Intematix

DOE Hydrogen Program

High Throughput Combinatorial Chemistry Development of Complex Hydrides

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Intematix Corporation

In Association with the DOE/SNL Metal Hydride Center of Excellence

Project ID #STP25

Overview

Project Timeline

- Start date: March 2005
- End date: February 2010
- 40% Percent complete

Barriers

- Slow kinetic reaction
- Thermodynamic stability
- Low reversible storage
- In-situ thin film characterization

Budget

- Total project funding
  - ✓ DOE share: $720K
  - ✓ Contractor share: $180K
- Funding received in FY06: $300K
- Funding for FY07: $300K

Partners

- HRL
- Sandia National Lab
- Additional MHCoE partner collaborations in future

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Objective

Overall

- Identify and synthesize novel metal hydride systems using high-throughput combinatorial technique
- Identify catalysts to achieve fast reaction kinetics for metal hydride systems and thus support DOE's 2010 targets for start time (4 s), flow rate (0.02 (g H_2/s)/kW) and refill time (3 min)

2006

- Validate combinatorial nano-synthesis systems for catalyst discovery
- Screen and identify better catalysts for MgH_2 + Si system
- Screen and identify better catalysts for complex $LiBH_4$ + MgH_2 dehydrogenation and hydrogenation

2007

- Synthesize and characterize novel complex hydride materials in thin films format
- Continue catalyst screening on $LiBH_4$ + MgH_2 system based on leads obtained in 2006
- Screen catalysts for various other partners/systems (GROUP A and GROUP B of MHCoE)

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Accomplishments

- Validation of two combinatorial synthesis techniques
- Validation of three high throughput screening techniques
- Catalyst screened: >50 metals and alloys
- Found better catalyst for MgH_2 + Si dehydrogenation
  - High throughput screening did not identify any effective rehydrogenation catalyst up to reactor's P&T limitations
  - System down-selected due to lack of rehydrogenation
  - High throughput screening enabled a rapid decision on system, enabling focus on newer, possibly regenerable systems
- A few catalyst leads found for LiH+MgB_2 system
- Thin film materials syntheses underway on both known and novel materials
- Patents filed: 2

- Intematix has accomplished validation of its tools for high-throughput combinatorial catalyst screening roughly nine months ahead of schedule

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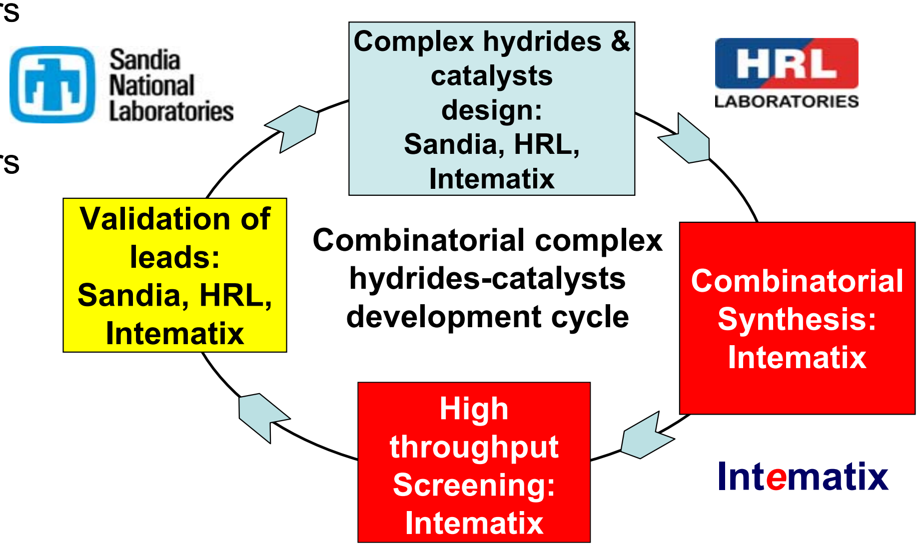
Please see following slides for details

Approach

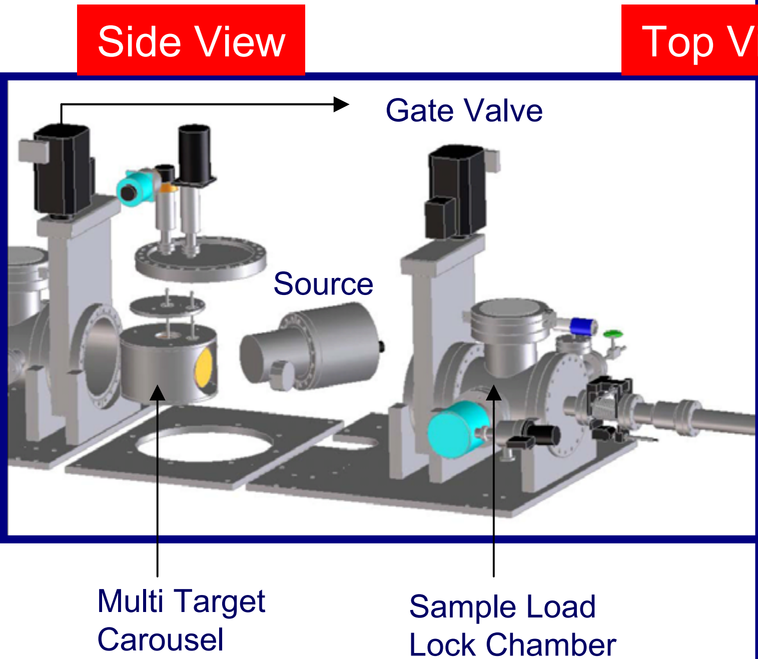
Methodology used for metal hydride synthesis and combinatorial catalyst screening

