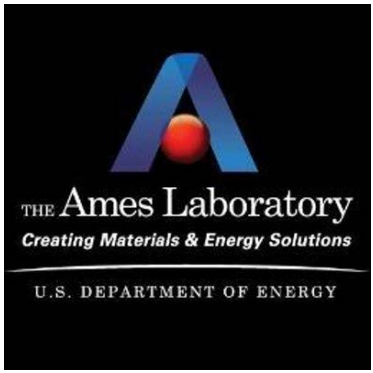
High-capacity Hydrogen Storage Systems via Mechanochemistry

PI :Vitalij K. Pecharsky

Co-PIs: Duane Johnson, Marek Pruski, Shalabh Gupta

(Ames Laboratory)

and Eric Majzoub (UMSL)



Presenters– Vitalij Pecharsky and Shalabh Gupta

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Project ID # ST119

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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-H_2 capacity solids for PEMFC
  - High cost of synthesis and raw materials
  - High (>250 °C) discharge temperature
  - Poor reversibility at low H_2 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)

UMSL

The Ames Laboratory
Creating Materials & Energy Solutions
U.S. DEPARTMENT OF ENERGY

Relevance

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

<u>Objectives:</u> 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 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 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.

Storage parameters	DOE Technical Targets*	Our Targets**
Gravimetric capacity (KgH_2/Kg)	0.075	>0.100
Volumetric capacity ($Kg\ H_2/l$)	0.070	>0.130
*Ultimate (2020) system level targets, **material basis		

Approach

1. Computational Screening:

Prototype Electrostatic Ground State Crystal Structure Prediction (PEGS)

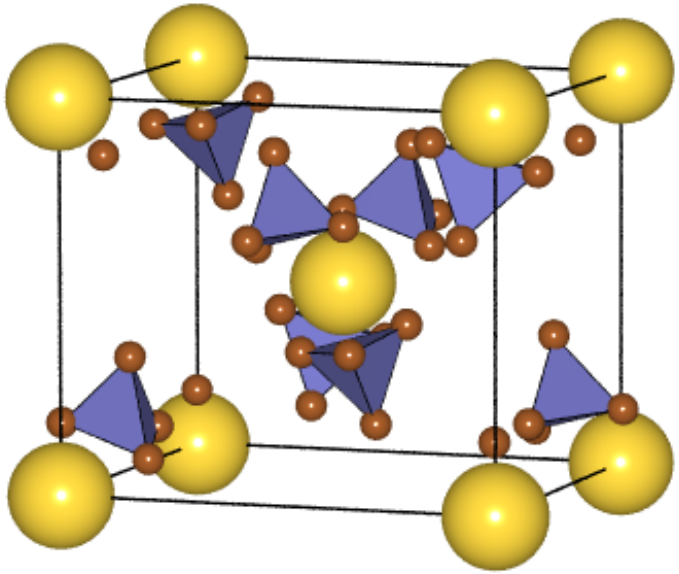
- Energy functional:

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

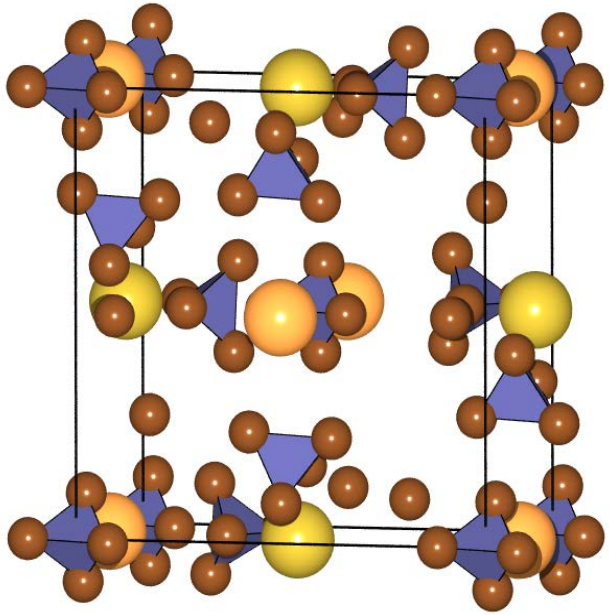
- Simulated annealing Monte Carlo energy minimization
- Generally obtains ground state and polymorph structures for complex ionic hydrides
- **Majzoub & Ozolins, Phys. Rev. B, 77, 104115, (2008)**
- **Over 20 peer reviewed publications using PEGS**

