High Throughput Combinatorial Chemistry Development of Complex Metal Hydrides

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– A participant of the DOE Metal Hydride Center of Excellence –

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Project ID #
STP29

Overview

Timeline

- Project start date: 01/2005
- Project end date: 09/2009
- Percent complete: New Start

Budget

- Total project funding expected
  - DOE: $720K
  - Intematix: $180K
- Funding for FY05: $150K

Overview

Barriers

- Hydrogen capacity and reversibility
- Limited selection of materials to meet gravimetric targets
- Volumetric densities trend opposite to gravimetric gains
- Safety in use of light-with reactive materials
- Cost of hydrogen storage systems
- Energy transfer requirements for H_2 storage systems
- Kinetics of solid-state reactions
- Cycle life, reliability and durability

Partners

- Collaboration with Sandia Lab and HRL on complex hydrides and catalysts
- Other collaborations with Center partners based on future discoveries

Objectives

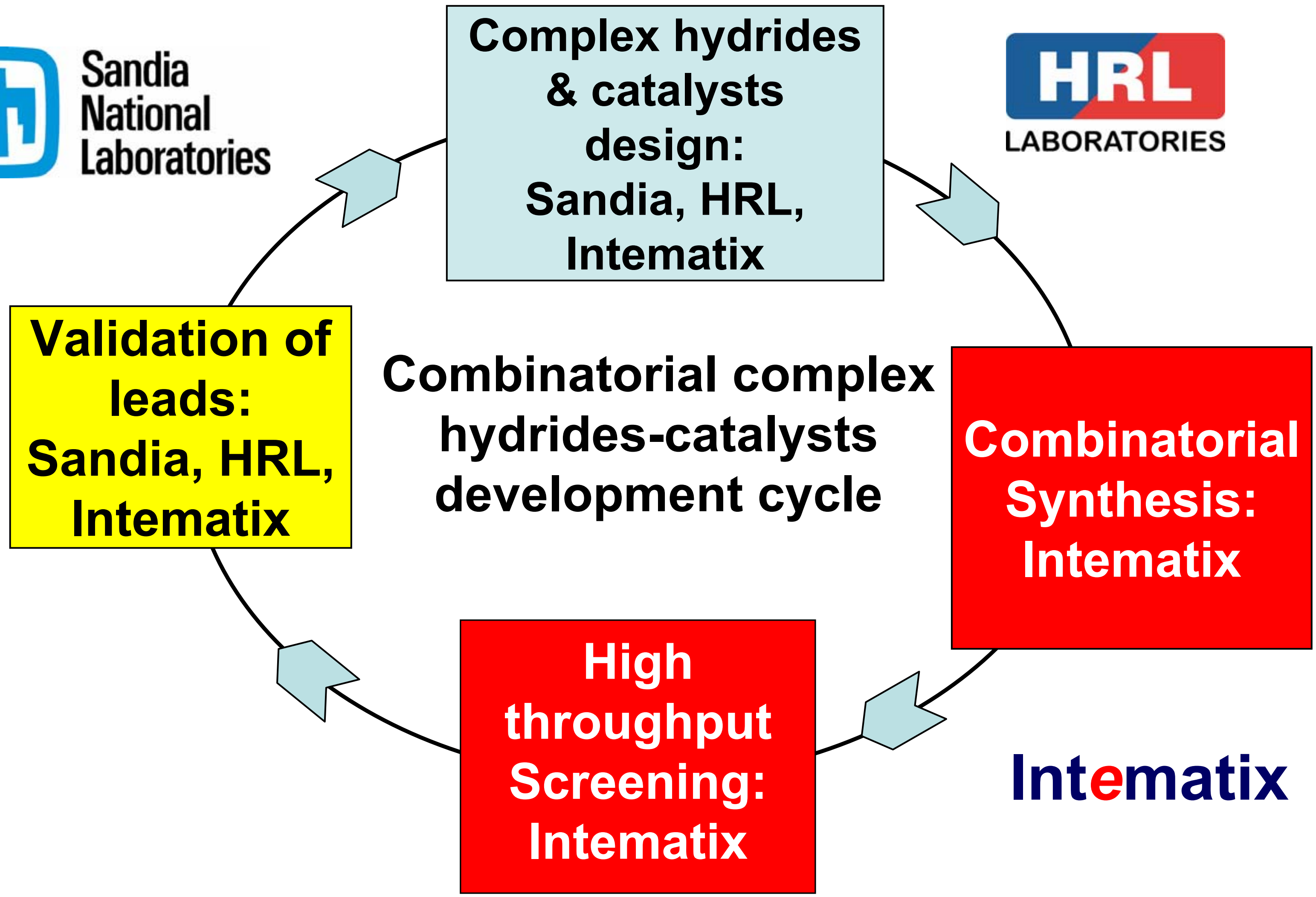
To assist DOE in achieving the DOE/ FreedomCAR target of a hydrogen storage system of 6.0 wt.% by 2010