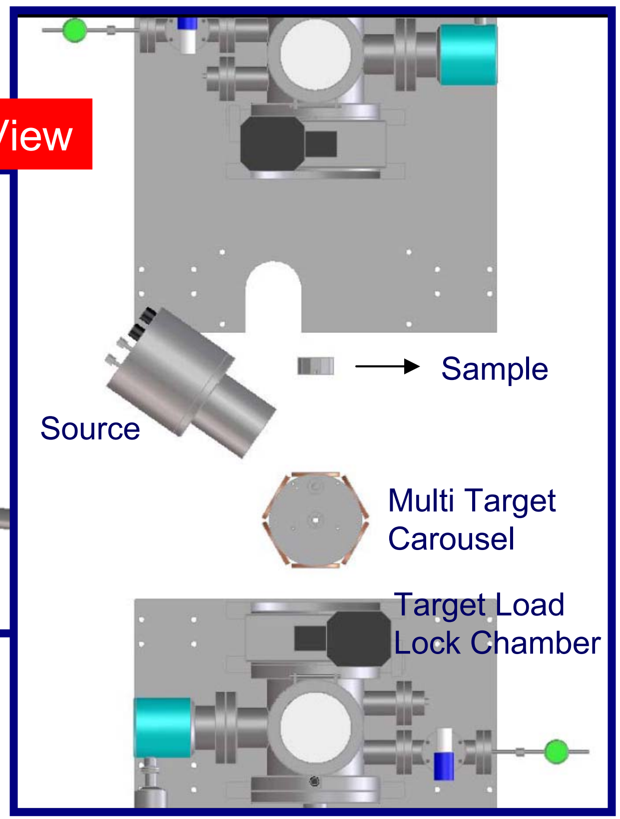
- Search Thermodynamic Database to Identify Metal Hydride Candidates ⇐ Intematix
- Metal Hydride Materials Synthesis ⇐ MHCoE partners
- Verify Reaction Pathway Identify Reaction Barrier ⇐ MHCoE partners
- Design Combinatorial Catalyst Synthesis Methods ⇐ Intematix
- Design High Throughput Screening Methods ⇐ Intematix

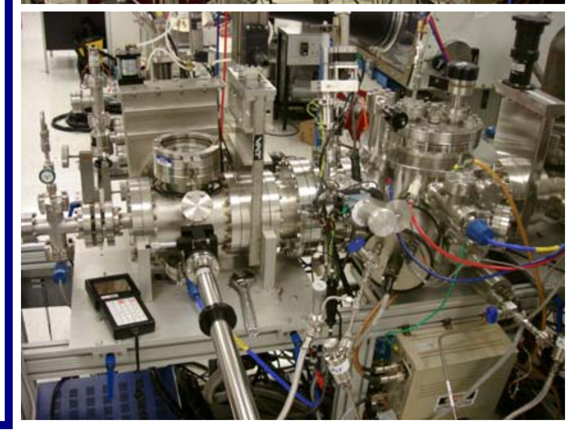


Combinatorial Synthesis Approach-1

Validated Combinatorial Ion Beam Sputtering (CIBS) technique for metal hydride catalyst synthesis







Successful identification of effective catalysts for MgH_2 + Si and $LiBH_4$ + MgH_2 systems

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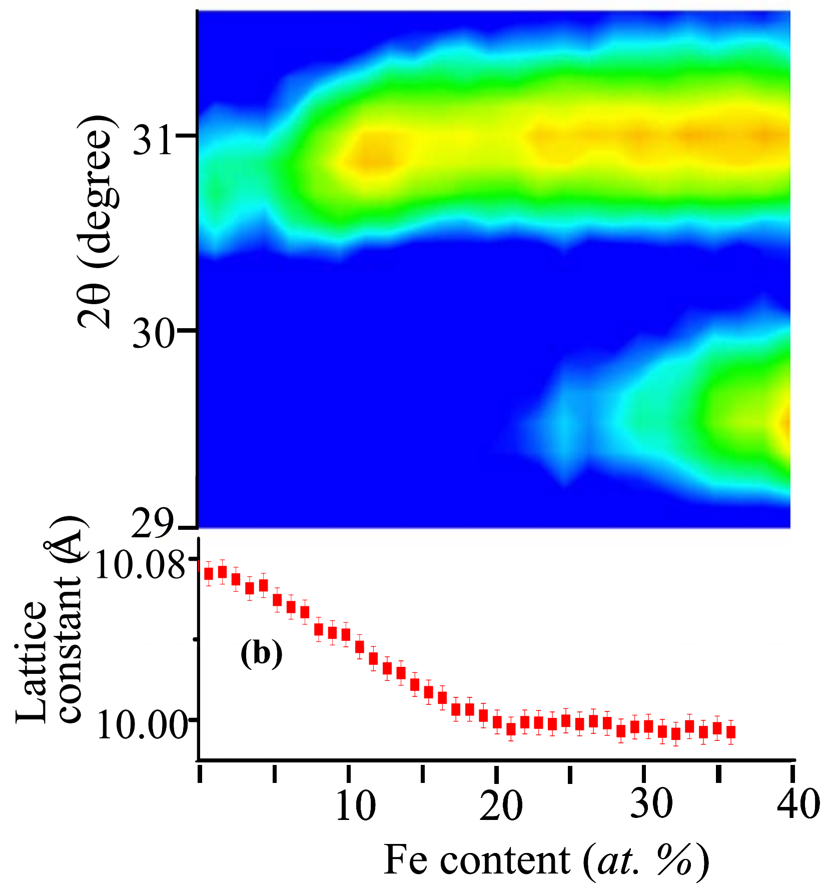
Materials grown by CIBS and its Validation

