

# Chemical Hydrogen Storage using Ultra-High Surface Area Main Group Materials & The Development of Efficient Amine-Borane Regeneration Cycles

(part of the DOE Chemical Hydrogen Storage Center of Excellence)



Philip P. Power (pppower@ucdavis.edu) and Susan M. Kauzlarich (smkauzlarich@ucdavis.edu)

University of California

April 13, 2007

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Project ID #  
STP 14

# Overview--Innovation Beyond Boron

## Timeline

Project Start Date: FY05  
Project End Date: FY09  
Percent complete: 40%

## Budget

- Total project funding for Phase I (05-08)
  - DOE Total \$813,924
  - Contractor share \$203,481
- Funding for FY05
  - \$155K (DOE) \$ 38.75K (cost share)
- Funding for FY06
  - \$193K (DOE) \$48.25K (cost share)
- Funding for FY07
  - \$320K (DOE) \$80K (cost share)
- Funding for FY08
  - \$146K (DOE) \$36.5K (cost share)

## Barriers

- Cost
- System weight and volume
- Regeneration Processes

## Direct Collaborators

- Participant in the DOE Chemical Hydrogen Storage Center of Excellence
- LANL, PNNL, U. Alabama, and Rohm and Haas Company

# Objectives – Innovation Beyond Boron

## Overall

- To identify new hydrogen storage material enabling DOE targets and increase the understanding of synthetic approaches and physical properties of main group element clusters, such as Si, B, Al, and alloys thereof. To identify new methods for regeneration of chemical hydrides.

## 2005-2006

- To design simple routes to such compounds using mild conditions to provide commercially viable materials.

## 2006-2007

- To investigate the viability of the synthesized materials for commercial application by studying weight and volume as well as the reversibility of hydrogen uptake. Provide new materials, compounds, and support for chemical regeneration of amine-boranes or boron amides from B-X (X= halide or oxide) compounds.\*

## 2007-2009

- To analyze measurements to identify compounds that offer relatively lightweight, easily handled solid materials capable of hydrogen storage that are synthesized, activated and regenerated in a simple manner.

# Timeline

Task	Year 1	Year 2	Year 3	Year 4	Year 5
<b>Task 1: Nanoparticle Synthesis</b> Synthesis of SiH and Si(NH <sub>2</sub> ) Characterization of SiH and Si(NH <sub>2</sub> ) Synthesis of Si <sub>1-x</sub> M <sub>x</sub> H and Si <sub>1-x</sub> MNH <sub>2</sub> Characterization of Si <sub>1-x</sub> M <sub>x</sub> H and Si <sub>1-x</sub> MNH <sub>2</sub> composition and reactivity Optimization of reaction to provide material to partners					
<b>Task 2: Main group Compound Synthesis</b> Synthesis of (H <sub>2</sub> BXH <sub>2</sub> ) <sub>n</sub> Characterization of composition and reactivity explore main group analogs					
<b>New 06/07: Task 2: Regeneration of E-H Materials (E = B, Al, Si, Ge, Zn)</b> Synthesis of compounds containing E-H, E-NH <sub>2</sub> , E-OC(O)H moieties Characterization of compounds and regeneration under mild conditions					
<b>Task 3: Characterization and Testing</b> Test reactivity, thermolysis, and regeneration of various alloys and main group compounds					

New/revised

# Plan & Approach

## Novel High Surface Area Main Group Materials

- To test the concept of a high surface area chemical hydride. Demonstrate proof of concept with Si nanoparticles.
- Key issue is to minimize weight by incorporation of light elements, thus changing the chemical bonding at the surface and increase the amount of hydrogen.

## Chemical Regeneration of Amine-Boranes

- Conversion of E-X to E-H (E= B,Al,Si,Sn or Zn; X = halogen or oxygen ligands)
- Cf. Sneddon and Yoon *J. Am. Chem. Soc.* **2006**, *128*, 13992-13993.

## Task 1.

To design and test a high yield synthesis of light element main group nanoparticles.<sup>1</sup> To control size and surface capping. To test for hydrogen release. Based on these results: to revise and optimize new light element main group nanoparticles. Demonstrate the feasibility of 4 wt % hydrogen production from nanoparticles with a plan to achieve 8 wt %. Explore other novel light element containing materials for hydrogen storage.

## Task 3.

To test the materials for hydrogen storage and regeneration by collaboration with other members of the Center.

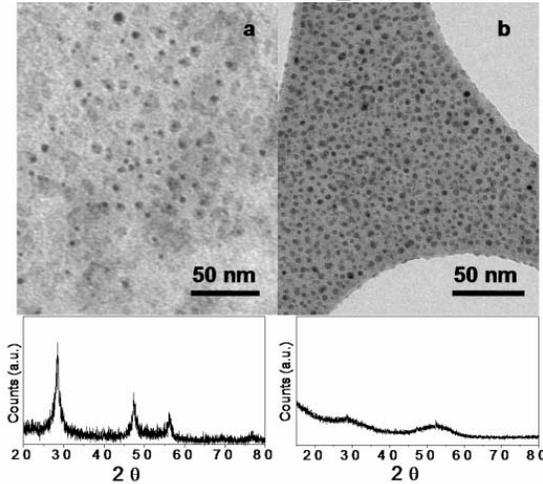
## Task 2.

To synthesize and characterize compounds with E-H, E-NH<sub>2</sub>, E-X (E = halogen or O), and E-C(O)OH moieties (E = B, Al, Si, or Zn containing groups). To investigate their interconversion under mild reaction conditions with the object of creating a simple chemical cycle to regenerate E-N bonds that will facilitate the storage of hydrogen.

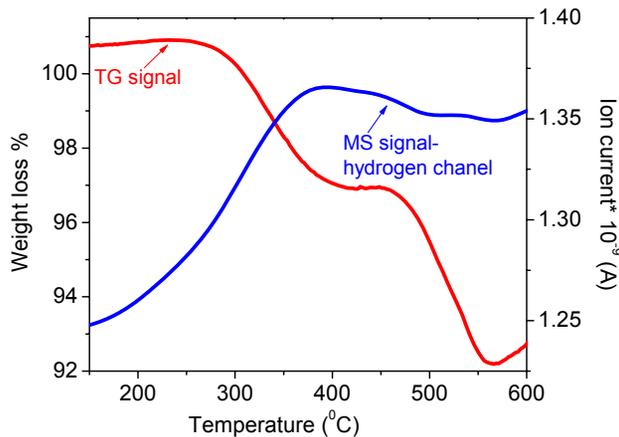
<sup>1</sup> Neiner, D.; Chiu, H.W.; Kauzlarich, S.M. *Journal of the American Chemical Society*, **2006**, *128*, 11016-11017.