- To validate the combinatorial synthesis tools and develop the high throughput screening techniques for metal hydrides-catalysts (current FY)

- To conduct high throughput, systematic and comprehensive investigations of catalyst effects on metal hydrides for optimization of reversibility and kinetics (next FY and beyond)

- To explore ternary and quaternary phases metal hydride systems (next FY and beyond)

Approach


Complex hydrides & catalysts design: Sandia, HRL, Intematix
Combinatorial Synthesis: Intematix
High throughput Screening: Intematix
Validation of leads: Sandia, HRL, Intematix
Combinatorial complex hydrides-catalysts development cycle

Concept of Approach

- **Combinatorial Synthesis**
  - Intematix proprietary combinatorial synthesis technology can generate hundreds of different hydrides/catalysts combinations (thin film or nano-particles) in one experiment under oxygen free environment

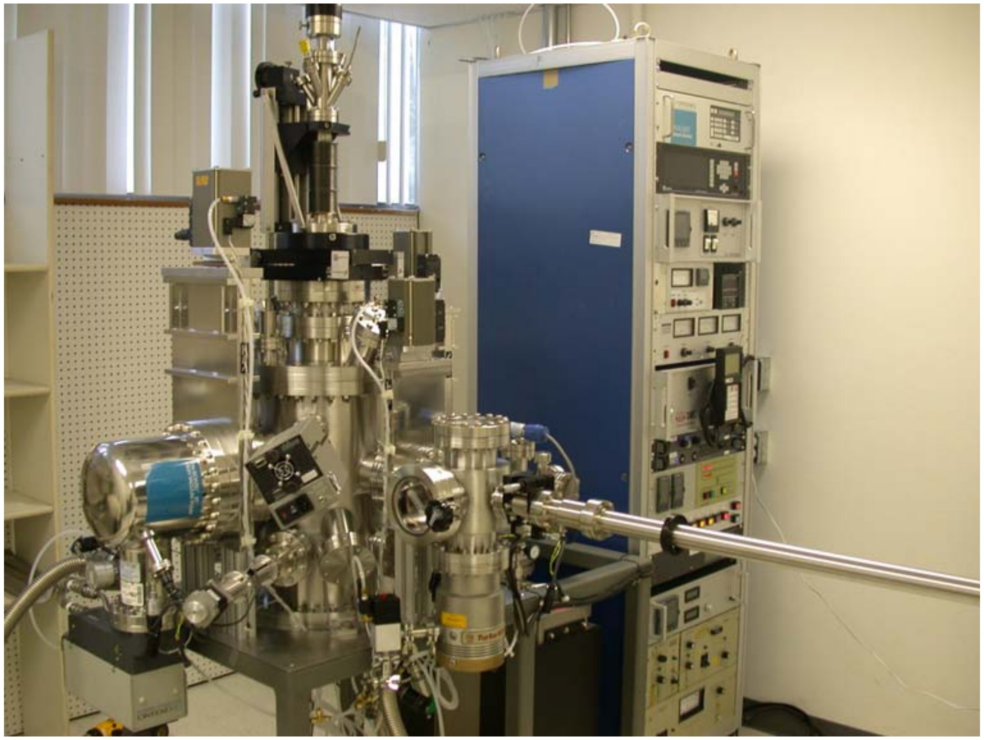
- **High-throughput Screening**
  - Intematix proprietary combinatorial high-throughput screening technology can test promising catalysts under realistic reaction conditions (high pressure, elevated temperature, and oxygen-free)

