

IV.A.1n High-Throughput Combinatorial Chemistry Development of Complex Hydrides

Darshan Kundaliya (Primary Contact) and Jonathan Melman

Intematix
46410 Fremont Blvd.
Fremont, CA 94538
Phone: (510) 933-3300; Fax: (510) 668-0793
E-mail: dkundaliya@intematix.com

DOE Technology Development Manager:
Ned Stetson

Phone: (202) 586-9995; Fax: (202) 586-9811
E-mail: Ned.Stetson@ee.doe.gov

DOE Project Officer: Paul Bakke
Phone: (303) 275-4916; Fax: (303) 275-4753
E-mail: Paul.Bakke@go.doe.gov

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- Validation of three high throughput screening techniques.
 - Validation of optical screening.
- Catalyst screened: ~100 metals and alloys.
- Found better catalyst for $\text{MgH}_2 + \text{Si}$ dehydrogenation:
 - Did not identify any effective rehydrogenation catalyst.
 - System down-selected due to lack of rehydrogenation.
- A few catalyst leads found for $\text{LiH} + \text{MgB}_2$ system, however, this entry point into the system is not very promising.
- Catalyst screening for $\text{LiBH}_4 + \text{MgH}_2$ dehydrogenation.
- Thin film materials synthesis on both known and novel materials (e.g. LiBH_4 and $\text{Ca}(\text{BH}_4)_2$).
- Intematix has accomplished validation of its tools for high-throughput combinatorial catalyst screening ahead of schedule.



Objective

- To implement high throughput, combinatorial material research, investigation of metal hydrides in order to facilitate and meet the DOE targets of on-board hydrogen storage.
- To perform systematic catalytic studies of known metal hydrides.
- To explore the hydrogen storage potential of new ternary, quaternary, or higher-order complex metal hydride systems.

Technical Barriers

This project addresses the following technical barriers from the Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Multi-Year Research, Development and Demonstration Plan:

- (E) Charging/Discharging Rates
- (J) Thermal Management
- (P) Lack of Understanding of Hydrogen Physisorption and Chemisorption
- (Q) Reproducibility of Performance

Accomplishments

- Validation of two combinatorial synthesis techniques.

Introduction

In this project, we synthesize and identify new metal hydride systems, as well as catalysts, using combinatorial techniques. Combinatorial synthesis enables preparation of arrays of materials with multiple elements and various ratios in one batch. To screen these materials we have developed high-throughput screening techniques and equipment which allow these materials to be studied in parallel for targeted properties via their optical and reflective properties. During this year we have combined combinatorial synthesis and high-throughput screening for metal hydride catalyst discovery.

In this year, the materials systems we have chosen, in conjunction with Center partners, for catalyst screening were NaAlH_4 , $\text{LiBH}_4 + \text{MgH}_2$, and LiBH_4 in powder, slurry and/or thin film formats. We screened more than 100 catalysts in these systems to look for the kinetic improvements required to meet DOE targets for on-board hydrogen storage systems.

Approach

Rational design is adopted for metal hydride and catalyst screening. First, metal hydride systems are screened based on thermodynamic calculation. Then, the identified metal hydrides are synthesized

in an approach suitable for catalyst synthesis and screening. In some cases, metal hydride powders are received from a Metal Hydride Center of Excellence (MHCoE) partner to identify suitable catalyst. These materials were applied on suitable substrates by making a uniform layer for subsequent deposition of catalyst on it. Combinatorial ion beam sputtering and high-throughput screening techniques are used to incorporate the catalyst. Thermodynamic calculation, thin film synthesis, catalyst deposition and subsequent screening are carried out independently. After obtaining initial leads for effective catalysts from screening, we work in close collaboration with MHCoE partners to confirm the results more quantitatively.

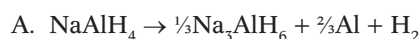
Experimental Details & Results

Powder Methodology - Validation of optical imaging technique for NaAlH_4 , a complex hydride system:

The aim of the study presented in this section is to validate both our optical technique to image hydrogen release/uptake and our thin film sputtering methodology for testing catalysts in the metal hydrides systems.

Scanning electron microscope images of metal sputtered onto fibrous substrates, such as the alumina paper used here, show small, well separated metal particles in the 100–500 nm regime. Additionally, due to the nature of the substrate and the ion beam sputtering used for deposition, the catalyst particles are well distributed through the system, not just sitting on the top surface, as would be expected if it were simply a thin film on a flat substrate. Additionally, it should not be necessary to have complete conversion of the metal hydride in order to observe a change in the system and thus establish a lead for further catalytic investigation; so while high catalyst coverage is desirable, excellent screening results can be obtained even without high catalyst coverage.

