High Throughput Combinatorial Chemistry Development of Complex Hydrides

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Intematix Corporation

In Association with the DOE/Metal Hydride Center of Excellence

Project ID #STP17

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Overview

Project Timeline

- Start date: March 2005
- End date: February 2008
- 100% Percent complete

Budget

- Total project funding
  - ✓ DOE share: $870K
  - ✓ Contractor share: $218K
- Funding received in FY07: $270K

Partners

- HRL
- Sandia National Lab

Barriers

- Slow kinetic reaction (E)
- Thermodynamic stability (J)
- Low reversible storage (P)
- In-situ thin film characterization (Q)

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
- Support other MHCoE partners for thin film deposition

2008

- Validate Combinatorial Optical Screening technique for complex hydrides such as $NaAlH_4$ and $LiBH_4$

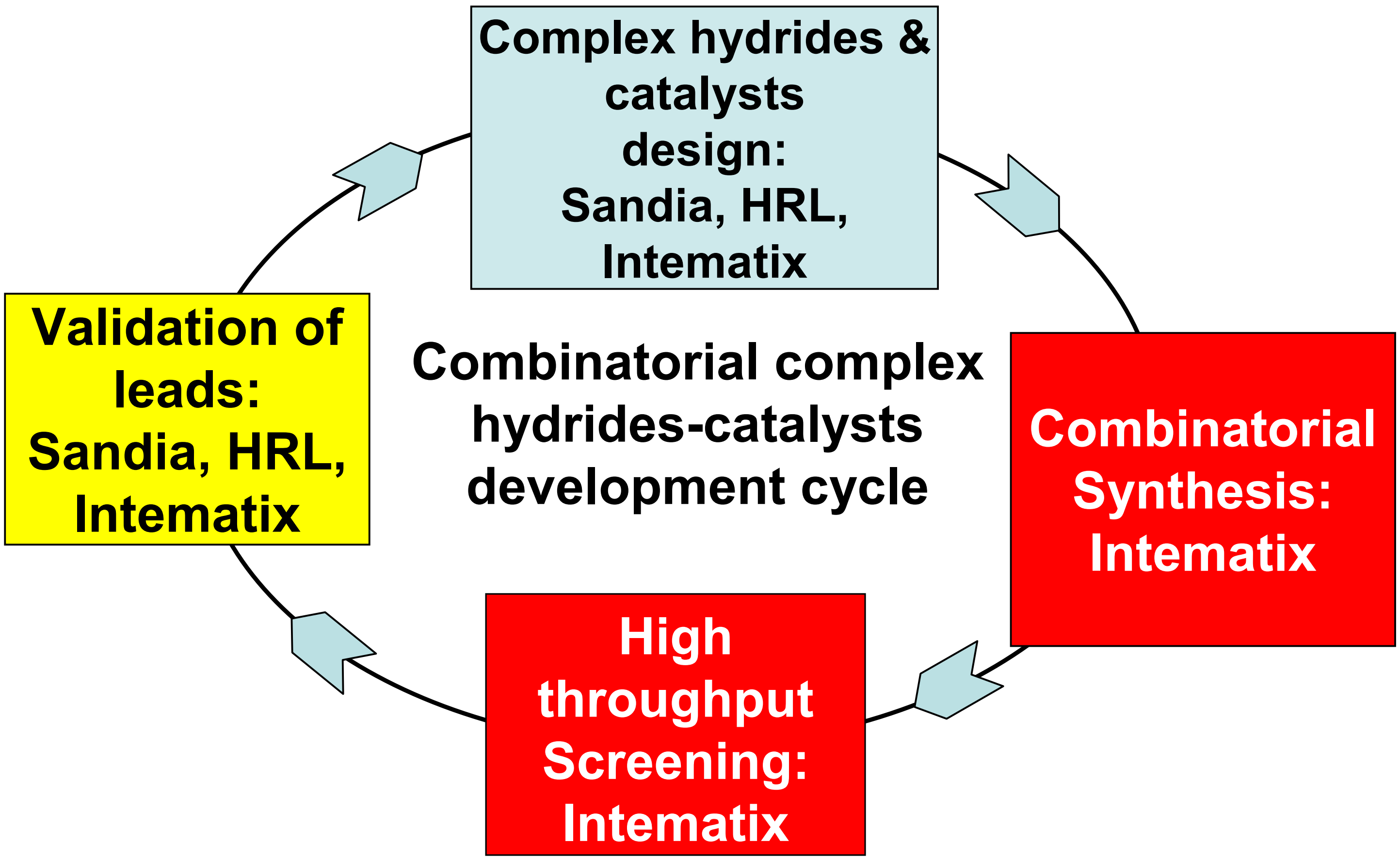
Accomplishments

- Validation of two combinatorial synthesis techniques
- Validation of three high throughput screening techniques
- Validation of Optical Screening for complex and simple hydrides
- Catalyst screened: ~100 metals and alloys
- Found better catalyst for MgH_2 + Si dehydrogenation
  - Did not identify any effective rehydrogenation catalyst
  - System down-selected due to lack of rehydrogenation at IMX or other Center Partners
- A few catalyst leads found for LiH+MgB_2 system hydrogenation, however, this entry point into the system is not very promising
- Catalyst screening in progress for $LiBH_4$ + MgH_2 dehydrogenation
- Proven successful synthesis of thin film materials on both known and novel complex hydride materials [e.g. $LiBH_4$ and $Ca(BH_4)_2$]
- Patents filed: 2
- Intematix accomplished validation of its tools for high-throughput combinatorial catalyst screening ahead of schedule

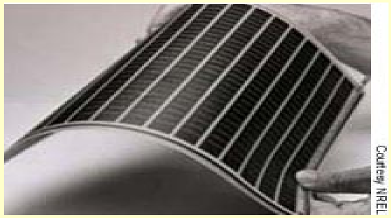
DOE Hydrogen Program

The Partner Approach

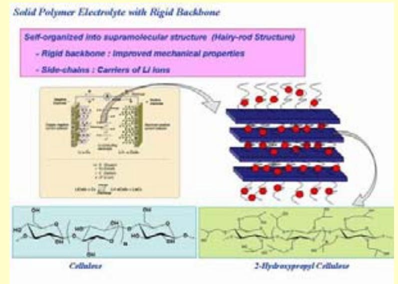
Methodology used for metal hydride synthesis and combinatorial catalyst screening



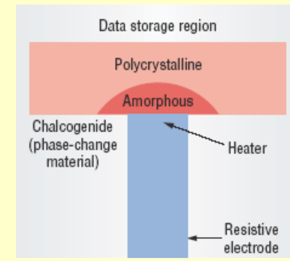
Intematix's Joint Development Program



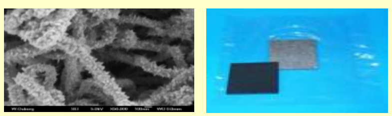
Thin Film Solar Cell & Down Conversion Technology



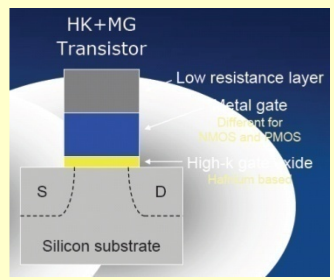
Li Battery Materials



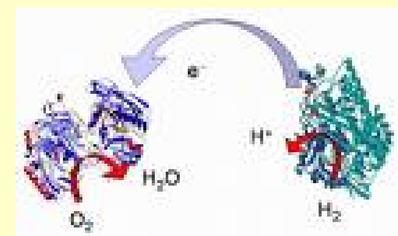
Non-Volatile Memory



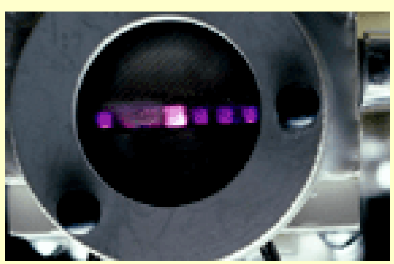
Fuel Cells, H_2 Generation and Storage



High-k Metal Gate



Catalysts for Biofuels



Security Phosphor Materials &System

LED, PDP, CCFL Phosphors

Catalysts Screening for Metal Hydride

Methodology

- Combinatorial thin film deposition of catalyst library and in-situ annealing using Ion Beam Sputtering System (primary tool)
- Combinatorial growth of metal nanoparticles using Laser Pyrolysis
- Laser Annealing of metal library in hydrogen pressure cell (Near Future)