Challenging Issues

- Dilemma between increasing interacting surface and surface contamination – *in situ* oxygen free transfer between synthesis and screening
- Difficulty in high-throughput screening of arrayed samples at high pressures (up to 150 atms) and elevated temperatures (up to 400^{o}C)
- Defining initial screening parameters (hydrogen concentration, end products, reaction rate, etc.) for the arrayed samples

Technical Accomplishments

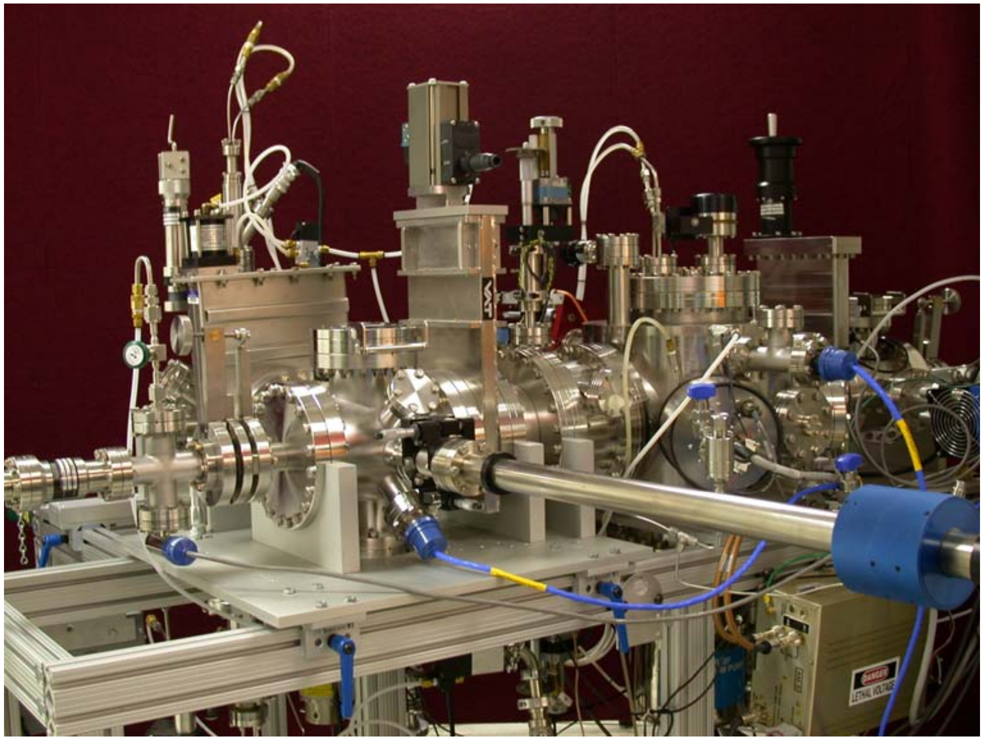
Validated combinatorial molecular bean epitaxy (MBE) system for synthesizing thin film complex hydrides containing air-sensitive elements, such as Li, Na, Mg



A high temperature effusion cell (up to 1900ºC) has been installed for catalyst elements (such as Ti) incorporation