Metal catalyst library, new materials growth and confirmation

1) Deposit uniform thin layer of the metal hydride material received from MHCoE partner on desired substrate under inert atmosphere
2) Transport to CIBS sample chamber for metal library deposition (alternately, metal library can be grown at the bottom and annealed for alloy formation before applying hydride materials)
3) Confirmation of alloy formation on identically grown library by XRD
4) For new material synthesis, multiple targets have been used to obtain desired compositional spread.

Typical example of solubility confirmation of $In_{2-x}Fe_xO_3$ materials grown by CIBS



J. He et al., APL **86**, 052503 (2005)

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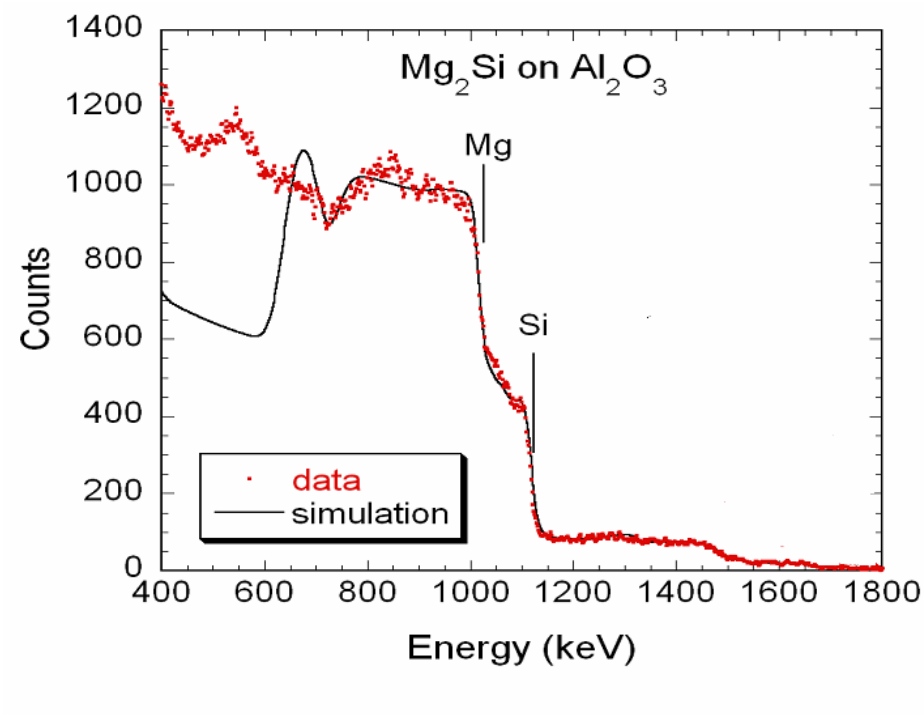
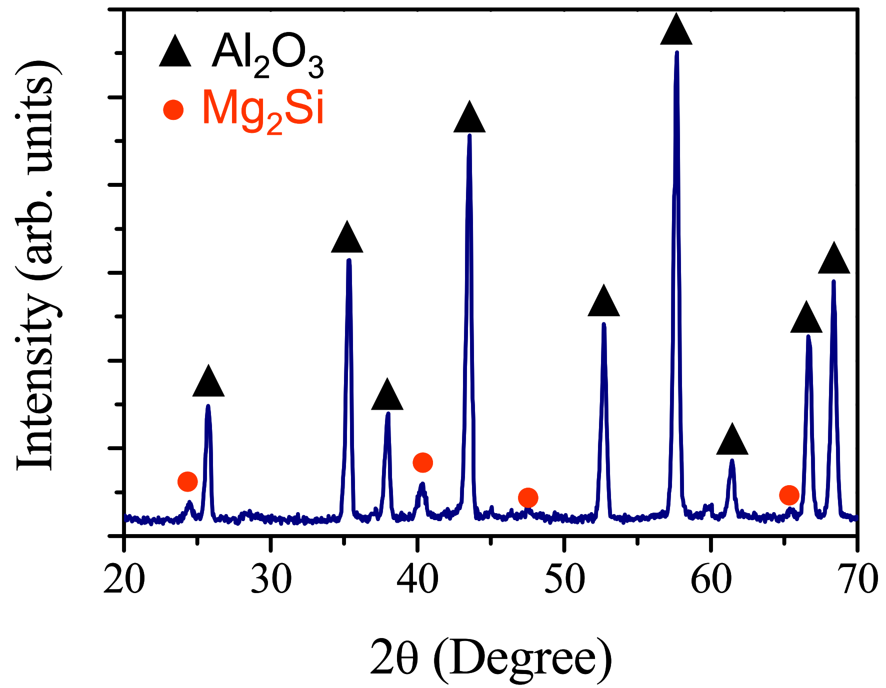
Materials grown by CIBS and its Validation