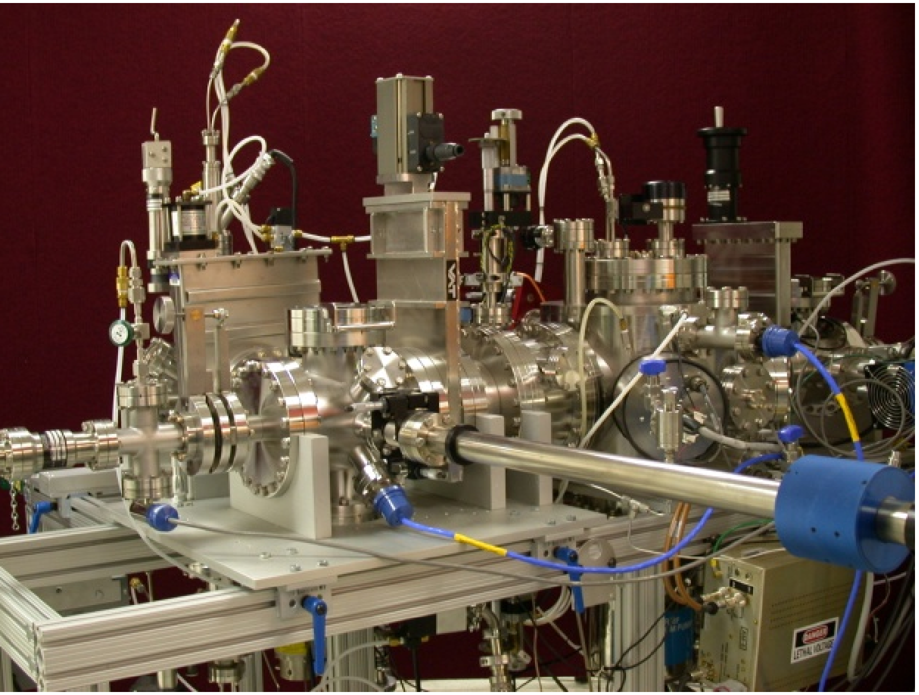
Techniques

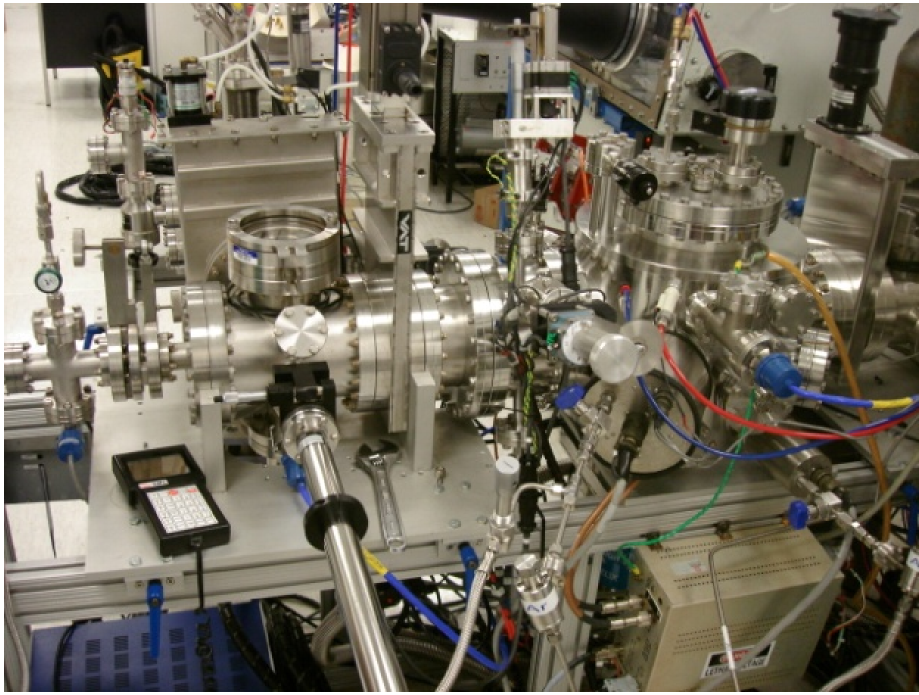
- Real-Time monitoring of optical variations with temperature under different environments
- Optical reflectivity determination (Only for thin film samples)
- Ex-situ scanning X-ray diffraction

Confirmation

MHCoE partners collaboration (HRL, SNL)

Ion Beam Sputtering: A Combinatorial Approach





Advantages	**Ultra-fast combinatorial materials synthesis**
Capabilities	**Combinatorial synthesis of metal hydrides and/or catalysts thin films**
Status	**Validated for metal hydride and catalyst synthesis**

Experimental Details – Catalyst Screening

Catalysts deposition by CIBS on metal hydride on substrates

Transfer to the reactor with optical window

Variations in optical properties recorded versus temperature

For hydrogenation, catalyst library was first screened under Ar and then H_2

Results determined by image processing; compared to any existing data*

Confirm the formation of product by XRD
$NaH + Al$ / $NaAlH_4$
Mg_2Si / $MgH_2 + Si$

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

DOE Hydrogen Program

High Throughput Screening Tools-1

Optical Screening

1) Using High Pressure Optical Chamber
2) Max. Pressure: 600 psi
3) Max. Temperature: 350 ºC
4) Max. Sample Size: 3 x 3 cm

Mg thin film (250 nm) before hydrogenation

MgH_2 thin film after hydrogenation

Methodology:

At constant pressure:
Change in optical properties versus temperature

At constant temperature:
Observe the of change in optical properties versus pressure

Conclusion:

A change in color, as indicated by image processing, at a particular catalyst, indicates that a reaction may have taken place (lead generated for further catalysis study)

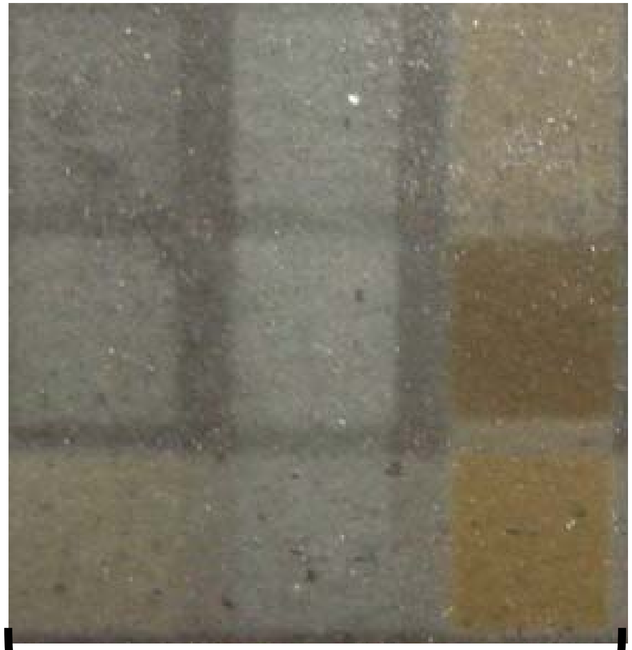
Change in optical property is a combination of change in reflectivity and the respective transmission stemming from change in underlying band structure.