# Novel Nano-Materials for Hydrogen Storage

- Light element main group nanoparticles (hydrogen capped nanoparticles such as Si,  $\text{Si}_{1-x}\text{Al}_x$ ,  $\text{Si}_{1-x}\text{C}_x$ , and  $\text{Si}_{1-x}\text{B}_x$  – chemical hydrides)
- Light element open frameworks (inorganic clathrates with  $\text{H}_2$  inside cages – similar to  $\text{H}_2\text{O}$  clathrates)<sup>2</sup>



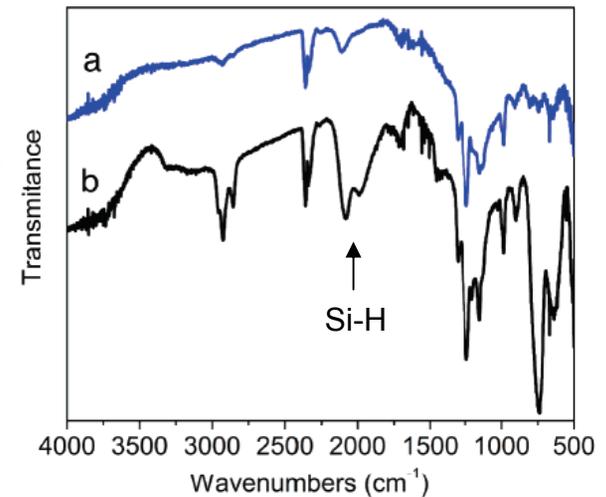
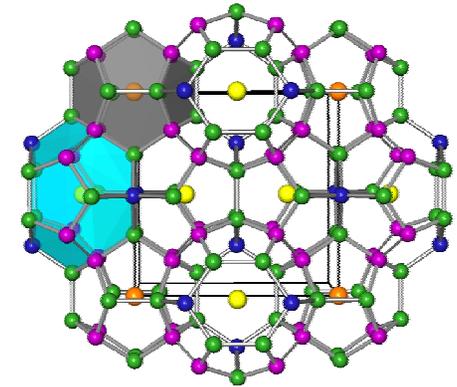
~5 nm diameter Si nanoparticles



TEM and X-ray powder patterns for the powders obtained from the reactions in (a) DME and (b) DOE. The powder diffraction of (a) can be fully indexed as diamond-structured silicon. Broad peaks are amorphous Si. What are the best structures for  $\text{NH}_3\text{BH}_3$  regen? Control structure by chemistry.

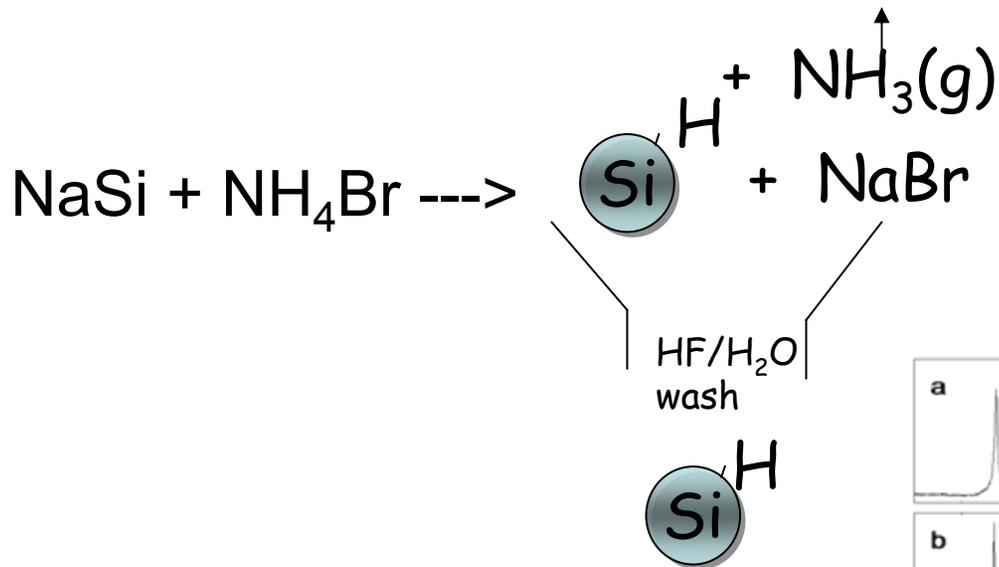
FTIR spectra for Si nanoparticles from (a) DME and (b) DOE

TG/MS showing ~3 wt %  $\text{H}_2$  between 200-350  $^{\circ}\text{C}$ .

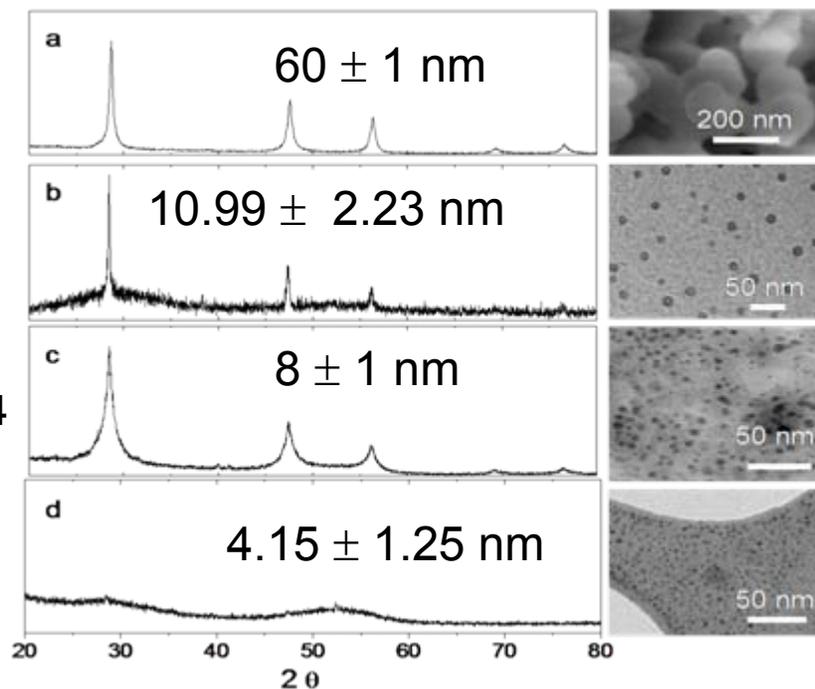


<sup>2</sup>"Hydrogen Encapsulation in a Silicon Clathrate Type-I Structure:  $\text{Na}_4(\text{H}_2)_2\text{Si}_{46}$ : Synthesis and Characterization" D. Neiner, N. L. Okamoto, C. L. Condon, Q. M. Ramasse, P. Yu, N. D. Browning and S. M. Kauzlarich, *Journal of the American Chemical Society*, submitted.