Compositional confirmation of Mg_2Si system by Rutherford backscattering



Structural confirmation of formation of Mg_2Si by XRD



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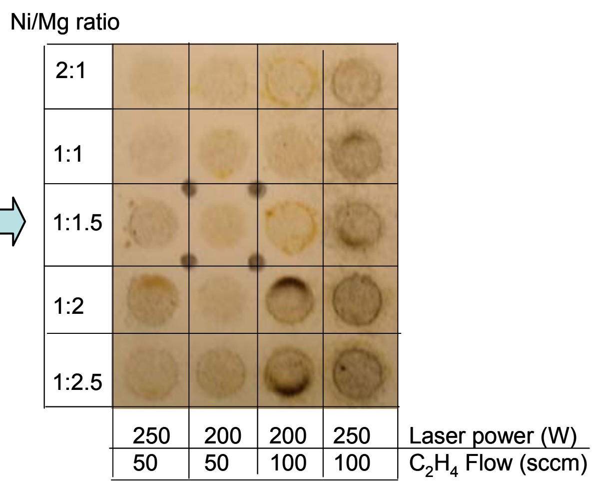
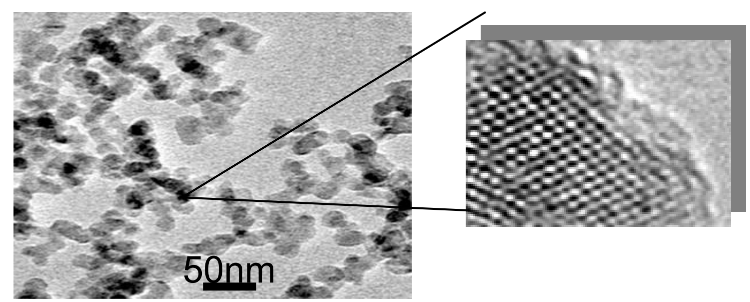
Complementary Synthesis Technique – Combinatorial Nano-particle (CNP) System

Capabilities:

- Synthesis of nanoparticles of metals, oxides, hydrides, nitrides, carbides, sulfides, etc.
- Reproducible high crystalline quality nanoparticles with narrow size distribution (< ±30%)
- Synthesis of combinatorial nano-particle libraries with controllable parameters:
  - particle size
  - material composition
  - synthesis conditions
- System has been validated for bimetal alloy libraries

Typical Example





This system has been used to generate Ni particles for Mg_2Si

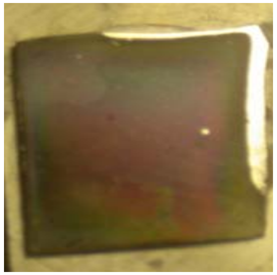
High Throughput Screening Approach-1

Optical Measurements

1) Using high pressure Optical Chamber
2) Max. Pressure: 600 psi
3) Max. Temperature: 350 ºC
4) Maximum size: 1.3” x 1.3” sample

Validation on Mg film

Mg thin film (250 nm) before hydrogenation



MgH_2 thin film after hydrogenation

Methodology:

At constant pressure:

Observe the change in optical properties of the sample with temperature

At constant temperature:

Observe the of change in optical properties of the sample with pressure

Conclusion:

A change in color at a particular catalyst, indicates that a reaction may have taken place with the sample (lead generated for further catalysis study)

Limitations: *Max. Pressure: 600 psi; Temperature: 350 ºC*
Leads require quantitative confirmation by MHCoE Partner collaboration