Griessen & coworkers, Scripta Materialia 56, 853 (2007)

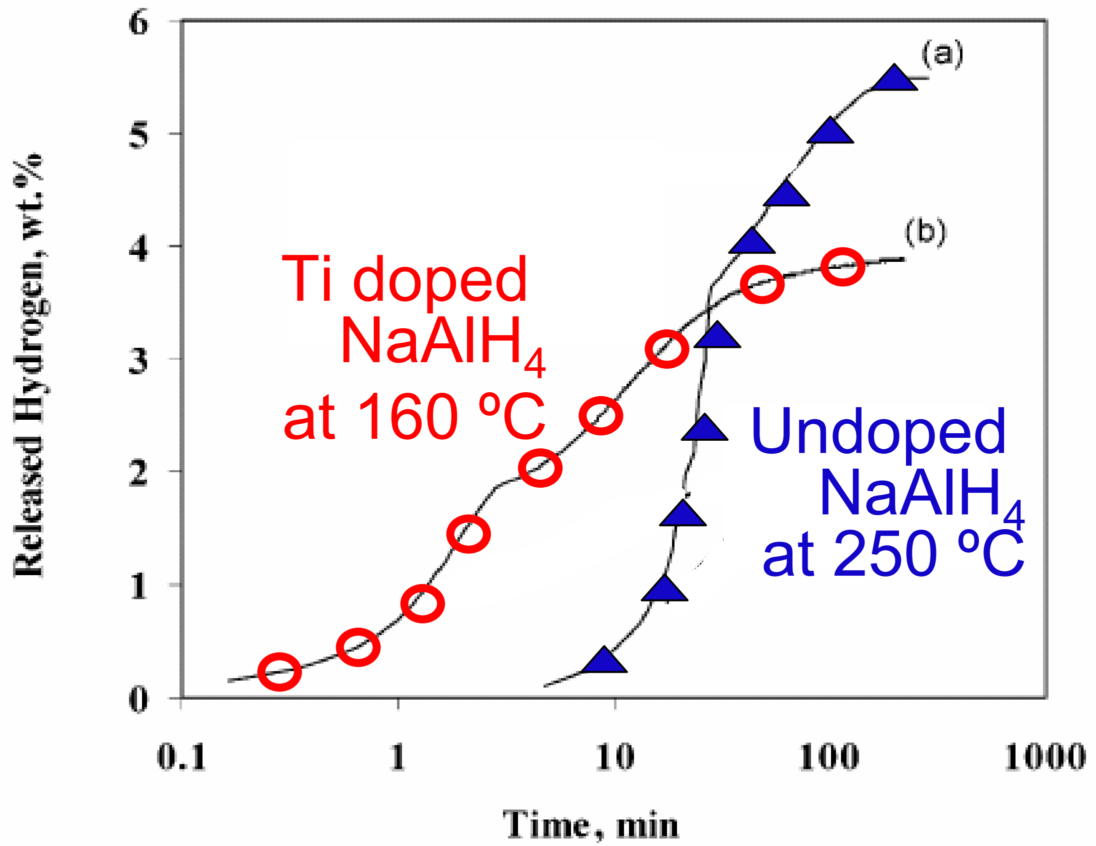
Example Libraries

Library 1

Library 2



$NaAlH_4$ Literature



Ti known to catalyze H_2 release from $NaAlH_4$

Jensen & coworkers, J. Phys. Chem. B 107, 10176 (2003)

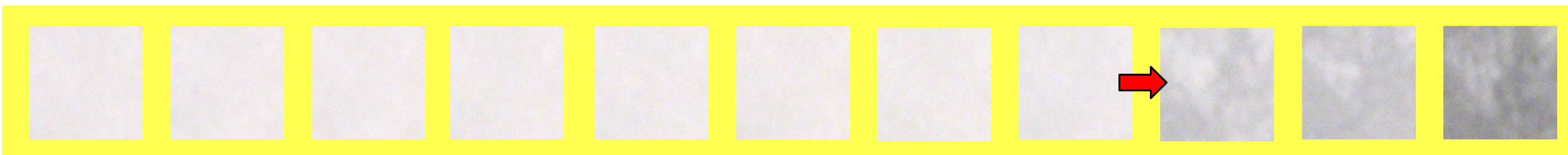
Validation of Method with $NaAlH_4$

Experimental Conditions

Gas Environment: Vacuum   Temperature: RT to 200 ºC   Rate: 3 ºC/min

Temp (ºC)	25	50	75	100	125	150	175	185	185 5 min	200	200 90 min

$NaAlH_4$ As available

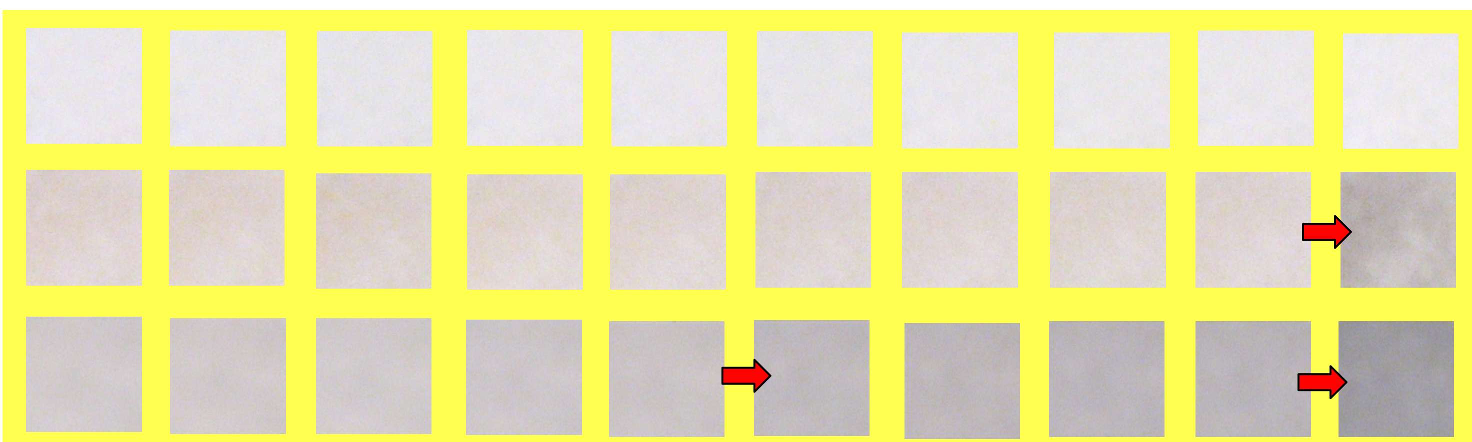


Temp (ºC)	25	50	75	100	125	130	140	150	160	160 (30 mins)

No Ti — No change

100Å Ti film — H_2 release at 160 ºC

5% $TiBr_4$* — H_2 release at 160 ºC



$NaAlH_4$ deposited on the substrate as a slurry in hexane or anhydrous toluene

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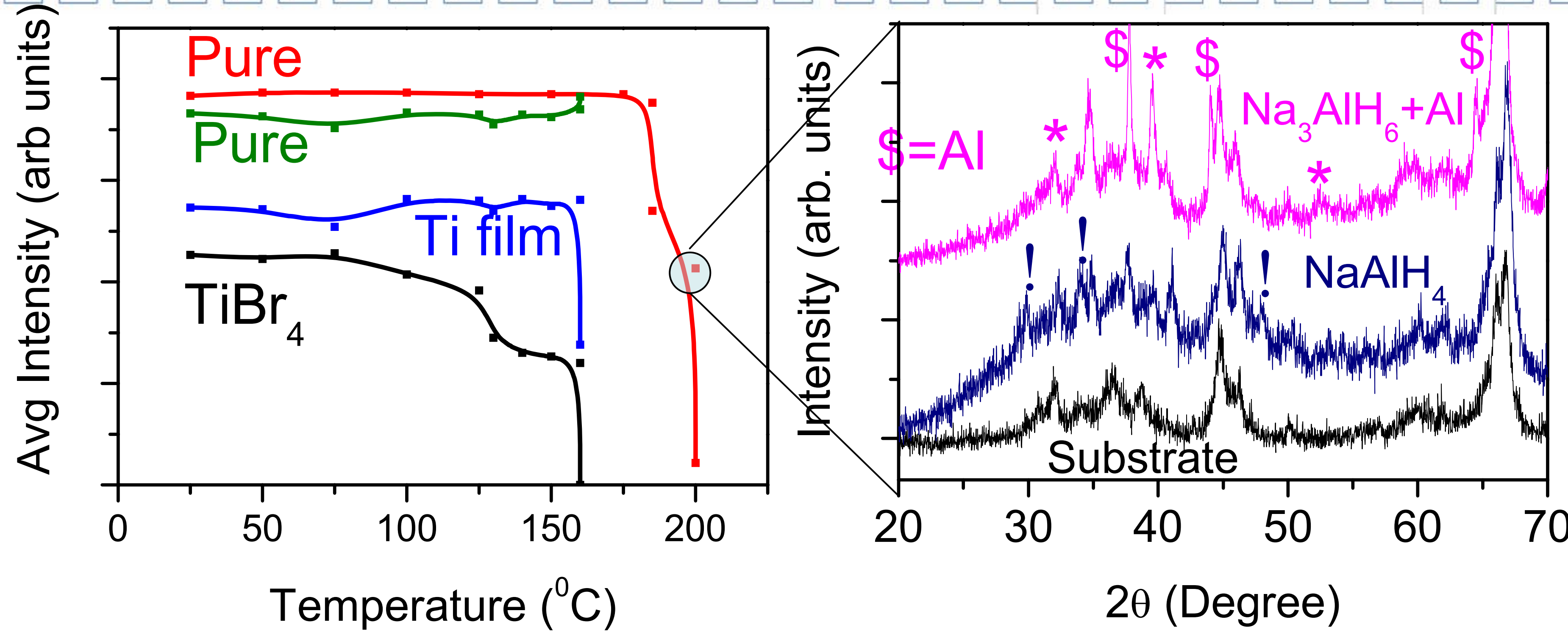
Intematix Results: Image Processing and XRD