Approach

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

Compound	Formation Energy $\Delta E_f°$ [kJ/mol]
$Si(BH_4)_4$	 **Increasing Stability**
$LiSi(BH_4)_5$	
$NaSi(BH_4)_5$	
$KSi(BH_4)_5$	

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}

Approach

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

- MGCLP: J. Phys. Chem. C., 118, 14759 (2014).
- 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_2H_6, SiH_4, CH_4, NH_3, and H_2**

Approach

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 $Si(BH_4)_4.nNH_3$

Equipment available

A combination of mills supplying varying milling energies will be utilized:

1. Magnetic Ball-mill (allows milling at -30 °C)
2. Planetary style Micro Mill (P7, Fritsch)
3. 8000 M SPEX mill

- Allows rapid and solvent-free synthesis of solids
- Offers opportunity to access non-equilibrium products with improved properties
- Synthesis is usually carried at room temperature and is easily scalable to 25–100 g scale
- Provides facile route for microstructural refinement, nano-sizing and structuring of hydrides
- Enables solid-solid, solid-liquid and solid-gas reactions under broad range of reaction parameters.

Approach

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 m^2g^{-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, CO_2, SO_3 etc.) will be further processed along with various high capacity hydrides (including alanates and borohydrides) using high-energy ball milling.

Approach

2c. Characterization:

- Newly synthesized borohydrides and hydride/graphene composites will be characterized by:

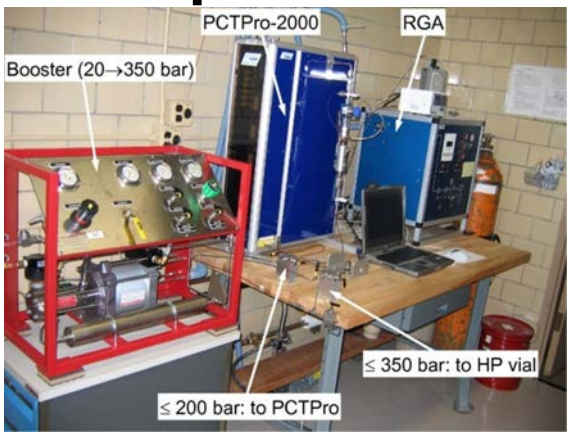
-X-ray and neutron (NIST, ORNL) diffraction

-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.

Capabilities



Sievert's type apparatus (PCTPro-200, HyEnergy, LLC) with extended pressure and residual gas analysis (RGA) capabilities

The newly installed 9.4 T DNP SSNMR spectrometer at the Ames Laboratory.

Approach

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

Collaborations

- **University of Missouri, St. Louis**

  Public University, outside DOE Hydrogen and Fuel Cells Program

  Co PI: Eric Majzoub

Task #	Task Title	Task description	Approach
1	Screening, Synthesis and characterization of Novel Silicon-based Borohydrides via Hypersalt Stabilization	Calculate thermodynamic stability of Si^{4+}-borohydride hypersalts with either alkali or alkaline earth cation additions	DFT and PEGS calculations
2	Graphene/hydride composite-based storage of metal hydrides	Computational identification of candidate Si-borohydride hypersalts for synthesis	DFT and PEGS calculations
4	Graphene/hydride composite-based storage of complex metal hydrides	Calculate thermodynamic stability of graphene/hydride composites to minimize composite degradation	MGCLP calculations

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:**