# High Yield Synthesis, XRD, SEM/TEM



- High yield, low cost synthesis.<sup>3</sup>
- Reaction conditions control size.<sup>4</sup>
- Hydrogen capped surfaces.



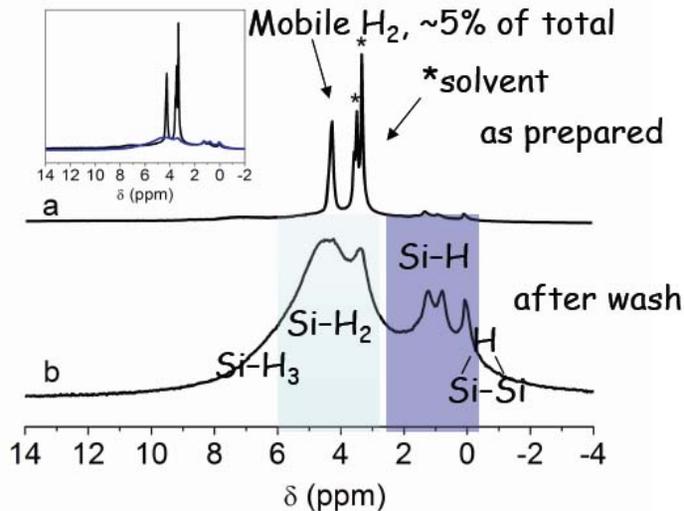
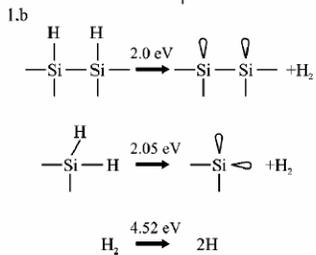
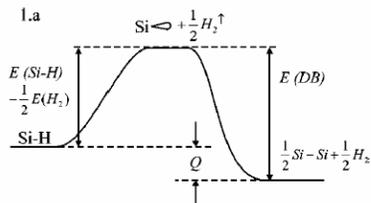
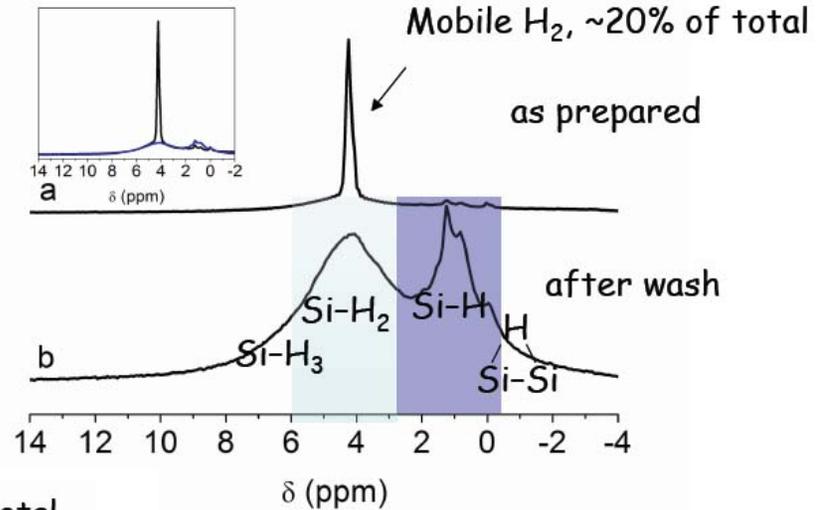
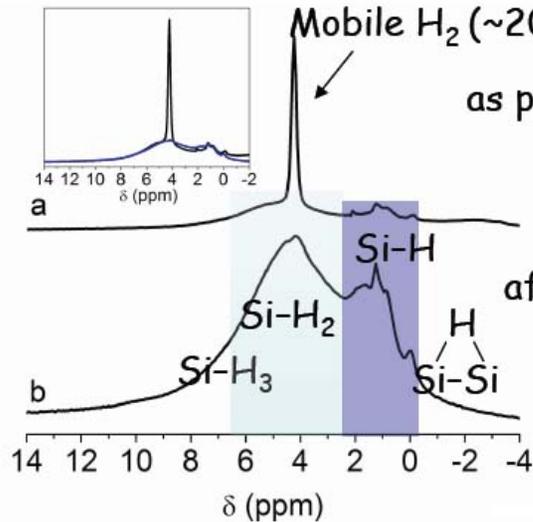
3. Patent Pending, UC2006-735

4"Hydrogen Capped Silicon Nanoparticles as a Chemical Hydride: Synthesis and Characterization" D. Neiner, and S. M. Kauzlarich, *Journal of the American Chemical Society*, in preparation.

# <sup>1</sup>H MAS NMR

60 nm

11 nm



8 nm diameter

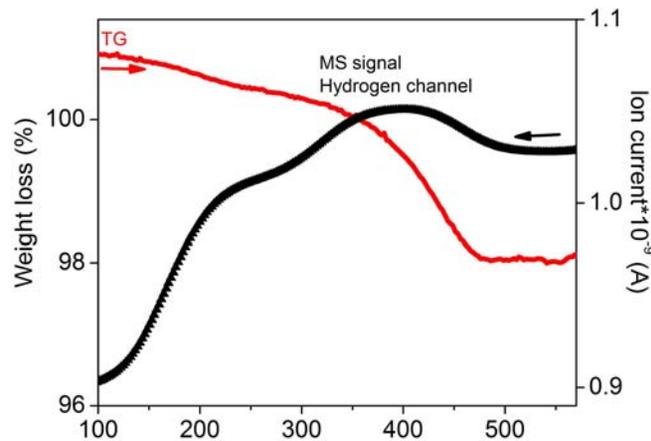
DME (8 nm particles) is physisorbed to the surface and appears to protect the particles from oxidation in air.

J. Farjas et al, *Phys. Rev B*, 65, 115403 2002.

**NMR shows that there is covalently bonded hydrogen on the surface.** Some is present as SiH<sub>2</sub> which is important for mechanism of H<sub>2</sub> release.