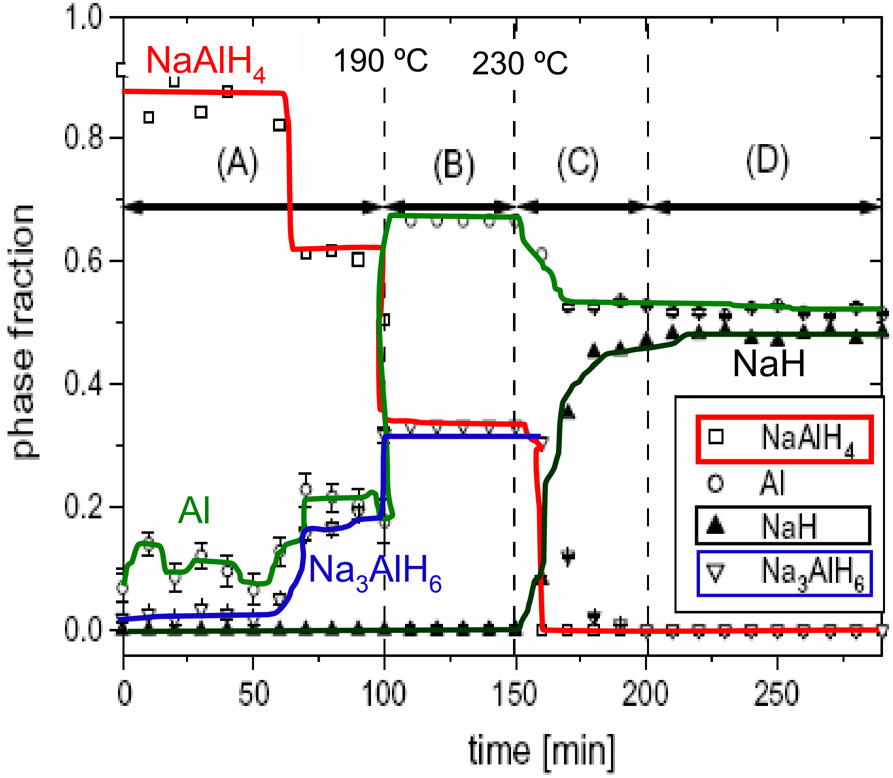
Ti identified as a catalyst for the system

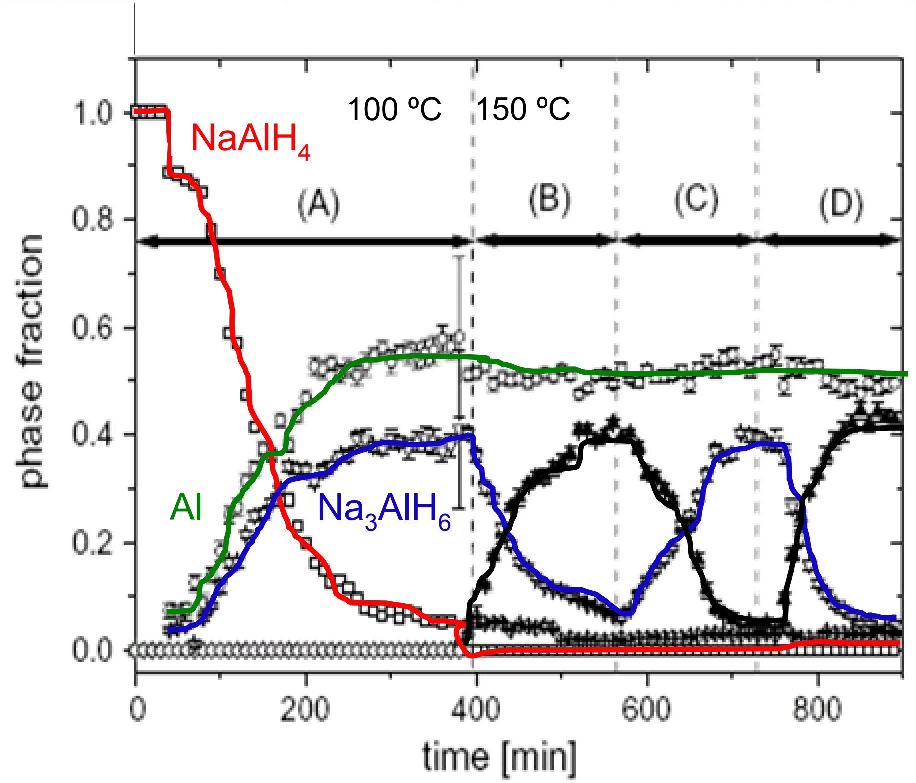
XRD confirms phase change and hydrogen release:

$3NaAlH_4 \rightarrow Na_3AlH_6 + 2Al + 3H_2$

Rehydrogenation attempted but unsuccessful as 500 psi H_2 is below the 1500 psi where facile reaction would be expected

NaAlH$_4$ Literature Matches Experimental Results





Pure NaAlH$_4$ transforms to Na$_3$AlH$_6$ ~190 ºC

Ti catalyzed NaAlH$_4$ transforms ~150 ºC

Singh et al., Acta Materialia **55**, 5549 (2007)

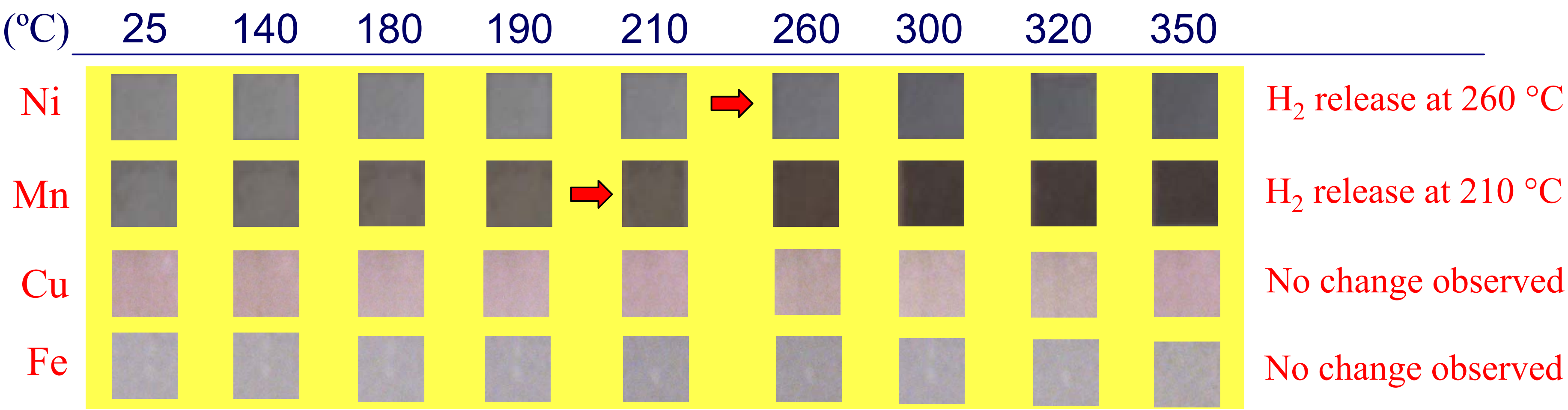
DOE Hydrogen Program

Validation

- Methodology validated on $NaAlH_4$ system; results both with and without Ti match expected behavior
- Observation of catalysis in “bulk-like” sample
- Observation of catalysis by thin film deposited catalyst sample on a complex hydride
- XRD can be used as direct confirmation of product formation
- These results enable us to trust both the thin film catalyst deposition approach and the sample preparation methodology