Technical Accomplishments

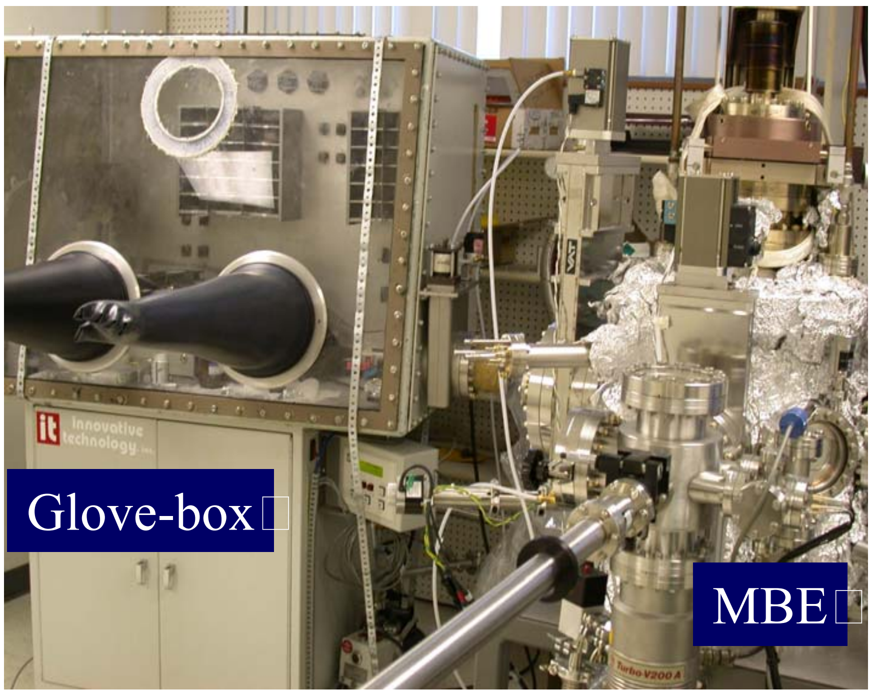
Validated combinatorial ion-beam sputtering (IBS) system for synthesizing complex metal hydride alloys containing air-sensitive elements, such as Li, Na, Mg



A getter pump on the combi-IBS system has been installed to reduce the residual O_2

Technical Accomplishments

Set up an air-tight oxygen-free glove box for *in situ* sample transfer and characterization



The glove box and the MBE growth chamber are directly connected to allow samples be transferred in oxygen-free environment

Technical Progress

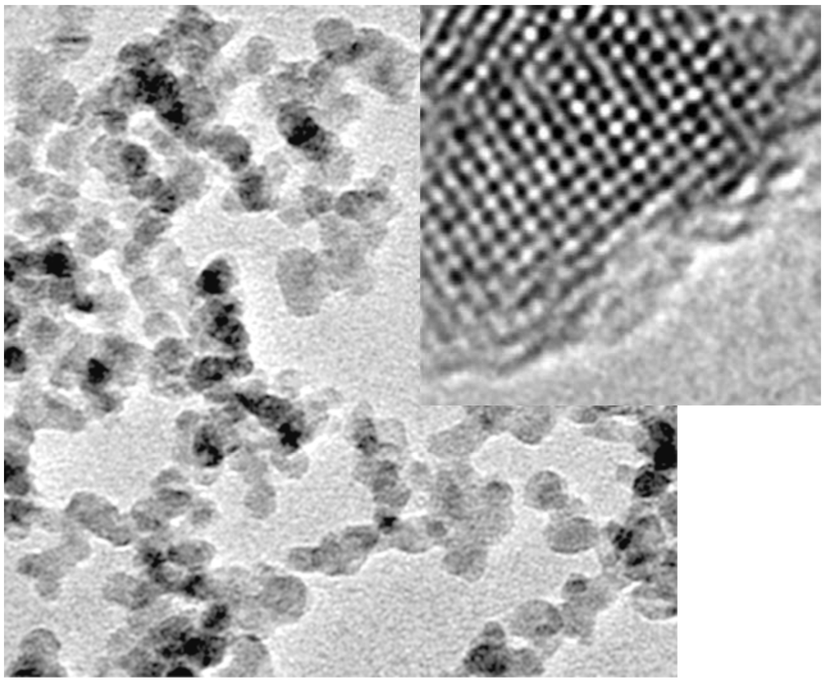
Validating combinatorial nano-particle (CNP) synthesis system as the third synthesis method - a proprietary combinatorial materials synthesis technique Intematix has recently developed

The advantages:

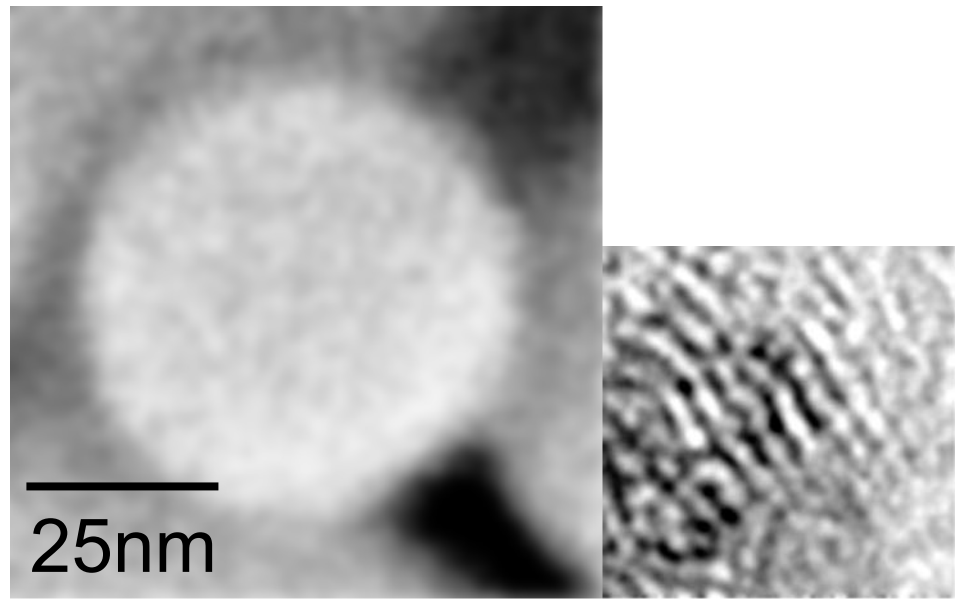
- Small particle size~10-50nm
- Narrow particle-size distribution
- Accessible to most elements
- Can optimize size and composition rapidly

Technical Results

The CNP system is very unique and powerful in high-throughput synthesis of nano-particles



TEM images of TiO_2 nano-particles prepared by CNP under optimized conditions.



YIG nano-particle prepared by CNP under preliminary condition. Particle has well-defined circular shape. The left image shows the crystal structure is not well-ordered.

Technical Progress

Designed and developed a high pressure/ temperature optical testing system for hydriding, dehydriding, screening of libraries

- Pressure range (H_2): 1-150 atms
- Sample temperature: up to 400^{o}C
- Portable for easy transferring between sample preparation/loading and testing/measurement stations
- Suitable for the high-throughput screening of combinatorial hydride library using a variety of optical measurements during hydriding/dehydriding

Addressing Barriers

- Hydrogen capacity and reversibility – *new complex metal hydrides may provide higher hydrogen capacity and reversibility*
- Safety in the use of light-weight reactive materials – *new complex hydrides together with new catalysts may require lower pressure and temperature for hydriding and dehydriding*
- Cost of hydrogen storage systems– *lower P&T will reduce the cost of storage systems*
- Energy transfer requirements for H_2 storage systems - *new catalysts may enable high efficiency dehydrogenation and rehydrogenation*
- Kinetics of solid-state reactions - *new catalysts may accelerate solid-state reaction process*

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Future Plans

- **Remainder of FY2005**
  - *Catalysts screening*
    - Identify key parameters for high throughput *in situ* optical screening
    - Demonstrate effectiveness of catalyst screening methodology for model reaction, e.g.

$$3NaAlH_4 \xrightarrow{Ti} Na_3AlH_6 + 2Al + 3H_2$$

$$\hookrightarrow 3NaH + Al + 3/2H_2$$

$$\hookrightarrow 2Na + 3/2H_2$$

  - *Validate the capability of CNP for synthesizing metal hydride/catalyst nanoparticles*