# TG/MS

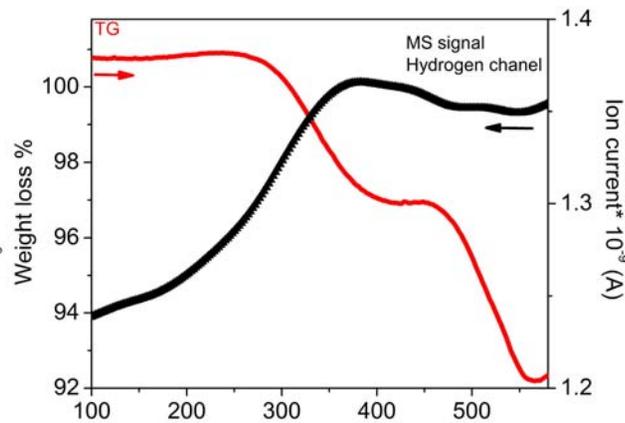
11 nm



➤ TG –weight loss ~ 3%,  
attributed to H<sub>2</sub>.

➤MS – 2 broad hydrogen signals,  
centered at 250 and 400 °C.  
Consistent with all hydrogen.

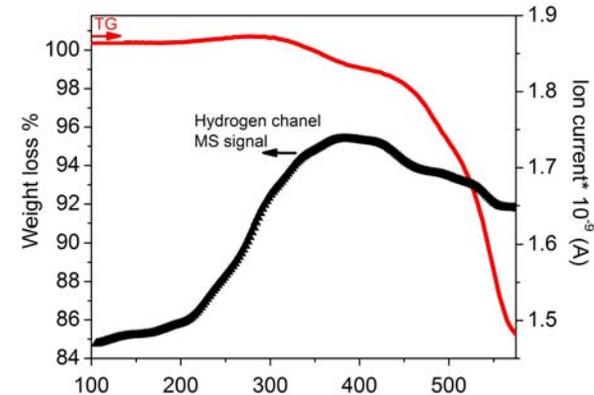
8 nm



➤ TG –weight loss ~ 8%,  
attributed to H<sub>2</sub>, and  
dimethoxyethane (DME)  
solvent loss above 400 °C.

➤MS – one broad  
hydrogen signal centered  
at 400 °C

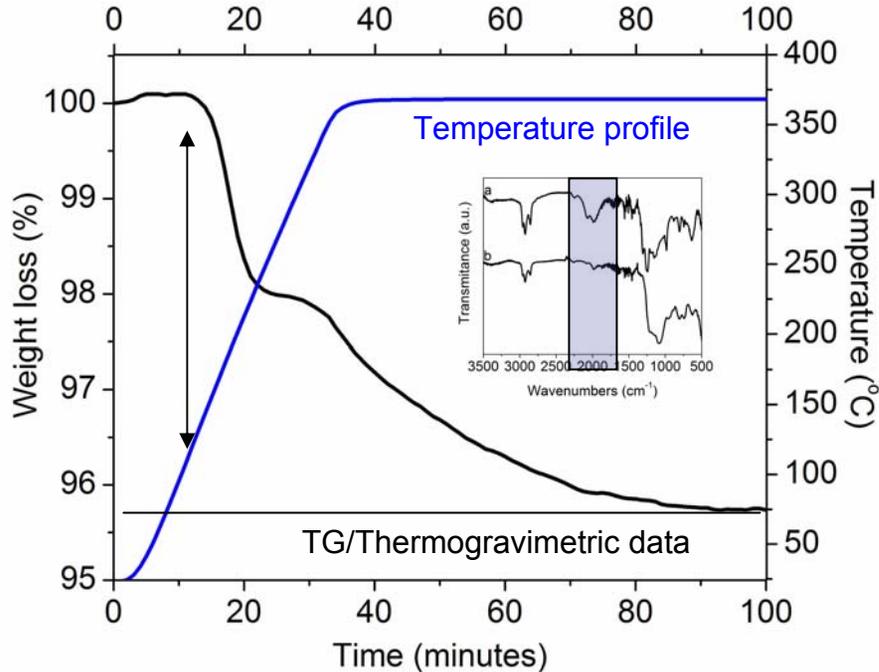
4 nm



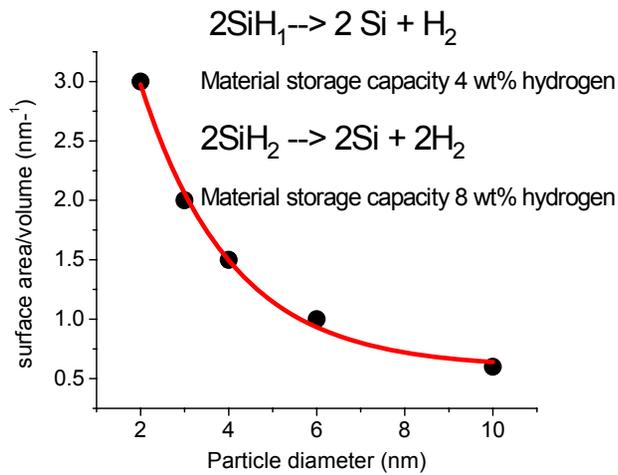
➤ TG –weight loss ~ 15%,  
attributed to H<sub>2</sub> and dioctylether  
(DOE)solvent loss above 400 °C.

➤MS – one broad hydrogen  
signal centered at 370 °C

# Isotherm TG for the 4 nm Si nanoparticles and predictions towards new nanomaterials



- Isotherm at 350 °C shows total of 4.5% weight loss. Suggests that a significant amount of hydrogen is present on the surface.
- FTIR on the sample before and after the isotherm confirms the disappearance of the SiH stretches in the 2000  $\text{cm}^{-1}$  region. There is some changes to the CH stretches also, perhaps due to concurrent oxidation of the sample.