Dehydrogenation – Catalyst Screening for MgH_2 + ½ Si Powder

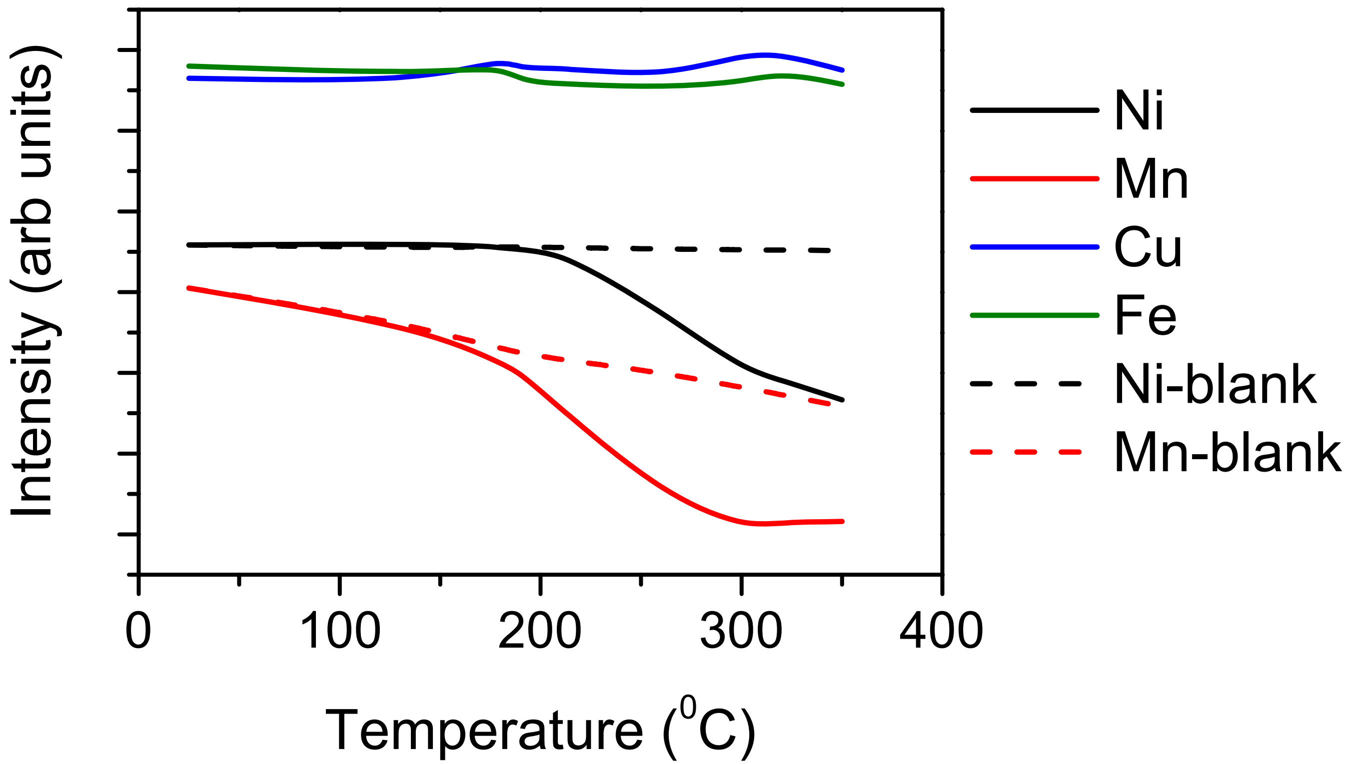
Optical Properties Screening (heated at 3 ºC/min):



- Catalytic effect observed with thin film metal deposited on covalent metal hydride
- Ni known by HRL, Mn previously unknown
- Non-reaction with Cu and Fe thin films confirms catalytic versus morphological nature of thin film Mn and Ni
- We have confirmed that there is no change in the optical properties of pure material under the similar conditions (1 bar Ar, time= 2 hrs, max T = 350 °C)

Catalysts screened: Ni, Mn, Cr, Fe, Ti, Nb, Pt, V, Cu, and
40 binary alloys

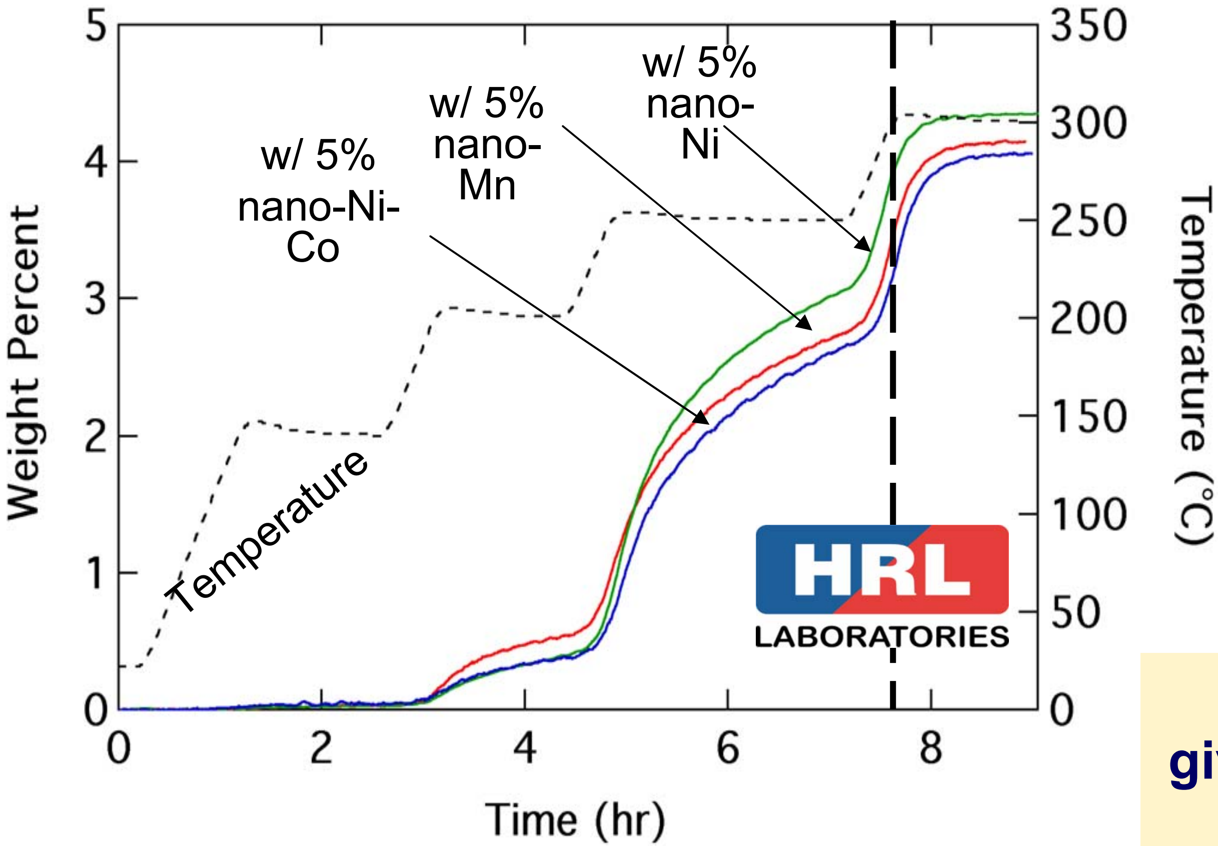
Image Processing of MgH_2 + Si optical screening



- Blanks show effect of heating catalyst in presence of argon
- No difference between blank and experiment for Ni or Mn
- Image processing quantitatively shows transition temperatures, which are key to interpreting results