Hydrogen release from NaAlH_4 , both pure and catalyzed, has been well studied in the literature [1,2] making it an ideal system to examine for this validation. Under inert atmosphere, NaAlH_4 (hydrogen storage grade, Aldrich) was mixed with anhydrous, non-coordinating solvent and homogenized. The resultant slurry was spread onto an alumina substrate and the solvent allowed to evaporate. After drying, the sample was transferred to the combinatorial ion beam system for the deposition of Ti catalyst. Ti was deposited on only half of the sample, leaving the other half bare as a control. In a separate experiment, TiBr_4 (~5 wt%) was first added to NaAlH_4 , ground together in a mortar and pestle, and slurry deposited on the substrate. In both experiments, the samples were transferred to a reactor cell fitted with an optical window, and heated at $3^\circ\text{C}/\text{min}$ up to 200°C in vacuum. The following reactions were expected to occur during the vacuum heating of the samples:



Reaction A is expected to take place around 190°C , whereas reaction B occurs at 250°C for pure NaAlH_4 . With a Ti catalyst, the onset temperature of reaction decreases substantially to $\sim 160^\circ\text{C}$ [1,2].

In our optical setup, the optical properties of libraries were monitored via digital photographs. Changes in both reflectivity and absorption have been established as indicators of hydrogen release by Griessen and co-workers [3], due to changes in the underlying band structure of the material. The visual change of the catalyst library is monitored during attempted dehydrogenation. As shown in Figure 1, it is evident that there are clear optical differences between the behavior of pure NaAlH_4 , Ti thin film on NaAlH_4 and TiBr_4 doped NaAlH_4 at the expected temperatures suggesting hydrogen release and hence, indicating how an effective

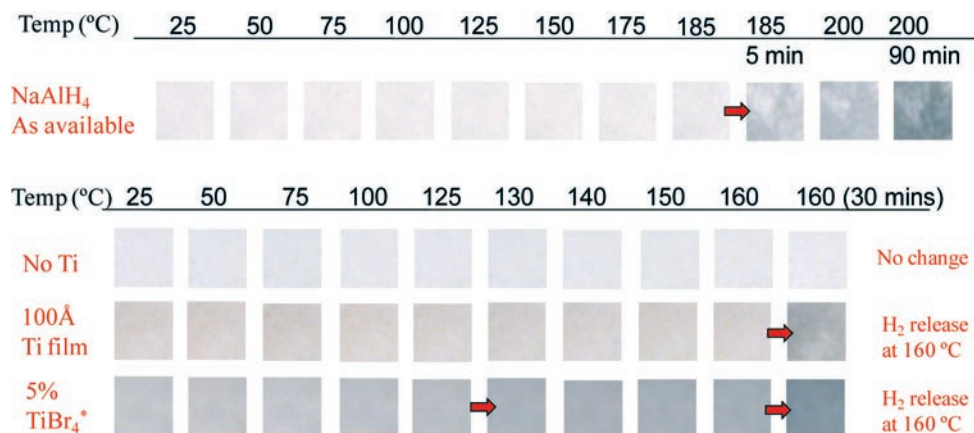


FIGURE 1. Optical images obtained at various temperatures for as available NaAlH_4 , NaAlH_4 with Ti thin deposition on top and NaAlH_4 mixed with TiBr_4 . Arrow indicates the onset of the hydrogen evolution.

catalyst will stand out in our combinatorial optical screening method. Furthermore, image processing (Figure 2, left image) is performed to provide a more quantitative measure of the color change and thus the temperature of reaction. X-ray diffraction of products (Figure 2, right image) after the dehydrogenation of pure NaAlH_4 confirms reaction A.

Similar image processing has been carried out on reactions in the $\text{MgH}_2 + \text{Si}$ and $\text{LiH} + \text{MgB}_2$ systems, where the hydrogen storage material was provided by HRL. The results provide further evidence of the catalyst screening results previously released to the MHCoe. The catalytic activity of Mn in the dehydrogenation of the $\text{MgH}_2 + \text{Si}$ system has been confirmed by HRL, while the catalytic activity of a Cr/Mn alloy for the hydrogenation of the $\text{LiH} + \text{MgB}_2$ system has not yet been investigated by HRL.