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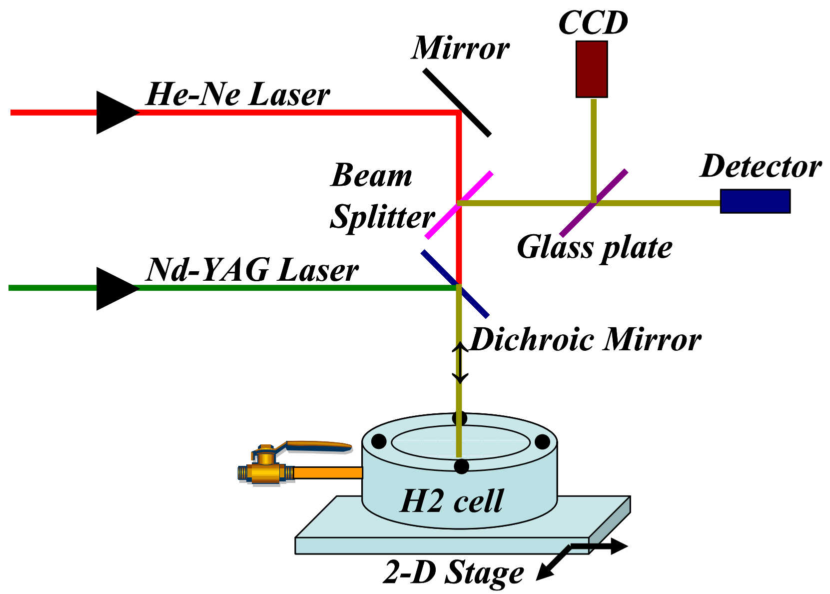
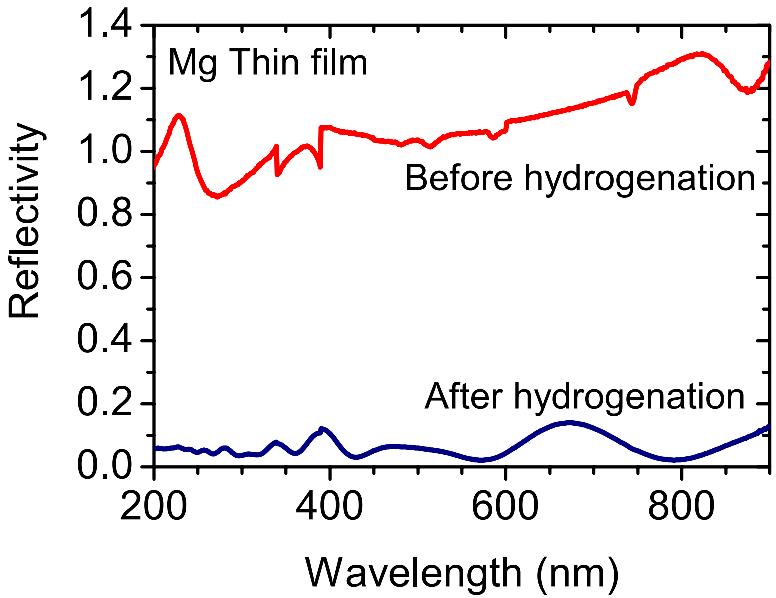
High Throughput Screening Approach-2

Reflectivity Measurements



Validation on Mg film



- Hydriding at 350 psi H_2 and 220 °C for 2 hours
- Metallic mirror-like Mg film converts to MgH_2 layer
- Drastic change in reflectivity during hydrogenation

Limitations: *Only thin film samples can be measured, not powders. No on-site high temp./pressure hydrogenation*