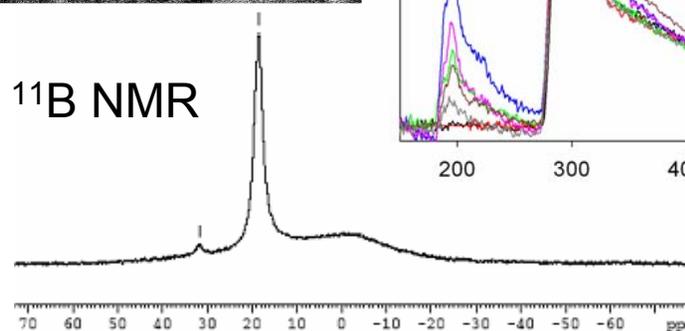
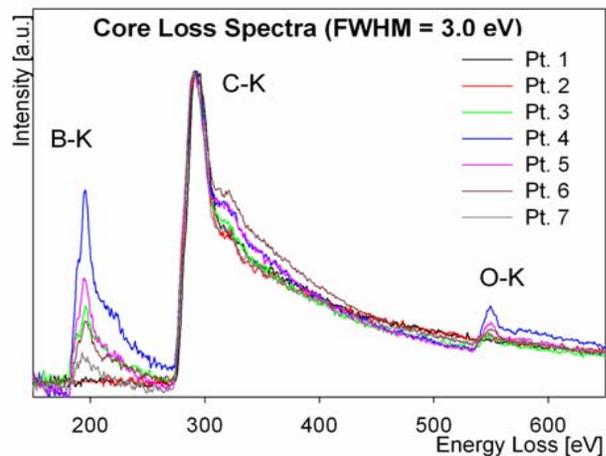
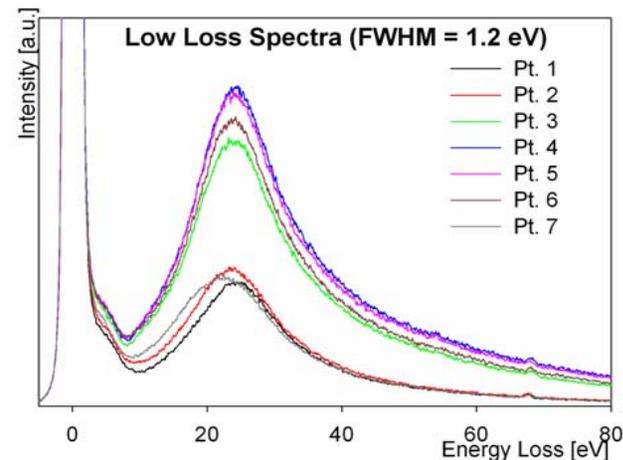
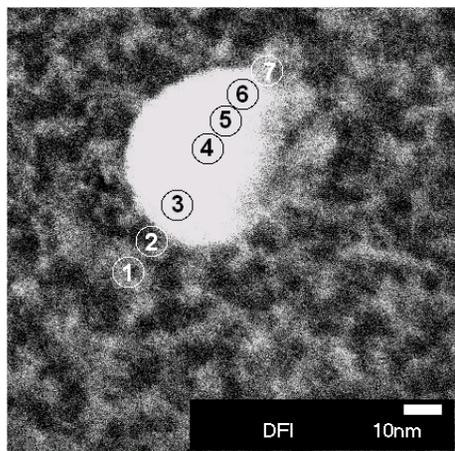
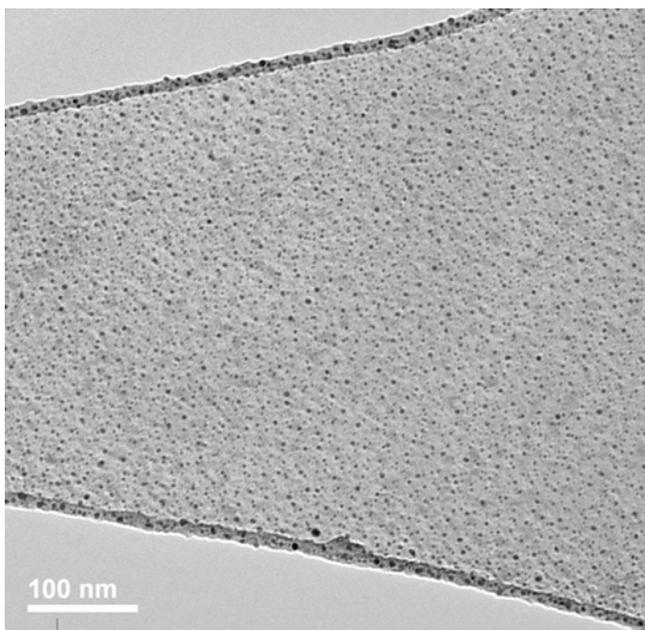
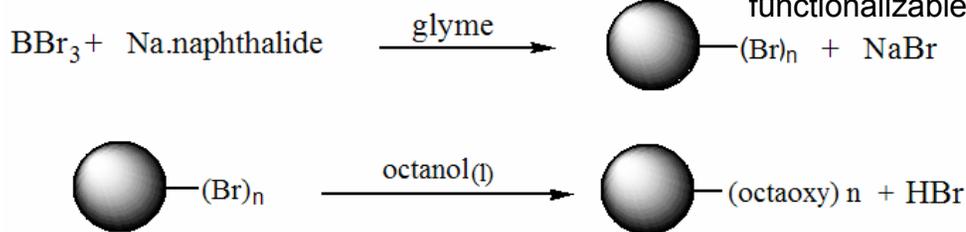


Lighter element nanoparticles and alloy nanoparticles of Si should provide different chemical reactivity and higher hydrogen content.

# Boron Nanoparticles: Room Temperature Synthesis and Characterization

## Lighter elements for larger weight % hydrogen

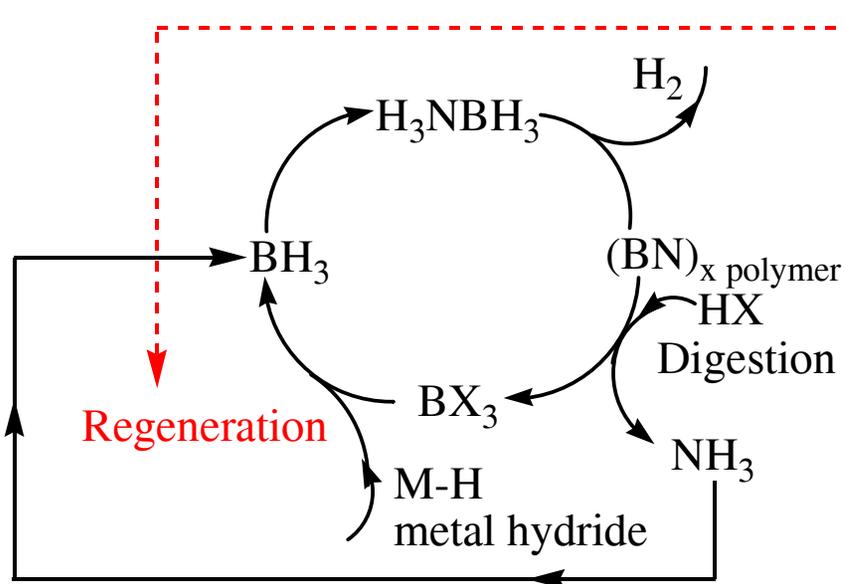
Proof of concept: 1st solution route to boron nanoparticles with functionalizable surfaces.



