/hydride composite-based storage of complex metal hydrides</td>
<td>M3.2</td>
<td>Optimize the kinetics and thermodynamics of composites using NMR characterization of the interactions</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td></td>
<td>M3.3</td>
<td>Demonstrate reversibility of Si-BH hypersalt with 11+ wt. % capacity and optimize thermodynamics</td>
<td>33</td>
</tr>
<tr>
<td></td>
<td></td>
<td>M3.4</td>
<td>Demonstrate reversibility of graphene/hydride composite with 10+ wt. % capacity and optimize thermodynamics</td>
<td>36</td>
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## Collaborations

- **University of Missouri, St. Louis**  
  Public University, outside DOE Hydrogen and Fuel Cells Program  
  Co PI: Eric Majzoub

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<td>MGCLP calculations</td>
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**Interactions**: Ames Laboratory will conduct teleconference calls involving all personals once every two weeks, and telephone discussions will be carried as frequently as needed. Computational efforts will allow rapid down selection of Si-B-H candidates and allow targeted synthesis.
Summary

• **Relevance:** Successful completion of the project will provide new high-capacity H-storage materials that will allow safer and cost effective implementation of hydrogen powered fuel-cells for onboard an portable applications

• **Approach:**

- PEGS Screening
  - Rapid down-selection of stable Si-borohydrides
  - Time Saving

- Mechanochemistry
  - Affords cost-effective scalable and benign synthesis and processing

- Graphene/hydride composite
  - Facilitate rapid sorption kinetics

Novel H-Storage materials: A holistic approach