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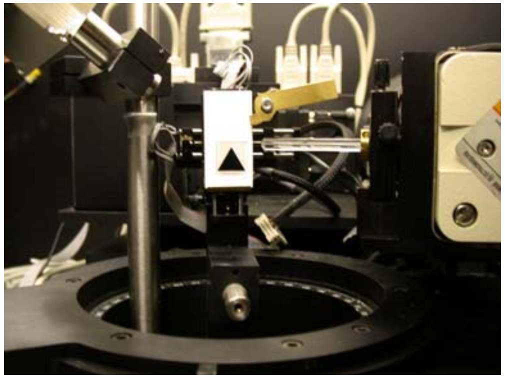
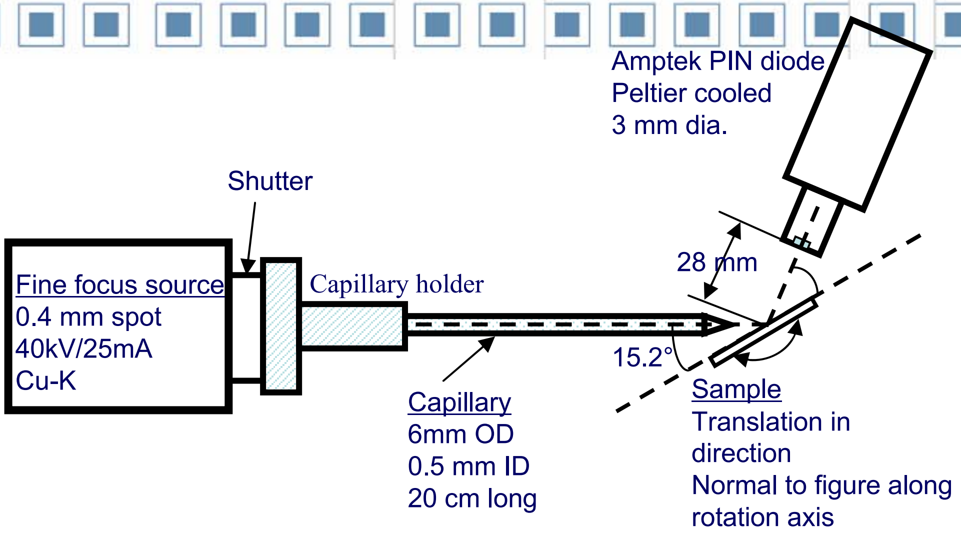
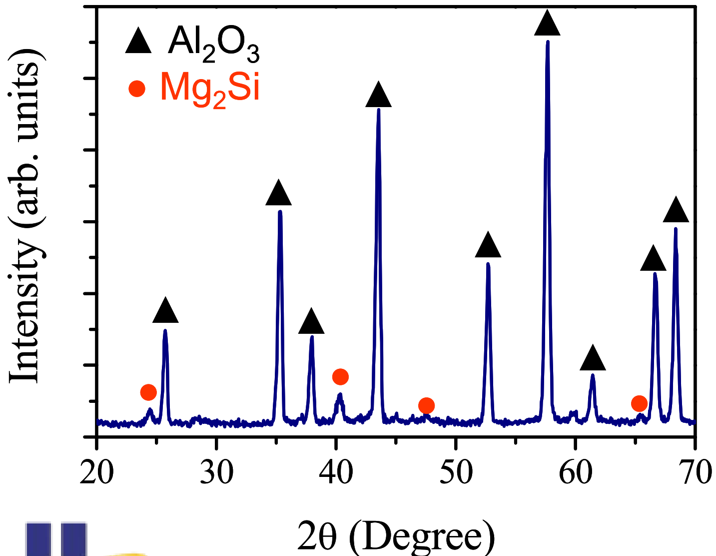
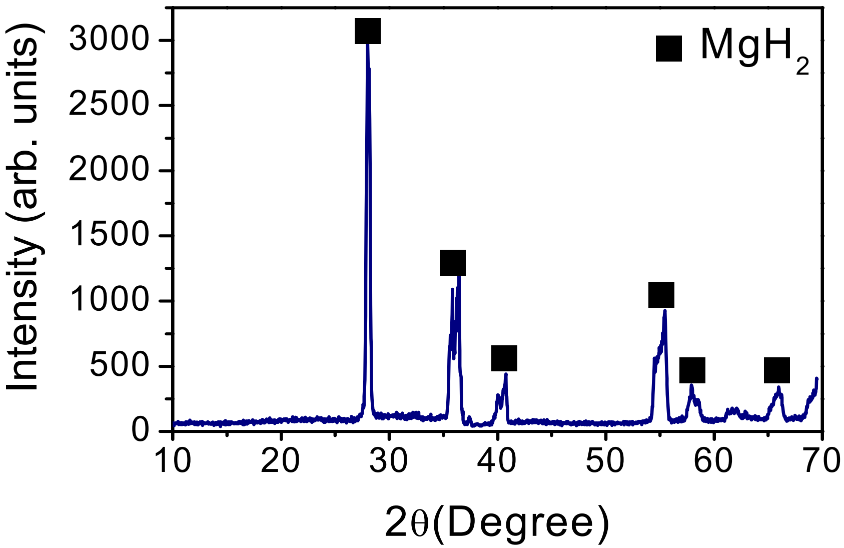
High Throughput Screening Approach-3

Micro-beam scanning XRD









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Limitation: *Not configured for highly air sensitive materials*

Experimental Detail
Catalyst Screening for MgH_2 + ½ Si – 1

- Ball-milled MgH_2+Si mixture without catalyst was obtained from HRL.
- The mixture was applied to a substrate without changing morphology or particle size. Catalysts were synthesized on the mixture.
- Under Ar atmosphere, the catalysts and hydride material were transferred to a reactor cell fitted with an optical window.
- For each catalyst library, three experiments were carried out.
  - Under conditions used by HRL, hydride materials with known catalyst were heated. The temperature profile of optical property variations matched previously reported results well.
    - ✓ *This supports the validity of the screening methodology.*
  - In a second experiment, catalyst libraries were heated at 5 ºC/min up to 350 ºC in 1.5 atm H_2. The optical properties of libraries were monitored; but no changes (recharge) were observed.
  - In a third experiment, the samples were heated under Ar at 3 ºC/min up to 170 ºC and then at 1 ºC/min up to 250 ºC. Temperature was held at 250 ºC for 20 minutes before cooling. Of the catalysts screened, a few showed obvious changes in optical properties.

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Experimental Detail
Catalyst Screening for MgH_2 + ½ Si – 2

- The temperature and pressure was varied widely from high to low to moderate for more experimental results.
- Catalyst screening for Mg_2Si hydrogenation was also performed. More than 20 catalysts were screened e.g., Mn, Ni, Ti, V, Cr, Nb, Pt, etc. and combinatorial alloys of the same.
  - *Unfortunately, none of the catalysts screened were found to be effective for hydrogenation of the material system.*

- *Without rehydrogenation – system is NO-GO.*

- *Methodology for catalyst screening validated by 'rediscovery' of known catalyst as well as discovery of a new, better catalyst.*

Intematix is using a similar strategy for the LiH + MgB_2 system and will continue to use this methodology for new metal hydride systems received from MHCoE partners