Hydrogen Desorption Catalyst Confirmation from Center Partner

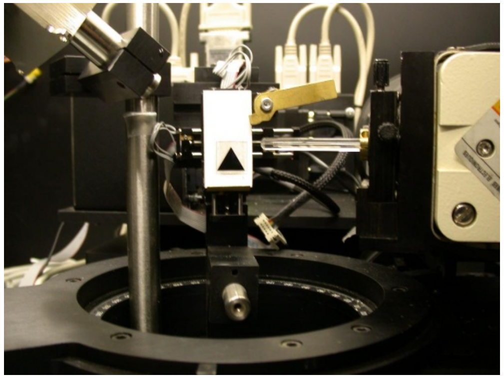
MgH_2/Si + Catalyst

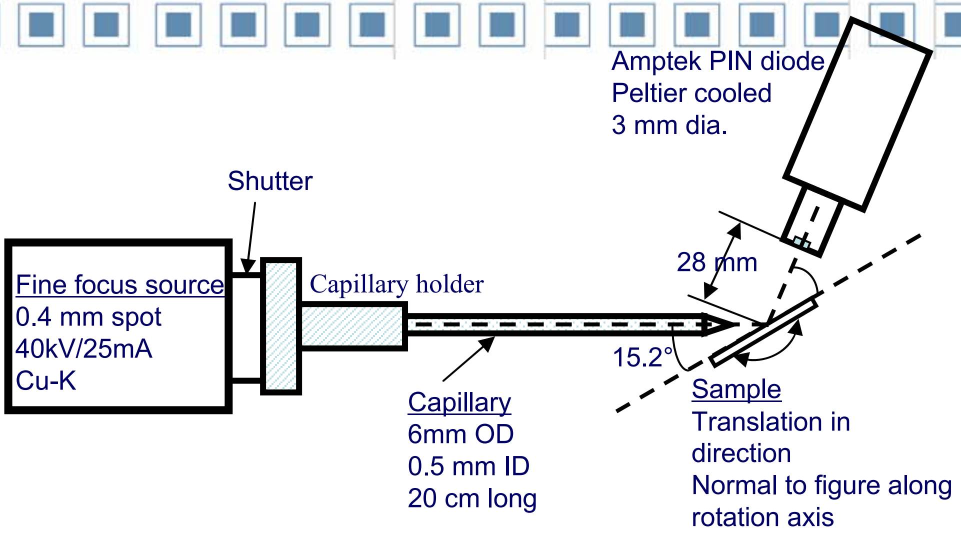


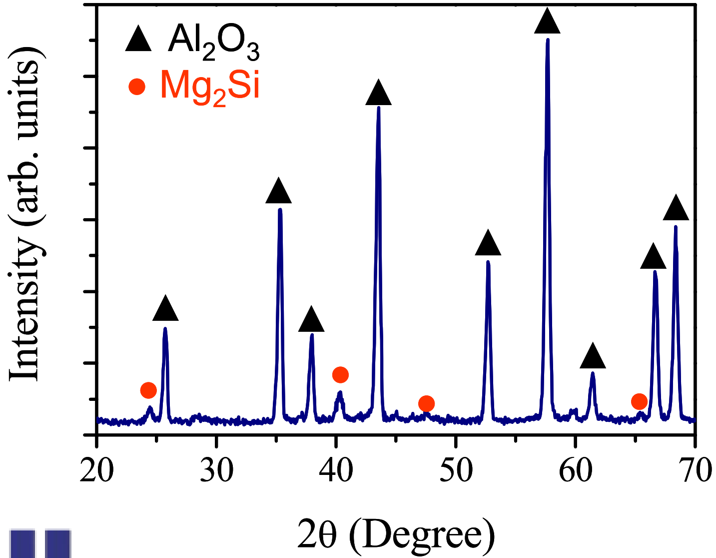
- A similar approach was used by HRL: heating at 2 ºC/min
- Pure MgH_2 + Si takes 7.5 hr for onset of decomposition (shown by vertical dashed line)

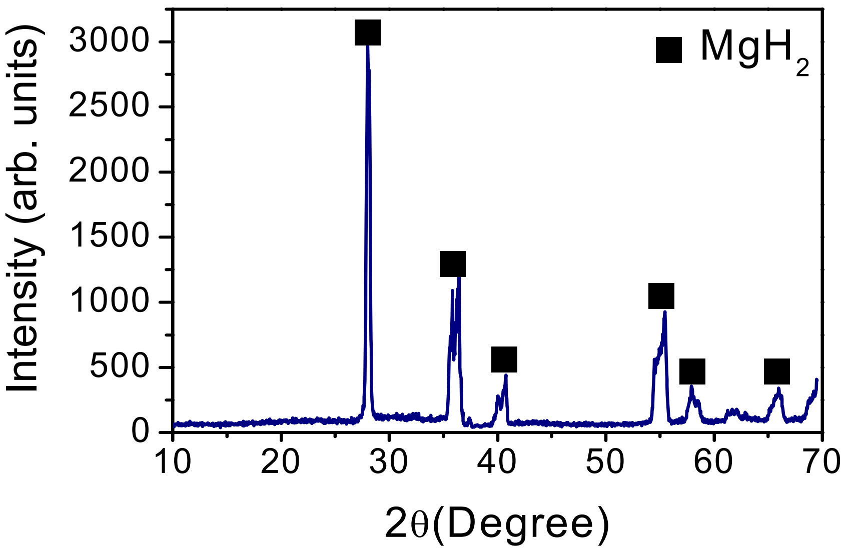
Nano-Mn, Ni and Ni-Co give similar enhancements for dehydrogenation

Micro-beam scanning XRD results



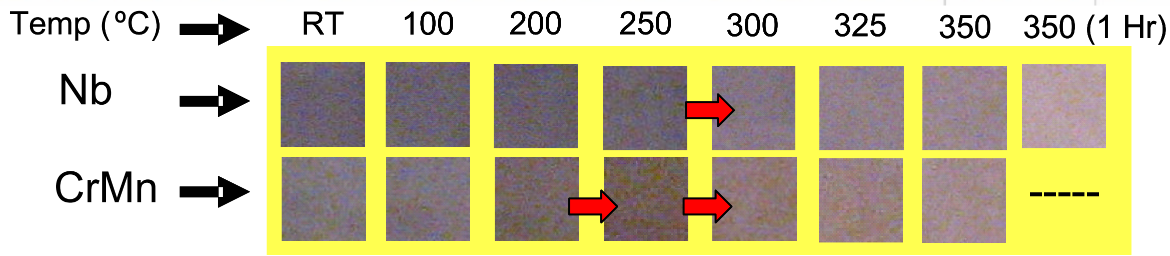


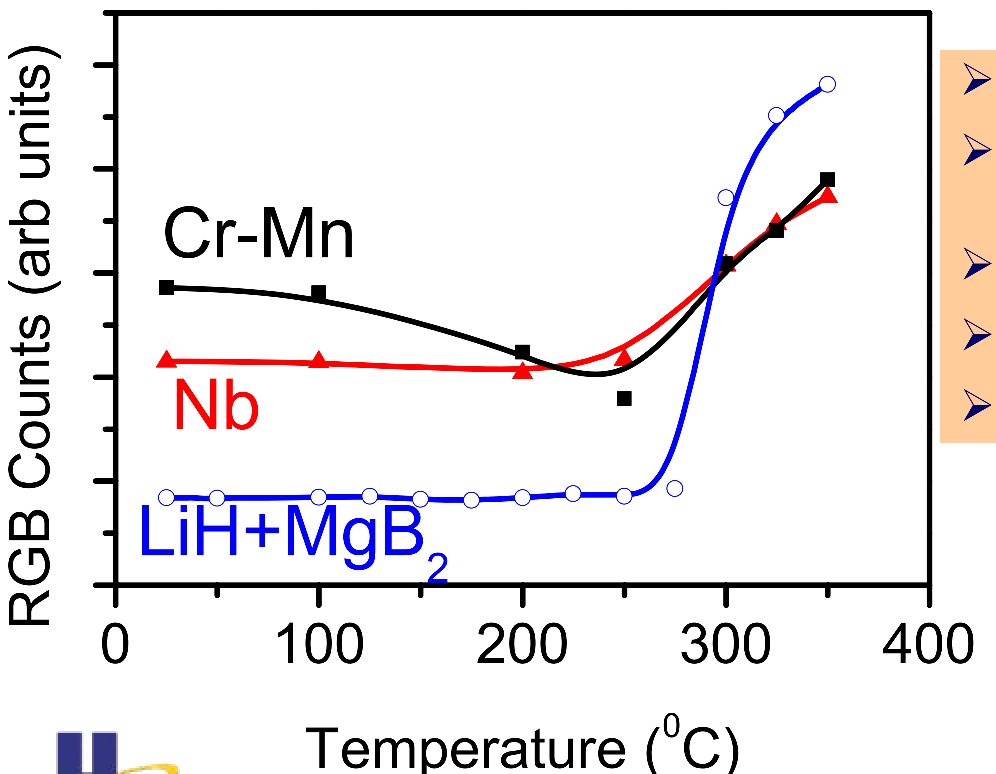




Limitation: *Not configured for highly air sensitive materials*

Hydrogenation – Catalyst Screening for LiH + MgB_2





- Evidence for Nb metal, CrMn alloy catalysis
- Screened ~50 catalysts combinations of Fe, Ni, Nb, Pt, Ru, Cr, Mn, Mg, V
- More careful analysis is required
- Most promising results shown here
- Further validation necessary

