Synthesis and Discovery of Nanocrystalline Reversible Hydrides by Vapor Phase Reactions

A Partner for Synthesis and Discovery

DOE

METAL HYDRIDE CENTER OF EXCELLENCE

THE UNIVERSITY OF UTAH

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Project ID #
STP26

Overview

Timeline

- Project start: FY05
- Project end date: FY09
- Percent complete: New start

Budget

- Total project funding (Expected)
  - DOE share: $645,438
  - Contractor share: $165,000
- Funding for FY05: $75,000

Partners

- Sandia National Lab,
- HRL
- U Nevada
- NIST & JPL
- U Pitts and CMU

Overview

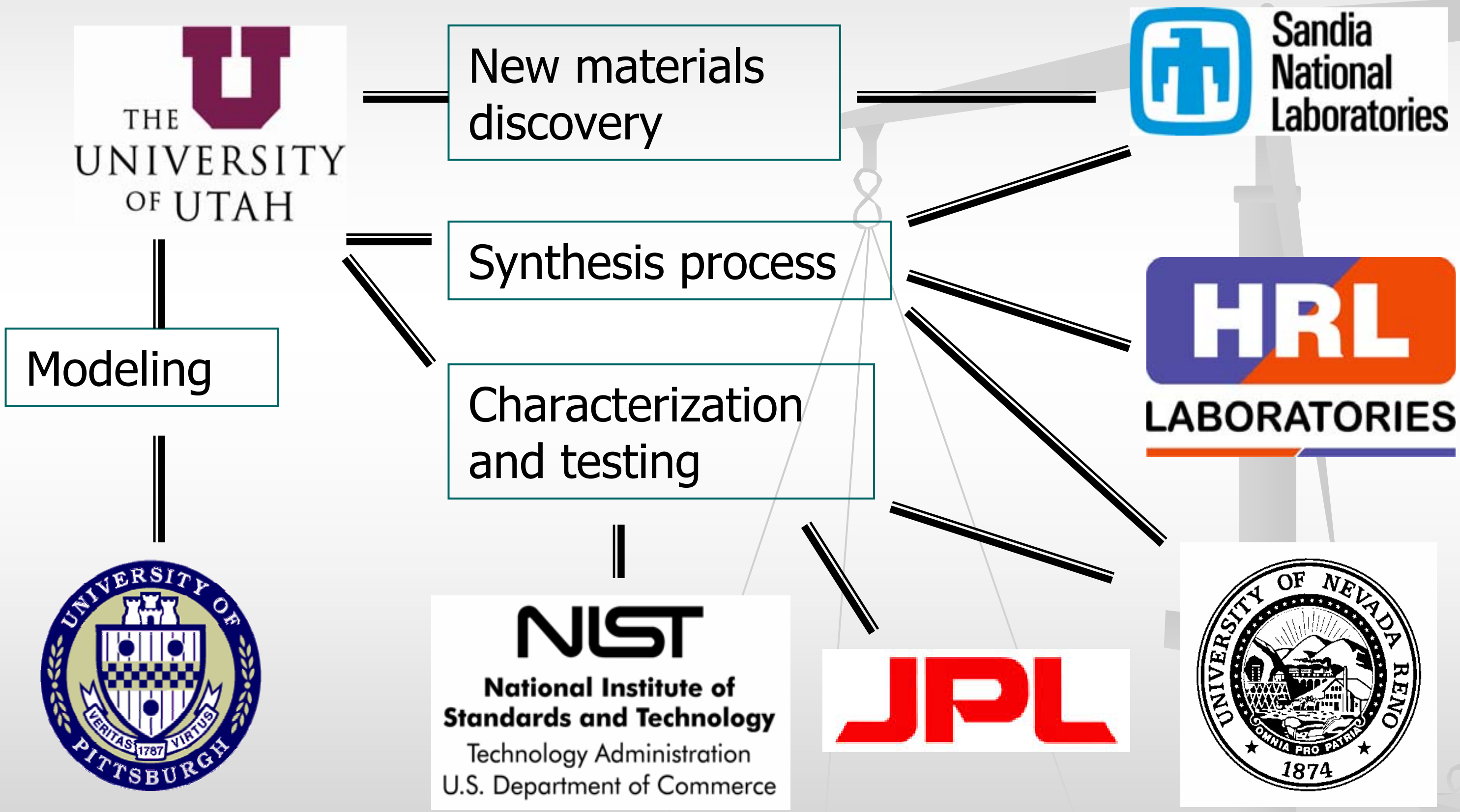
Barriers

- Kinetic properties of hydrogen release/uptake reactions of known metal hydrides are inadequate
- Reversible hydrogen content of known metal hydrides are not sufficient
- Effects of doping elements - hence the effects of the methods of doping - not fully understood
- Lack of commercially viable synthesis methods