Thin Film Methodology - Synthesis of Complex Metal Hydrides and Catalysts:

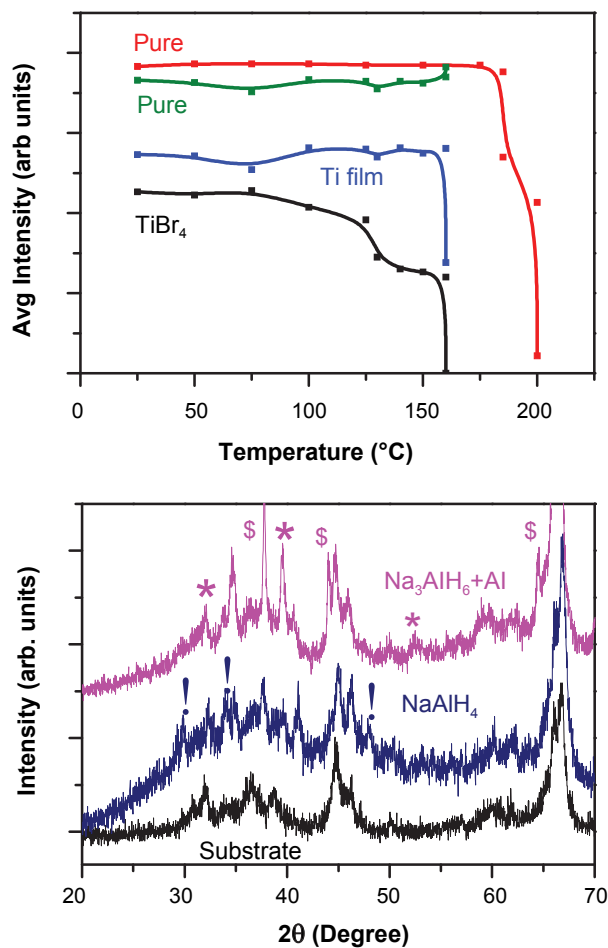


FIGURE 2. Image processing of NaAlH_4 with and without catalyst, showing temperatures of phase transition, and X-ray diffraction confirming formation of Na_3AlH_6 in uncatalyzed reaction.

It has been understood that if hydrogen-based energy is to become a practical alternative to fossil fuel, we must have efficient ways to store, restore and convert hydrogen into electricity, fuel, and heat. In terms of synthesizing metal hydrides for storage, the current methods are focused mainly on high energy ball-milling. This forms a bulk powder, which is the most likely deployment of a hydrogen storage material. Rapid screening for catalysts is limited to the optical imaging outlined above, which while effective, is not as direct and may not be the most sensitive. If the system were a true thin film, then optical reflectivity could provide a very sensitive measure of the changes in the material. In order to take advantage of this potential increase in sensitivity, it seems that there is a necessity to design a novel controlled approach for metal hydride and catalyst synthesis. A fully thin film approach can offer the following advantages:

1. Uniformity of sample compared to powdered (ball-milled) sample.
2. Opportunity to explore novel nano-material systems in a “controlled” fashion.
3. Catalysts can be sandwiched between the complex hydride layers increasing effective loading.
4. Data can be accumulated more accurately 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.

A. Li-B-Mg-Ti System (Method in Figure 3a)

Using the combinatorial ion beam sputtering technique, we endeavored to make LiBH_4 by depositing multilayers of Li, B, Mg and Ti based on literature reports of LiBH_4 formation. Figure 3 describes how thin film complex metal hydrides can be grown with effective catalyst loading, in either discrete or continuous libraries. More details are given in the June 2007 quarterly report.

For optical reflectivity, the laser spot size is $1 \mu\text{m}$ and the data were obtained every $100 \mu\text{m}$ throughout the sample. The sample size was approximately $2 \times 2.5 \text{ mm}^2$. A uniform intensity is expected if the sample is extremely smooth and without defects. Defects are the most likely cause of the high intensity spots seen on the sample before hydrogenation (Figure 4). Also, statistical error due to laser instability cannot be ruled out as the cause of such anomalies. As noted above, the observed change in optical reflectivity stems from a change in the underlying band structure of the