A.L. Pickering, C. Mitterbauer, N.D. Browning, S.M. Kauzlarich, P.P. Power, *Room Temperature Synthesis of Surface-Functionalised Boron Nanoparticles* **Chem. Commun.**, 2007, 580

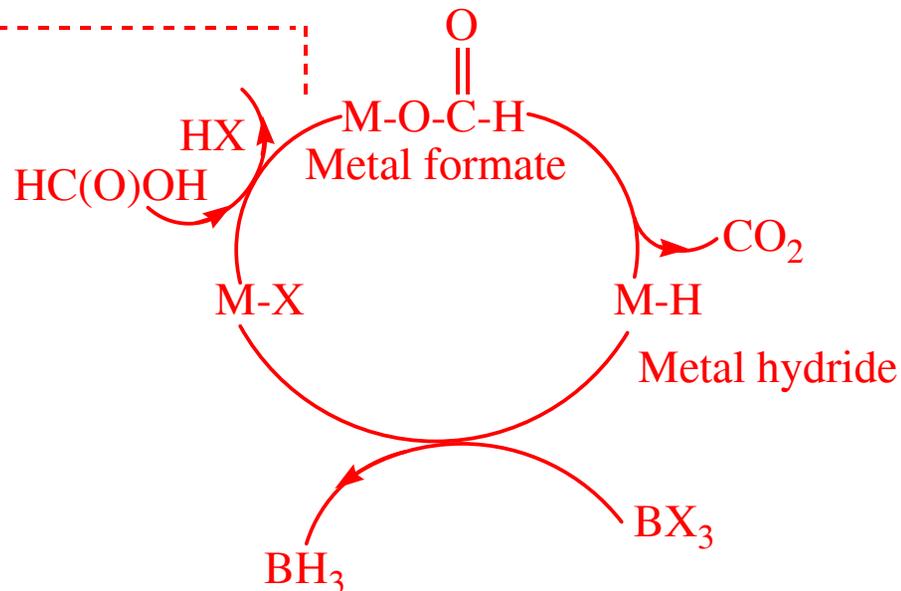
# Efficient Regeneration of the Amine-Borane H<sub>2</sub>Carrier is Essential to the Success of the Project

Metal Formate Based Regeneration Work at UC Davis



X = Halogen or oxo group

Simplified LANL H<sub>2</sub> Storage and Spent Fuel Regeneration Cycle



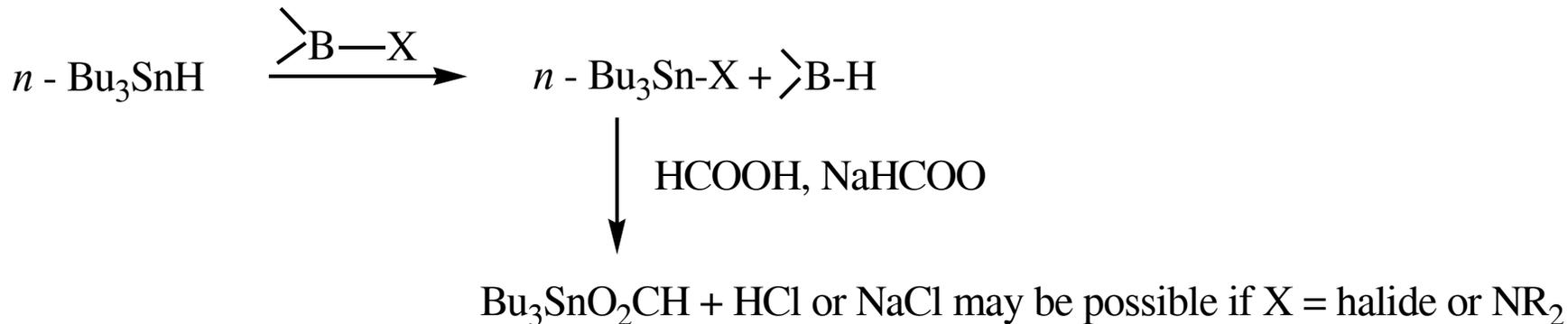
Simplified UC Davis Formate /Hydride Regeneration Cycle

# Efficient Synthesis of Metal Hydrides for the Regeneration of the H<sub>2</sub>(Amine-Borane) Carrier.

Use of Metal Formates as Shown by the n-Bu<sub>3</sub>SnH/n-Bu<sub>3</sub>SnOC(O)H System.



Klinger, R. J.; Bloom, I.; Rathke, J. W. *Organometallics* **1985**, 4, 1893.



## Energetics



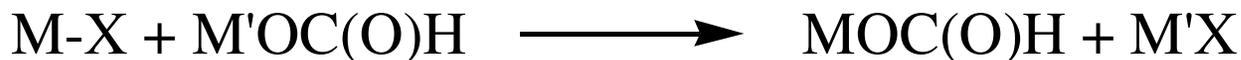
$$^2 H = -18.3 \pm 0.2 \text{ kcal mol}^{-1}$$

$$^2 S = -20.2 \pm 0.2 \text{ kcal mol}^{-1} \text{ deg}^{-1}$$

# Summary of Initial Work on Formates at UC Davis

(also cf. subsequent slides)

- Salt Elimination Reactions are an Inefficient Method of Metal Formate Synthesis

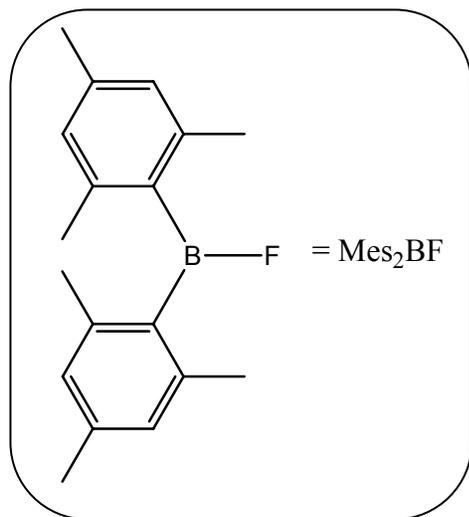


(M = Si, Ge, Sn, B, Al or Ga; X = F, Cl or Br; M' = Li or Na)