Objectives

- Develop chemical vapor reaction process (CVS) for synthesis and discovery of nanosized solid hydrides that meet reversibility and kinetics requirement
- Demonstrate the effectiveness and unique properties of nanosized solid hydride materials
- Demonstrate the feasibility and economical viability of the chemical vapor phase synthesis process.

Partnering with the Center Member Institutions -



Technical Approach

To address the technical barriers -

- Improve kinetics of hydrogen release/uptake reactions by using nanoscaled powders
- Synthesize solid hydrides via chemical vapor phase reactions (CVS) to achieve
  - Homogeneity at atomic level
  - Fine tuning of chemical formula
- Discover new solid hydrides taking advantage of the flexibility of vapor phase reactions

Technical Approach

R&D path for achieving the goals -

- Develop new synthesis process at bench scale
- Evaluate the materials made by the CVS process and demonstrate
  - Kinetic properties
  - Reversibility
  - Cycle life /stability
- Scale-up issues of the process

Technical Approach

Basic concepts of CVS

CHEMISTRY – e.g. hydrogen reduction

$$m\mathbf{MCl}_x(g)+n\mathbf{NC1}_y(g)+0.5(mx+ny)\mathbf{H}_2(g) = \mathbf{M}_m\mathbf{N}_n(s)+(mx+ny)\mathbf{HCl}(g)$$

*where **M**: **Al, Mo***   ***N**: **Ni***

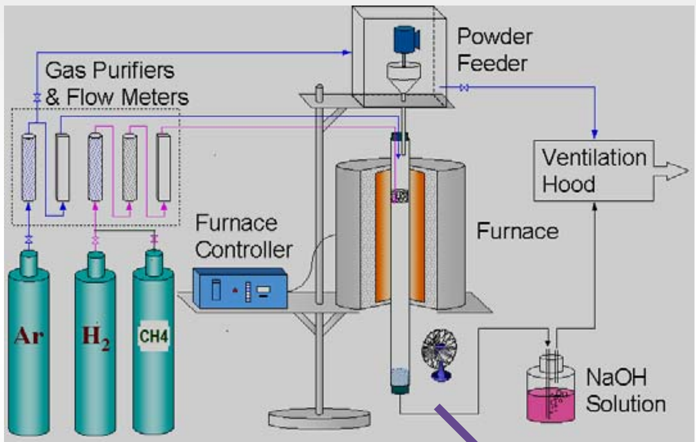
- A large number of **metallic**, **intermetallic** **or** **alloy** powders by **hydrogen** reduction
- An even **larger number** of different materials by **magnesium** reduction or a **plasma** process

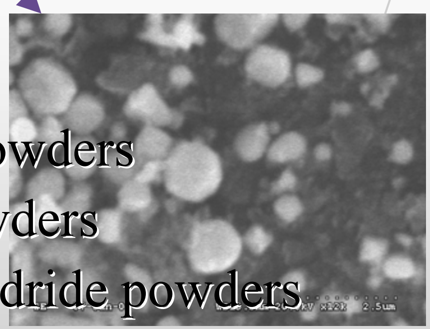
This project will exploit all or a combination of the options –

- *Reductions using H2 or Mg,*
- *Process using plasma or other high temperature processes*

Technical Approach

Chemical vapor synthesis of nanosized hydride powders





- Nano elemental powders
- Metal hydride powders
- Complex metal hydride powders
- Composite hydride powders

Unique advantages:

•Elements are mixed at the atomic level,
•Doping can be incorporated readily in the vapor phase,
•Compound formulations can be specifically engineered,
•Particle size from 10 to 200 nanometers,
•Composite of two can be made in one-step synthesis.