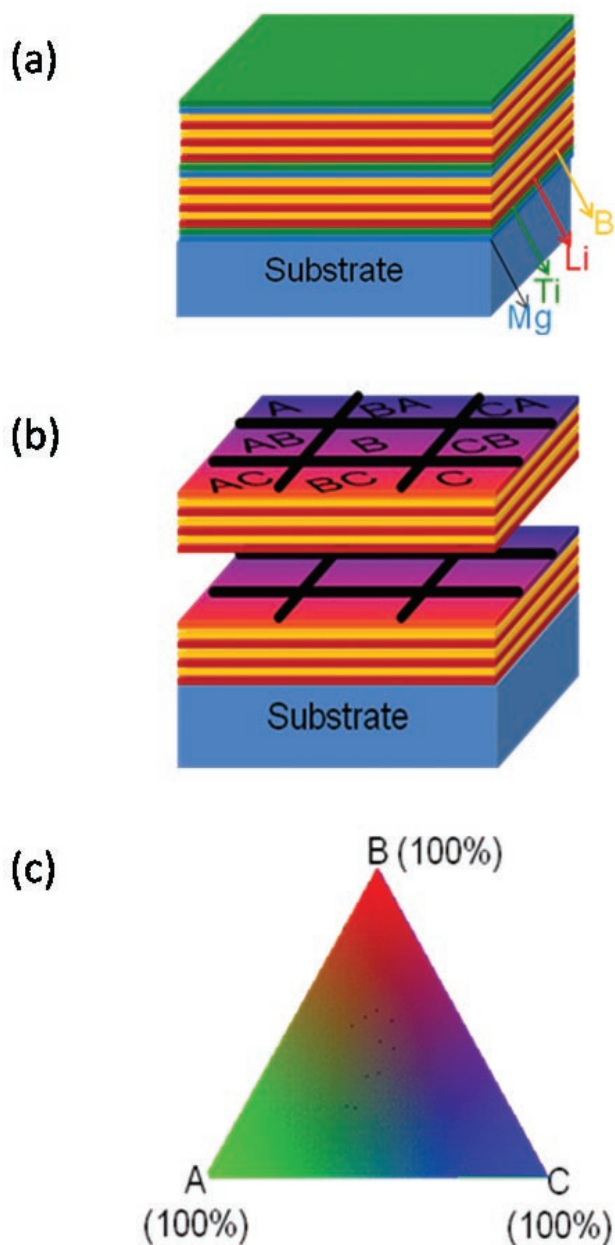


FIGURE 3. Schematics of how thin film complex metal hydrides can be grown with effective catalyst loading, in either discrete or continuous libraries fashion.

material [3]. Raman spectroscopy (Eric Majzoub, Sandia National Laboratories [SNL]) was utilized to determine formation of BH_4^- , and correlate the change in reflectivity to that formation. Raman shifts in the 2,000-2,500 cm^{-1} region correspond to B-H bonds. Figure 4 also shows Raman results of the Li-B-Mg-Ti thin film systems. The spectra were taken at various points before (red) and after hydrogenation (green, blue and magenta). Hydrogenation temperature was varied as indicated. It is evident that B-H bonds start to form even at low temperature i.e. 200°C (green). More

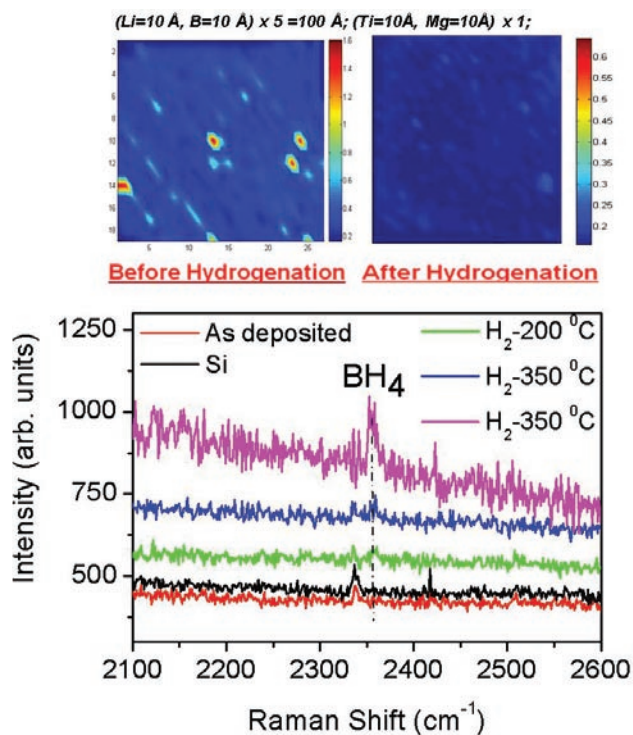


FIGURE 4. Optical reflectivity and Raman spectroscopy of Li-B-Mg-Ti thin film system before and after hydrogenation.

B-H is formed at 350°C (blue). However, the strongest indication of B-H bond formation is realized after two hrs of hydrogenation at 350°C (magenta). Overall, this approach will prove very important in realizing the efficient nano-catalysis of the **hydrogenation** of such complex borohydride systems.