- Reactions are often characterized by variable yields, sluggishness and difficulties in product separation.
- Two methods suggest much cleaner reactions possible
- $\text{M-NR}_2 + \text{HC(O)OH} \longrightarrow \text{MOC(O)H} + \text{HNR}_2$  (amine elimination)  
(R = H, Me, etc...)
- $\text{M-H} \xrightleftharpoons[\text{CO}_2]{\text{CO}_2} \text{M-OC(O)H}$  ( $\text{CO}_2$  insertion)

# Conversion of Boron Amides to Formates (A Step in the Regeneration Route)

Boron Formates can be generated by 2 efficient routes



Supporting Data:  
 $^1\text{H NMR } \delta = 8.2 \text{ ppm}$   
IR signal =  $1605 \text{ cm}^{-1}$   
Trace  $^{19}\text{F NMR}$  signal  $\delta = -14.6 \text{ ppm}$

Direct Addition of Formic Acid to E–NH<sub>2</sub> is quantitative for E–OCOH (E = boron)



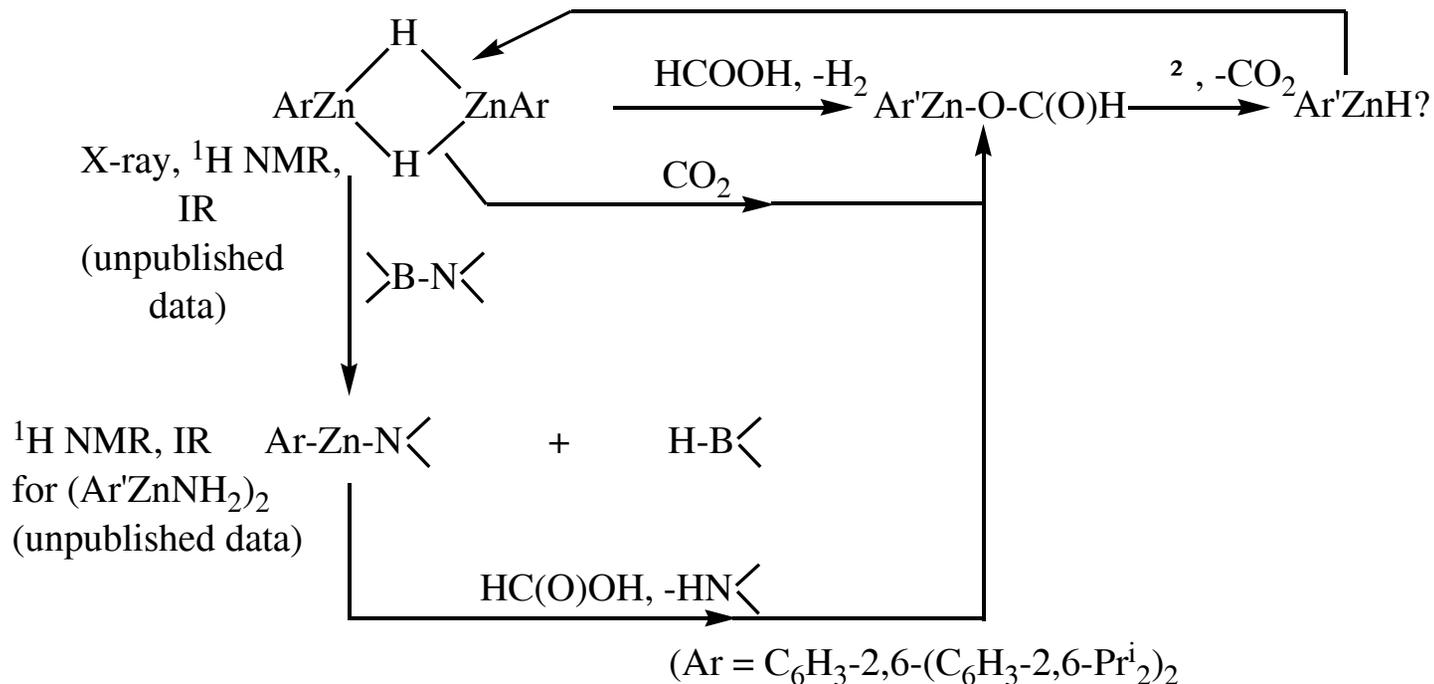
85% yield

>95% yield 15

# Several Metal Formate/Hydride Systems are being Investigated as Possible Regeneration Agents.

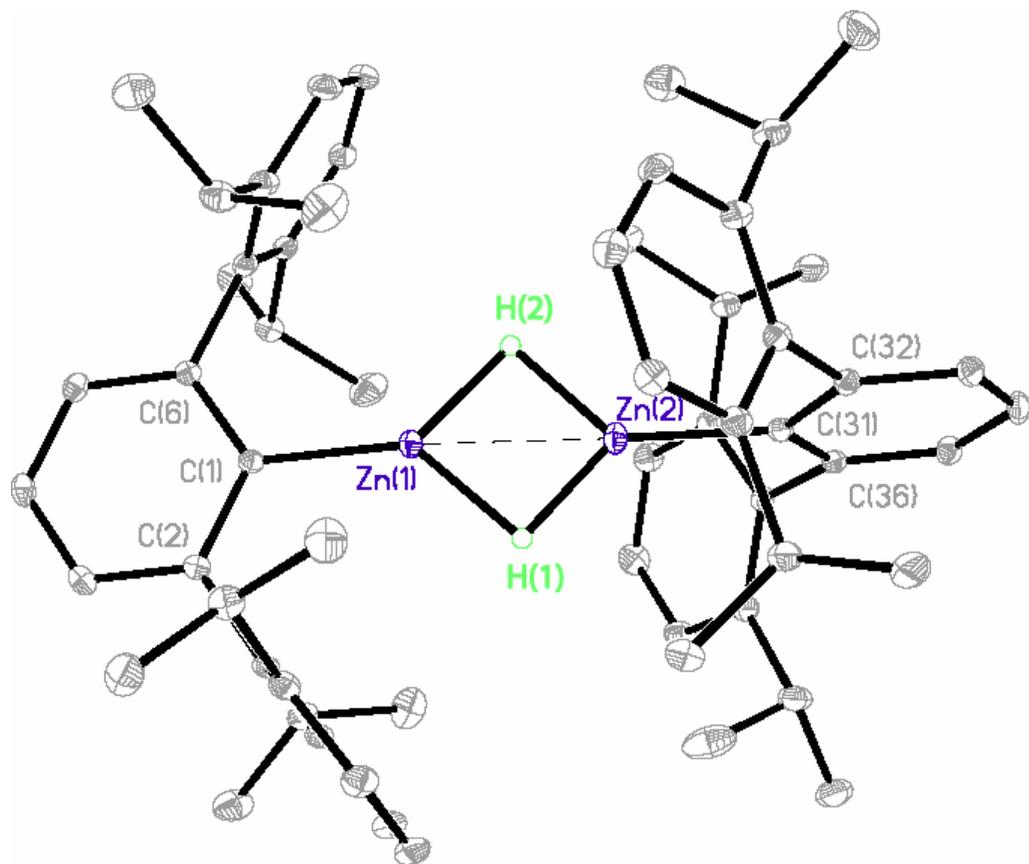
These include the use of Si, Sn, Al or Zn based reagents.