Also, screened 25 catalyst for Dehydrogenation of $LiBH_4$ + MgH_2

DOE Hydrogen Program

Intematix

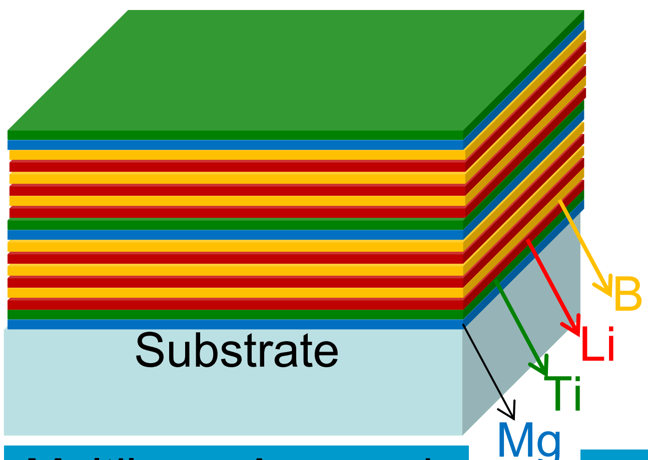
DOE Hydrogen Program

Thin film systems

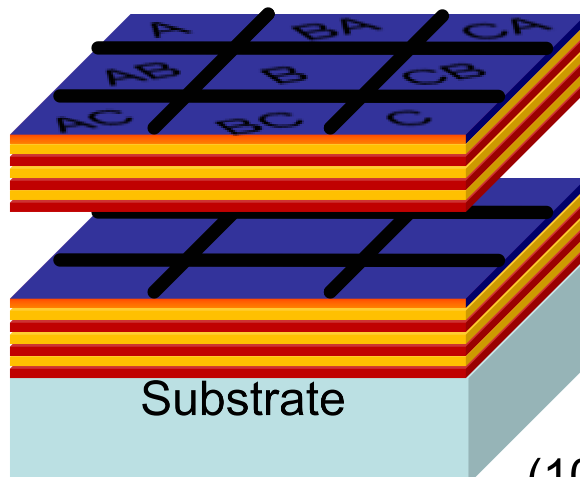
Combinatorial Thin Film Design Approach

Rationale:

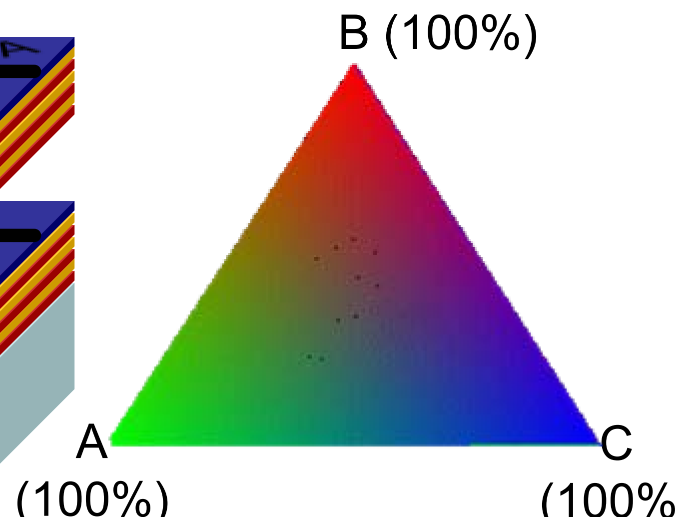
1)Addresses/solves non-uniformity of powdered (ball-milled) sample
2)Opportunity to explore novel nano-material system in a **"controlled"** fashion.
3)Catalysts can be sandwiched between the complex hydride layers increasing effective loading
4)More accurate data accumulation using automated optical reflectivity setup for hydrogenated and dehydrogenated samples.
5)Role of morphology, microstructure and stress on hydrogen storage can be studied effectively
6)Sensitive elements, such as Li, can be deposited very efficiently and effectively.
7)Sample size can be varied depending on the experiments



Multilayer Approach

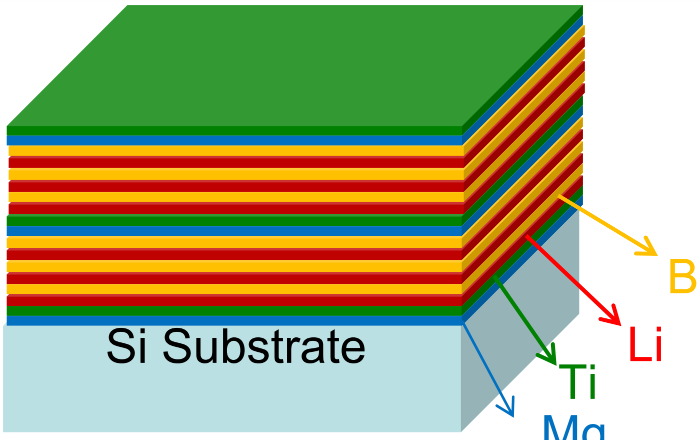


Multilayer + Discrete library

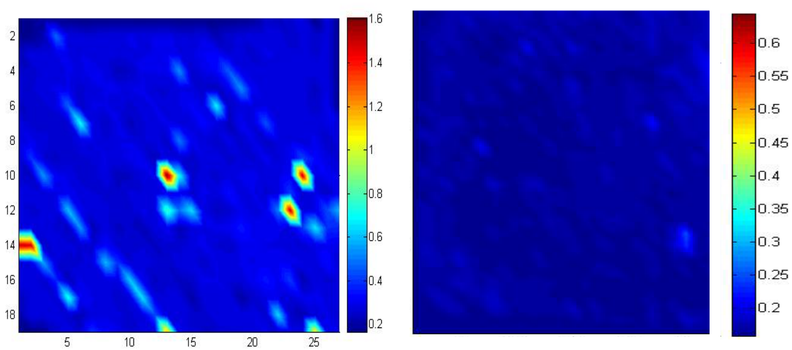


Ternary Continuous library

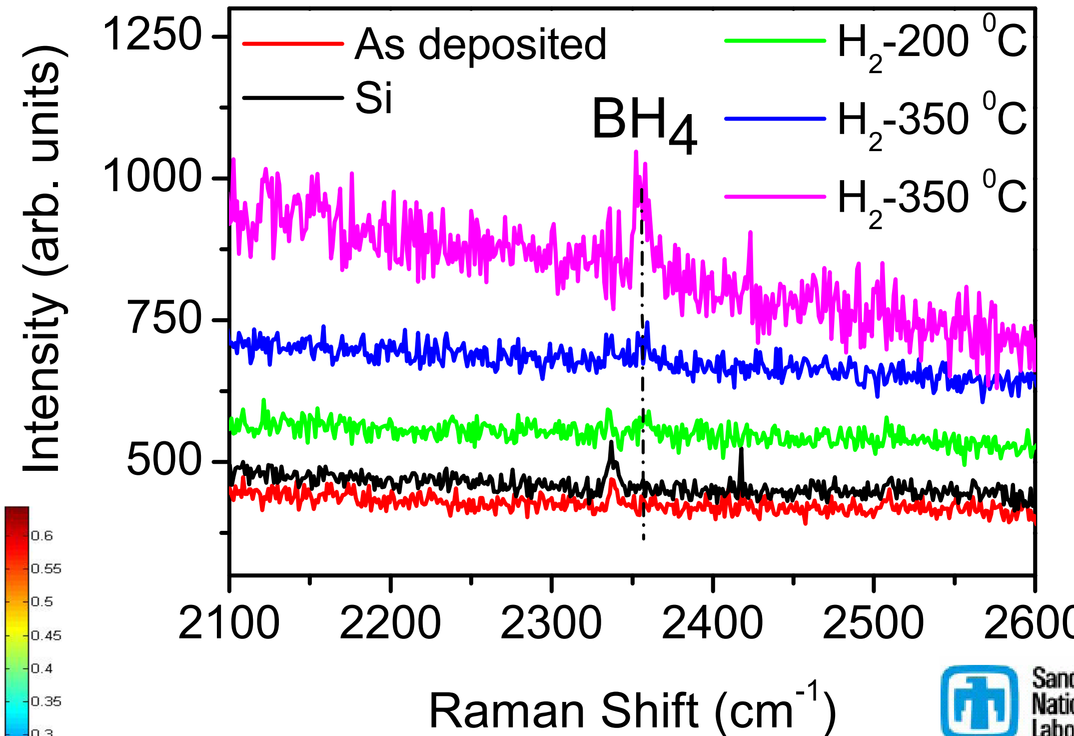
Li-B-Mg-Ti Thin Film, 350 ºC and 500 psi H_2