B. Ca, B Thin Film Mixture with Catalyst Library (Method in Figure 3b)

We also investigated the synthesis of $\text{Ca}(\text{BH}_4)_2$ by depositing a multilayer and a mixed composition of catalyst elements. This is similar to what was been done for the LiBH_4 thin film system but with a library of discrete catalysts. Further treatment is given in the September and December 2007 quarterly reports. Hydrogenation experiments have been carried out using a reactor cell at Intematix as well as at SNL; Raman spectroscopy (Ewa Ronnebro, SNL) was utilized to determine formation of BH_4^- . The preliminary data do show formation of BH_4^- vibration. The detailed analysis is underway and will be reported when available. The typical image of optical reflectivity and camera image before hydrogenation of one of the samples is shown in Figure 5. The different colors represented in Figure 5 reveal variation in the intensity of the photo-reflection from each discrete library entry (catalyst) deposited. The intensity is expected to reduce on hydrogenation as described in section A for Li-B-Mg-Ti system.

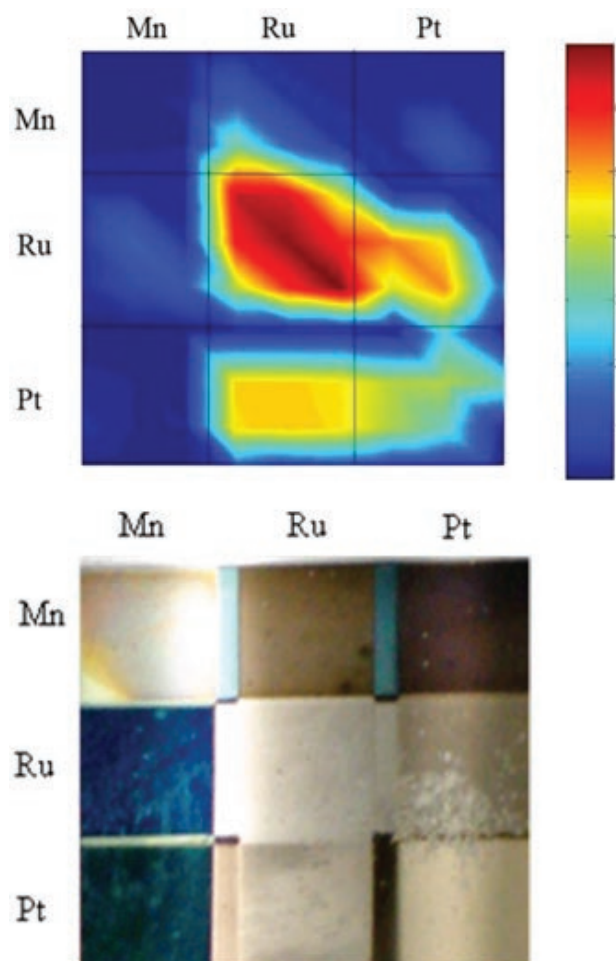


FIGURE 5. Optical reflectivity and an image of Ca, B mixture with discrete catalyst libraries.

Preliminary results of higher temperature and pressure hydrogenation (440°C and 15,000 psig) performed at SNL indicate B-H bond formation, though not necessarily BH_4^- . Based on the Raman spectra, it seems likely that a higher order $\text{B}_x\text{H}_y^{n-}$ compound was formed, such a compound could be an intermediate in the formation of BH_4^- from elemental B and H_2 .

Conclusions

- Intematix has successfully developed and applied its combinatorial synthesis and high-throughput screening techniques to rapidly find catalysts for dehydrogenation and/or hydrogenation of simple/covalent ($\text{MgH}_2 + \text{Si}$) and complex/ionic (NaAlH_4 , LiBH_4 , $\text{Ca}(\text{BH}_4)_2$) metal hydride systems.
- Our system was validated on the known NaAlH_4/Ti system, and was successfully applied to the $\text{MgH}_2 + \text{Si}$ system, discovering a dehydrogenation catalyst.
- In addition, we have developed the methodology to incorporate catalysts into thin films of metal hydrides, ensuring effective loading and nano-scale mixing. The initial results obtained from Raman spectroscopy are encouraging and generate a great level of confidence in our combinatorial tools capabilities.
- Intematix has developed the resources to perform the rapid discovery of active catalysts for metal hydride systems, either by modification of existing equipment, or construction of new facilities. The discovery of active, inexpensive, and light weight catalysts will be of prime importance for the successful advancement of hydrogen systems which can fulfill the DOE goals.

References

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3. Dam et al., *Scripta Materialia* **56**, 853 (2007).