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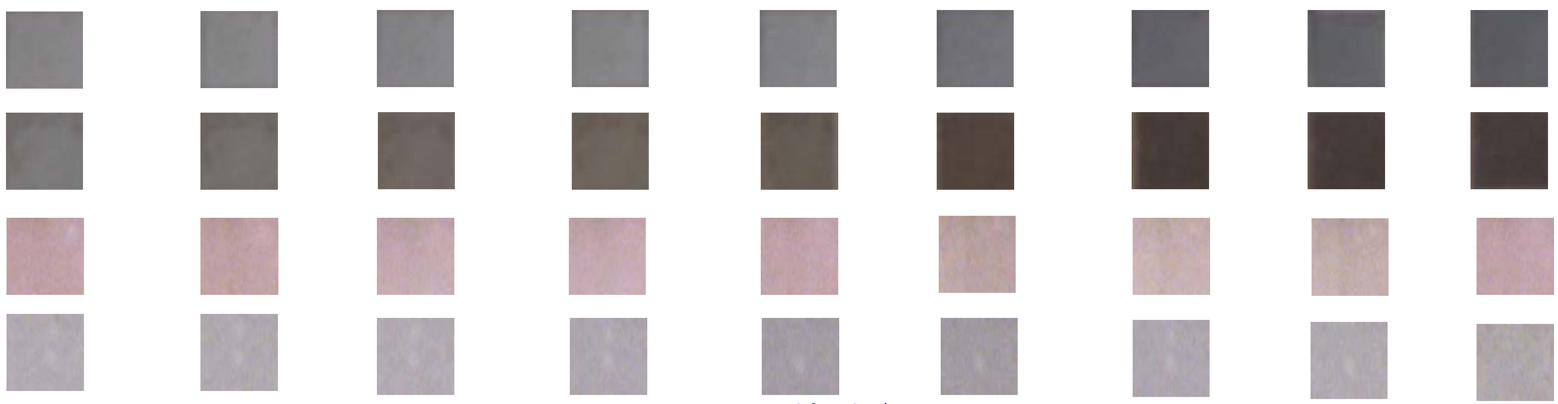
Results-Catalyst Screening for MgH_2 + ½ Si

Optical Properties:

Color changes of catalysts during high temperature/pressure dehydrogenation reaction suggests catalytic effect.

25 °C 140 °C 180 °C 190 °C 210 °C 260 °C 300 °C 320 °C 350 °C

Ni
Mn
Cu
Fe



- Reproducibility confirmed
- Screened Catalysts (~ 50 catalysts)
  1) 1st row transition metals
  2) Some 2nd row transition metals
  3) Combinational libraries of 1) and 2)

Catalysis screened: Ni, Mn, Cr, Fe, Ti, Nb, Pt, V, Cu, and alloys of all.

Cu and Fe NOT effective

Most Effective Catalysts: Ni and Mn

HRL has confirmed these results with their own experimental work

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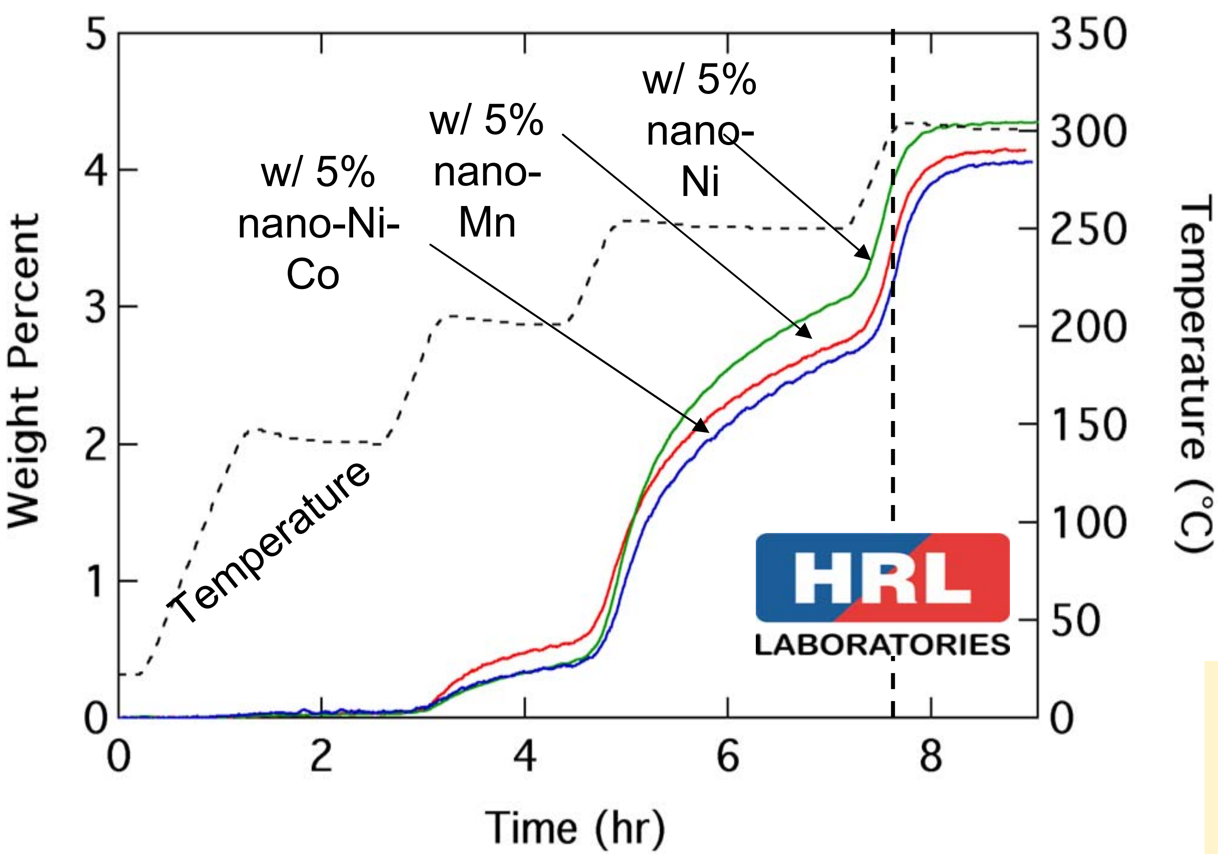
Hydrogen Desorption Results