(Li=10 Å, B=10 Å) x 5 =100 Å; (Ti=10Å, Mg=10Å) x 1;



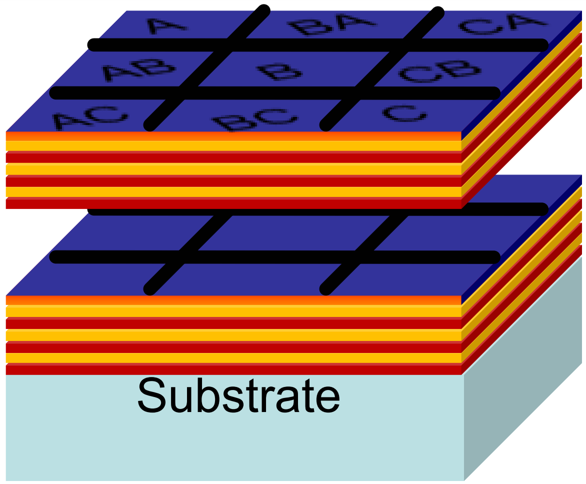
False color reflectivity mapping indicates hydrogen uptake (darkening from right to left); confirmed by Raman



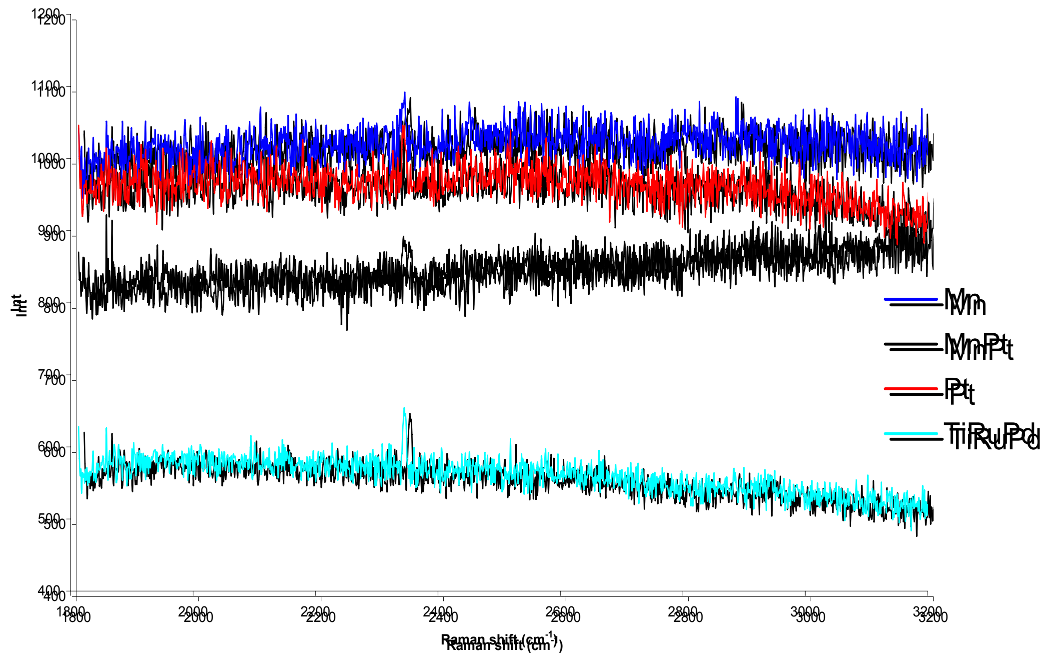
Mg & Ti were added as catalysts based on $LiBH_4$ bulk systems in the literature

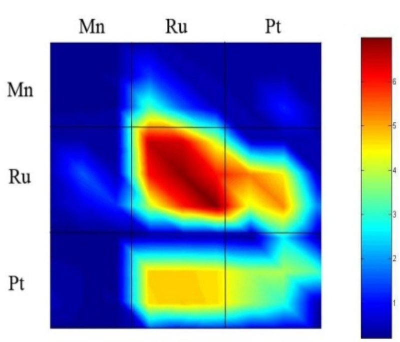
Vajo et al., J. Phys. Chem. B **109**, 3719 (2005)
Yu et al., Chem. Comm. 3906 (2006)
Au et al., J. Phys. Chem. B **110**, 26482 (2006)

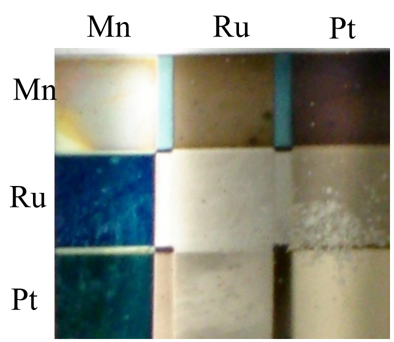
Ca-B Mixture Thin Film With Catalyst Library



Hydrogenation temperature=440 °C
Hydrogen pressure=15,000 psi







Optical reflectivity and an image of Ca, B mixture with discrete catalyst libraries.

Indication of B-H bond formation, but not necessarily BH_4^-, possibly a higher order $B_xH_y^{n-}$, based on the Raman spectra. Such a compound is likely an intermediate in the formation of BH_4^- from elemental B and H_2.

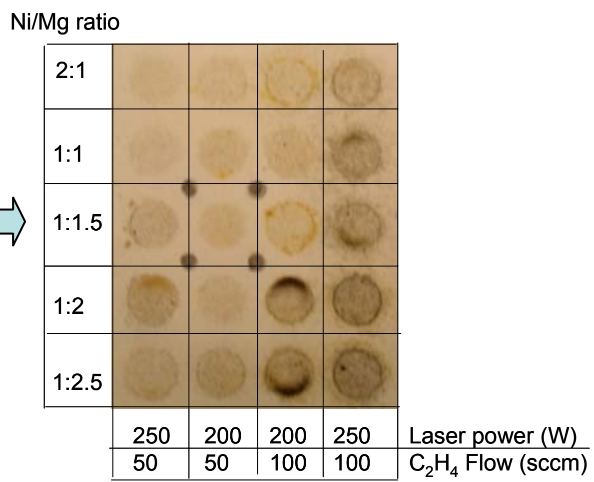
DOE Hydrogen Program

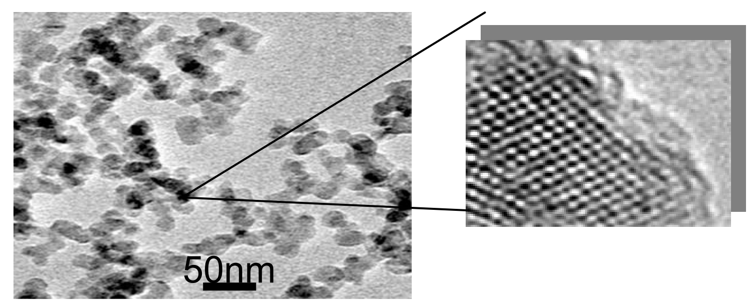
Complementary Synthesis Technique – Combinatorial Nano-particle (CNP) System

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





For example, this system has generated Ni particles for Mg_2Si

DOE Hydrogen Program

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) Validation of Optical Screening for complex and simple hydrides

(3) Proven successful synthesis of thin film materials on both known and novel complex hydride materials [e.g. $LiBH_4$ and $Ca(BH_4)_2$]

(4) 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.

(5) 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:

Project Complete

DOE Hydrogen Program