Future Plans

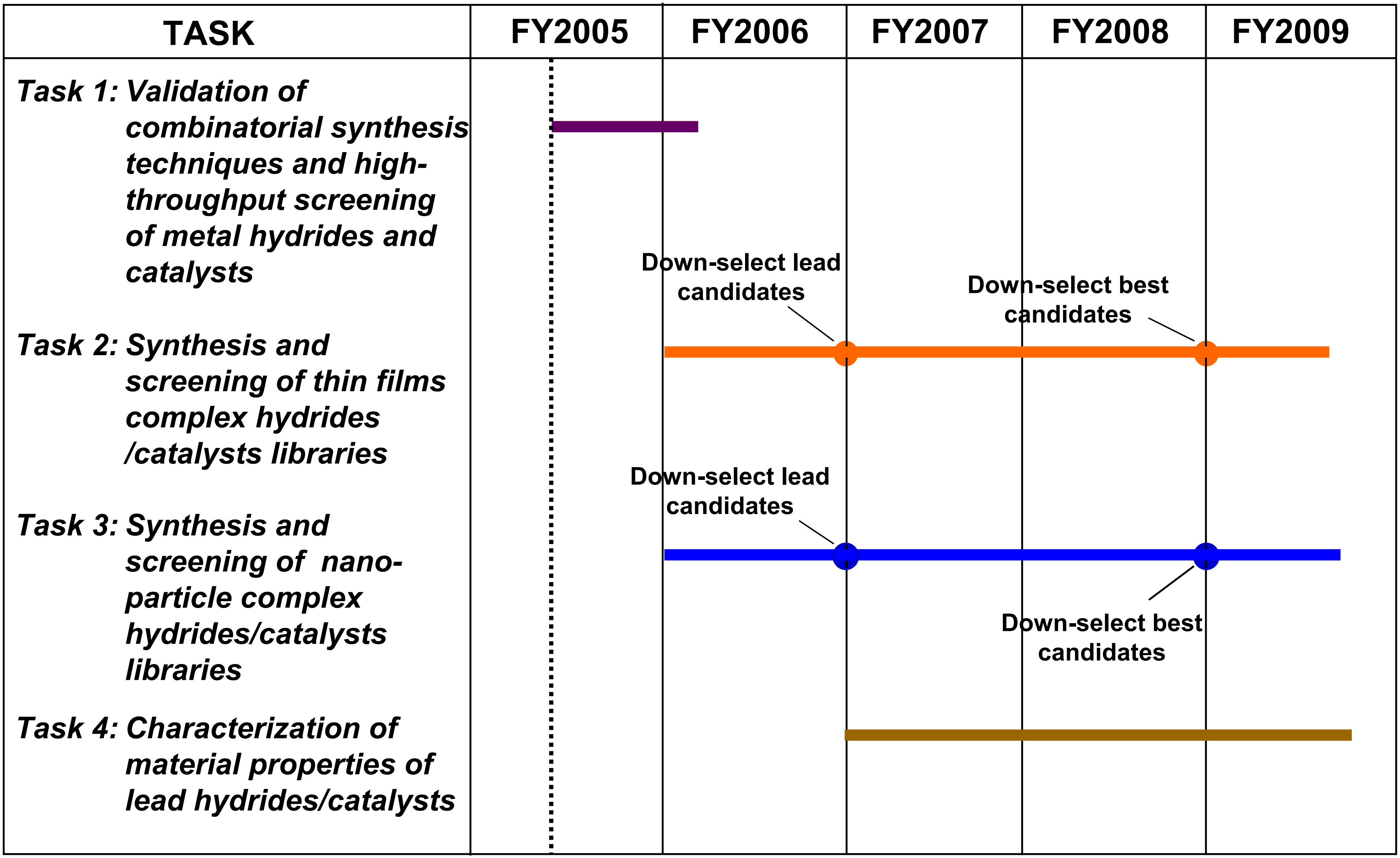
- **FY2006**
  - *Conducting high throughput, systematic and comprehensive investigations of catalyst effects on complex metal hydrides for optimization of reversibility and kinetics*, *e.g*.

$$2LiBH_4 + MgH_2 \longleftrightarrow 2LiH + MgB_2 + 4H_2$$

HRL has established this reversible system with a theoretical capacity of 11.4 wt %. However, the reaction is too slow and operating temperature is higher than desirable without catalyst. We will primarily focus on the catalysts for the reaction process.

  - *Nano-particle precursors/catalysts using CNP for the same reaction process*

Summary of Future Plans



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