MgH_2/Si + Catalyst



- Ramping rate of 3 ºC/min with dwelling time at intermediate steps (Intematix).
- A similar approach was used by HRL: 2 ºC/min.
- Pure MgH_2 + Si takes longer for onset of decomposition (approx. 7.5 hrs – shown by dashed line)

Nano-Mn, Ni and Ni-Co give similar enhancements for dehydrogenation

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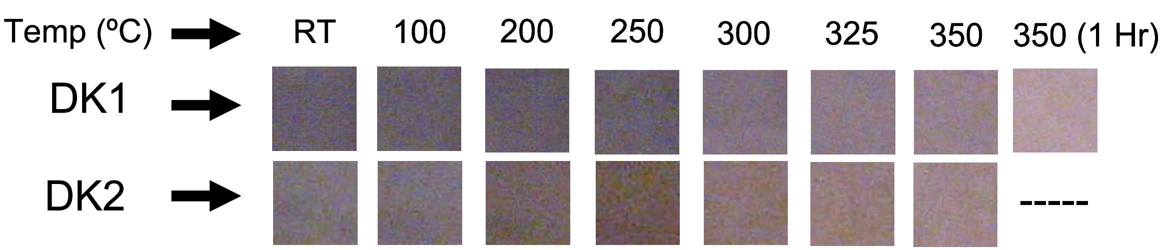
Results-Catalyst Screening for LiH + MgB_2

Strategy

1. Metal Hydride Powder from MHCoE partners ⇐ MHCoE partners
2. Preparation of uniform thin film layer on substrate ⇐ Intematix
3. Design Combinatorial Catalyst Library ⇐ Intematix
4. Verify catalysis reaction pathway using high-throughput Screening techniques ⇐ Intematix
5. Confirmation from MHCoE partner ⇐ MHCoE partners

Color changes of catalysts during high temperature/pressure reaction suggest catalytic effect



Effective Catalysts: DK1=pure metal, DK2=alloy

More catalyst screening is underway, desorption/sorption experiment will be carried out with HRL by end of this Year

Future Work

- Continue combinatorial *catalyst screening* for the $LiH+MgB_2$ system after further characterizing the current catalyst library in collaboration with HRL. (*through December 2007*)

- Try to understand HRL's observation that $LiBH_4+MgH_2$ melts during dehydrogenation by using Intematix's tools. It has been realized that starting with this mixture for desorption does not give good reversibility because $LiBH_4$ melts. *(August 2007)*

- Perform complementary characterization techniques such as *in-situ* XRD, Raman spectroscopy and high-temperature/high-pressure testing of metal hydride thin films in collaboration with SNL. (*through March 2008*)

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Future Work

- Synthesis of $Ca(BH_4)_2$ thin films and catalyst screening using Combinatorial Sputtering technique. However, prior to that, it is important to determine the reaction kinetics for the hydrogen desorption from $Ca(BH_4)_2$ in bulk. (*through March 2008*)
- Combinatorial synthesis and search of catalysis for new *complex* metal hydride materials. *(through September 2008)*

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Summary

Goal:

Identify catalysts which improve the kinetics and selectivity for desired metal hydride systems to enable an on-board hydrogen storage system which meets DOE 2010 targets.

Approach:

Combinatorial nano-catalyst synthesis and high throughput screening to speed up catalyst discovery.

Technical Accomplishment and Results:

(1) Improvement in design, setup and validation of combinatorial nano-catalyst synthesis and high throughput catalyst screening processes.

(2) Ni and Mn were found to be the most effective catalyst for MgH_2 + Si system for dehydrogenation. But, NO Reversibility. So, NO-GO system.

(3) Identified a few alloy leads which appear to improve kinetics of LiH + MgB_2 system. But more catalyst screening is necessary for further improvement.

Proposed Future Research:

Continue high throughput screening of catalysts for LiH + MgH_2 and other candidates systems such as $Ca(BH_4)_2$. Optimize & improve synthesis and screening methods.

Improved catalyst measurement sensitivity (using laser reflectivity).

More characterization and synthesis utilizing customized equipment built at Intematix.

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