For example, complex metal hydrides

➢LiH + B + 3/2H2 = LiBH4

Technical Accomplishments/ Progress/Results

Start-up Activities – Setting up the synthesis reactor and characterization tools

- Installed an atmosphere controlled glove box system
- Installed a thermal gravimetric analyzer
- Installed a high pressure (35 MPa) autoclave
- Designed a CVS reactor
- Studied the sensitivity of $NaAlH_4$ to experimental procedural details
- Recruited two doctoral students
- Allocated and established lab space

Future Work

Vapor Synthesis of nanocrystalline Metal Hydrides

TASKS

I. Development of the chemical vapor synthesis process
II. Synthesis of nanocrystalline metal hydrides
III. Test and evaluation of new materials,
IV. Synthesis of nanocrystalline complex metal hydrides
V. Modeling of synthesis process

- Nano elemental powders
- Metal hydride powders
- Complex metal hydride powders
- Composite hydride powders

- Doping of metal hydrides including simple and complex hydrides
- Nanosized powders

Near term Plan – Fiscal Year 05

Task I Experimental set-up – Process development

Task II Vapor Synthesis – Doping of known promising hydrides – $NaAlH_4$, $LiAlH_4$, and MgH_2

Task III Small quantity test and evaluations – XRD, TGA, PCT, etc.

Goals

- Establish laboratory processing set-up for synthesis below 1200^{o}C
- Demonstrate feasibility of vapor phase synthesis and doping of nanocrystalline metal hydrides
- Demonstrate the effectiveness of doping via vapor phase

Near term Plan – Fiscal Year 05

Task I

Experimental set-up – Process development

- Resistant heating thermal reactor,
- Flame synthesis,
- Thermal plasma synthesis system.

Near term Plan – Fiscal Year 05

Task II — Vapor Synthesis – Doping of known promising hydrides

For example,

$$NaAlH_4 \Leftrightarrow \tfrac{1}{3} Na_3AlH_6 + \tfrac{2}{3} Al + H_2 \Leftrightarrow NaH + Al + \tfrac{3}{2} H_2$$

The mechanism of the role of TiCl3 doping is the subject of intense studies.

What is the state of Ti with respect to NaH and Al after dehydrogenation?

Near term Plan – Fiscal Year 05

Task II — Vapor Synthesis – Doping of known promising hydrides

We plan to experiment doping of Al and NaH via vapor phase reactions.

For example, nanosized Al powder can be made with Ti doping by

$$AlCl3(g) + Mg(g) = Al + MgCl2(g) \quad \text{at} >1000^{o}C$$

↑ $TiCl_4$

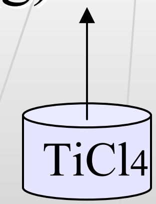
Near term Plan – Fiscal Year 05

Task II

Vapor Synthesis – Doping of known promising hydrides

And, nanosized NaH powder can also be made with Ti doping in the vapor phase by

$$\mathrm{Na\ (g, >800^{o}C) + H_2(g) = NaH\ (s, <400^{o}C)}$$



Near term Plan – Fiscal Year 05

Task II

Vapor Synthesis – Doping of known promising hydrides

- The doped Al and/or NaH can be used for cycling kinetic studies
- Other doping elements?

The results will be interesting from the perspectives of understanding the mechanisms of Ti doping, and different techniques for achieving optimum conditions, and the potential of nanosized powders.

Near term Plan – Fiscal Year 05

Task II

Vapor Synthesis – Doping of known promising hydrides

Explore the potential of other promising materials, e.g. doping $LiNH_2$ via vapor phase reactions:

$$LiCl\,(g) + NH_3(g) = LiNH_2 + HCl$$

$TiCl_4$

And

$$6Li\,(g) + N_2\,(g) = 2Li_3N$$

$TiCl_4$

Synthesis of Complex Metal Hydrides via the Chemical Vapor Synthesis Approach

Exploit unique advantages of the process:

- ✓Chemical elements involved in the reaction are mixed at the atomic level,
- ✓Doping elements or alloying additives can be incorporated readily in the vapor phase,
- ✓Compound formulations /atomic ratios can be specifically engineered,
- ✓Particle size can be controlled from 10 to 200 nanometers,
- ✓Composite of two or more compounds can be made in one-step synthesis.

Overall Plan