They combine high reduction potential and good thermal stability of the hydride.<sup>a</sup>  
 Current work at UC Davis uses the aryl zinc hydride (ArZnH)<sub>2</sub> as shown:



Zn-H bond enthalpy = ca. 80.0 kcal/mol : cf. Mavrides et al. *J.Phys. Chem. A* **2006**, *110*, 10899

# Thermal ellipsoid (30%) plot of $\text{Ar}' \text{ Zn}(\mu\text{-H})_2\text{ZnAr}'$



Zn(1)-Zn(2) 2.4084(3)  
Zn(1)-H(1) 1.67(2)  
C(1)-Zn(1)-Zn(2) 175.14(5)  
C(1)-Zn(1)-H(1) 138.3(9)  
Zn(2)-Zn(1)-H(1) 45.2(8)

$^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 300 MHz,  $25^\circ\text{C}$ ):  $\delta$  4.84 (s, 1H, ZnH)

# Summary of Accomplishments

## Nano-materials

- $^1\text{H}$  NMR before and after wash shows the presence of multiple hydrogen sites on the silicon surface, regardless of particle size and crystallinity.
- The TGA/DSC measurement under Ar reveals that the Si nanoparticle lose weight upon heating. TG/MS is consistent with this being  $\text{H}_2$ .
- The weight loss starts at  $300\text{ }^\circ\text{C}$  and it is over at  $\sim 400\text{ }^\circ\text{C}$  for the 10 nm and 5 nm diameter particles.
- The smallest nanoparticles (4 nm) show the largest weight loss.
- Boron nanoparticles can be synthesized via a low temperature solution route.

## Regeneration

- Amide, hydride and formate derivatives of the  $\text{Mes}_2\text{B-}$  ligand platform have been synthesized and spectroscopically characterized.
- Both the hydride and amide may be converted to formate in quantitative yield.
- A zinc hydride (X-ray structure) and amide have been synthesized and spectroscopically characterized. Their conversion to formate has been spectroscopically verified.

# Future Directions

## Nano-materials

- Collaborate with partners (R & H) to test nanoparticles for regeneration.
- Repeat TG/MS measurements at PNNL to ensure reproducibility and fully characterize the gases that evolve.
- Investigate the potential of these nanoparticles for regeneration of B–H bonds from B–X bonds (UCD).
- Synthesize  $\text{Si}_{1-x}\text{E}_x$  (E = B, C, Al) nanoparticles to affect the chemical bonding (lower dehydrogenation temperature), increase chemical reactivity (for ammonia borane regeneration), and increase the weight % hydrogen on the nanoparticles.

## Regeneration

- The syntheses of several more examples of metal hydrides, amides and formate derivatives of B, Al, Si, and Zn with a variety of coligands will be undertaken.
- The interconversion of such compounds under mild conditions will be investigated.
- Reversible generation of hydrides with use of formates will be the major objective of this work

# Project Summary

- **Relevance:** New materials for hydrogen storage and ammonia borane regeneration.
- **Approach:** Synthesis and characterization of novel nanomaterials and the synthesis of metal hydrides for efficient ammonia borane regeneration.
- **Technical Accomplishments and Progress:** Demonstrated significant wt % hydrogen on the surface of silicon nanoparticles for three different average sizes, synthesized boron nanoparticles and new compounds for ammonia borane regeneration.
- **Technology Transfer/Collaborations:** Active partnership with LANL, PNNL, Rohm & Hass, U. Alabama, U. Penn, presentations, publications, and patent applications.
- **Proposed Future Research:** Apply knowledge gained to new nanoparticles (alloys of silicon) and new compounds. Test nanoparticles for possible regeneration ability. Investigate the reversibility of amine-borane regeneration routes

# Quantitative Performance Metrics: Tracking Center Progress

Nanopart. DOE Targets	Si/NH <sub>2</sub>	B/OR	4 nm Si/H	8 nm Si/H	10 nm Si/H	60 nm Si/H	2010 Center Goal
2010 System Gravimetric Capacity (6.0 wt%)	No H <sub>2</sub> detected	-	4.5 g H <sub>2</sub> released/ 100g	3.7 g H <sub>2</sub> released/ 100g	3g H <sub>2</sub> released/ 100g	-	> 6.0 wt % Phase I: Material Phase II: System- 2010 Phase II: 9% Material- 2015
2010 System Volumetric Capacity 0.045 kg/L	-	-	0.1 kg H <sub>2</sub> /L laboratory vessel contents (4.5gX2.3g/c m <sup>3</sup> )/100g	0.08 kg H <sub>2</sub> /L laboratory vessel contents (4.5gX2.3g/c m <sup>3</sup> )/100g	0.06 kg H <sub>2</sub> /L laboratory vessel contents (3gX2.3g/c m <sup>3</sup> )/100g	-	> 0.045 kg/L Phase I: Material Phase II: System- 2010 Phase II: 0.060 Material-2015
2010 H <sub>2</sub> Flow Rate (0.02 (g/s)/kW) (80 kW stack)	-	-	-	-	-	-	Reactor volume Amount of catalyst

- not measured

# Co-operations

**LANL:** Synthesis of metal hydrides for cost effective regeneration

**PNNL:** Characterization of nanomaterials, theoretical calculations of regeneration cycle energetics.

**U. Alabama:** theoretical calculations of hydrogen storage cycles, application of nanomaterials to regeneration.

**Rohm & Haas:** scale-up and application of nanomaterials to regeneration.

# Acknowledgements

## Nanomaterials:

Doinita Neiner: Si nanoparticles

Alex Pickering: B nanoparticles,  
Si-NH<sub>2</sub> nanoparticles

Tom Autrey (PNNL): TG/MS

Alex Navrotsky (UCD): XRD

Ping Yu (UCD): MAS NMR

## Regeneration:

Audra Betzer

Bobby Ellis

Zhongliang Zhu

Don Camaioni (PNNL)

Tom Baker (LANL)

Fran Stephens (LANL)