HIGH THROUGHPUT SCREENING OF COMPLEX HYDRIDES FOR HYDROGEN STORAGE

John J. Low*, J.W. Adriaan Sachtler, Gregory J. Lewis, David A. Lesch, and Craig M. Jensen(1)

UOP LLC Research Center, 50 E. Algonquin Road, Des Plaines, IL 60017-5017 USA

(1)Hawaii Hydrogen Carriers, LLC, 3540 Kumu Street, Honolulu HI 96822 USA

Introduction

The discovery that dopants, such as Ti, cause $NaAlH_4$ to reversibly desorb H_2 at mild conditions has spurred a great deal of research into complex metal hydrides. However, no complex hydride meets the targets for automotive hydrogen storage. High throughput screening will accelerate the rate of discovery of improved hydrides and dopants through a combination of Virtual High Throughput Screening (VHTS) with Combinatorial Synthesis and Screening (CSS). Our CSS methods will allow us to screen thousands of samples in a year. VHTS exploits a molecular mechanics method to screen a thousand phases in a month. Combinatorial methods will lead to the discovery of the most promising complex hydrides for hydrogen storage. The results of our medium throughput CSS methods (8 samples simultaneously) are presented here and demonstrate the feasibility of high throughput screening (48 samples simultaneously).

Results and Discussion

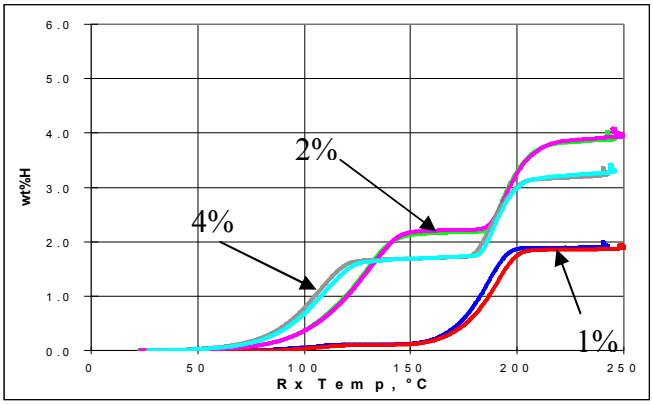

Figure 1. Hydrogen evolution from $NaAlH_4$ doped with 4 wt%, 2 wt% and 1 wt% Ti.

Medium throughput synthesis was carried out by ball milling mixtures of hydrides and dopants similar to the standard methods to preparing Ti doped $NaAlH_4$. Commercially available ball mills allow for the simultaneous synthesis of four to eight samples. Medium throughput screening was carried out in a commercially available reactor system. This system allows for the parallel testing of eight samples. The test involves increasing the temperature of the samples in a closed vessel. The pressure during the temperature increase was measured and then converted to H wt% assuming that the evolved gas is H_2. The sample is then rehydrided and then tested for reversibility. Typical results as shown in Figure 1.

The medium throughput synthesis and screening was used to screen mixtures of $NaAlH_4$, $LiAlH_4$ and $Mg(AlH_4)_2$. The reversible hydrogen content of these mixtures is shown graphically in Figure 2. None of the mixtures shown in Figure 2 has higher hydrogen content than $NaAlH_4$.

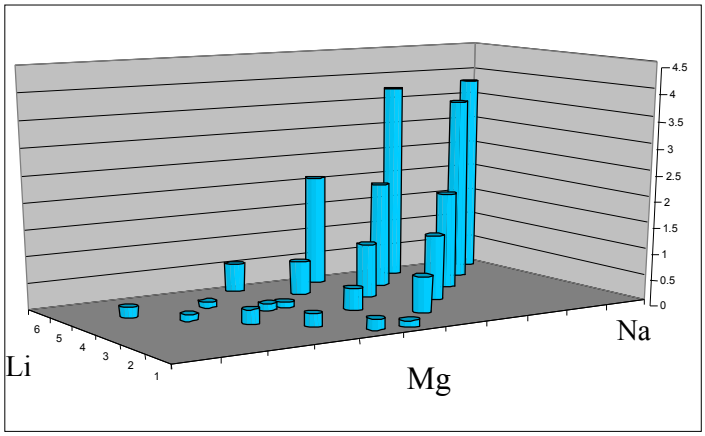

Figure 2. Reversible H_2 Content for Mixtures of $NaAlH_4$, $LiAlH_4$ and $Mg(AlH_4)_2$

Evidence for mixed hexahydride phases can be found in the X-ray powder diffraction patterns of rehydrided mixtures of $NaAlH_4$ and $LiAlH_4$ as shown in Figure 3.

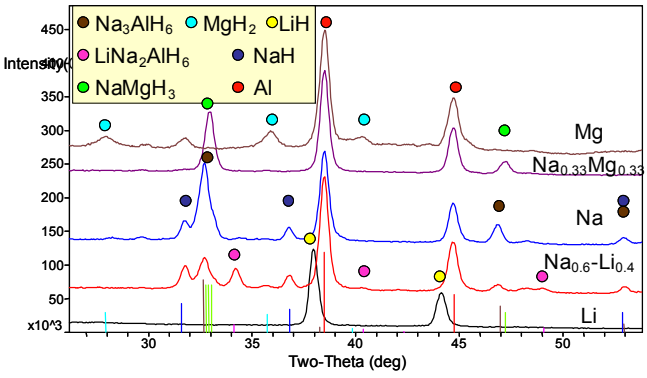

Figure 3. XRD power patterns for spent mixtures of $Mg(AlH_4)_2$, $NaAlH_4$ and $LiAlH_4$

VHTS has been carried out on mixtures of $NaAlH_4$, $LiAlH_4$ and $Mg(AlH_4)_2$. Molecular Mechanics were

used to estimate heats of mixing for VHTS. The parameters for he interatomic potentials used in the molecular mechanics were derived from potentials calculated by the electronic structure program DMOL3. These potentials have been shown to be qualitatively correct in they predict crystal structures and heat capacities which compare well to experiment. (See Figure 4.)

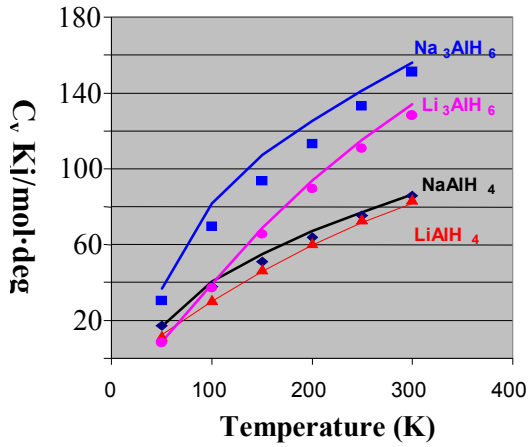

Figure 4. Comparison of predicted and experimental heat capacities. The predicted heat capacities are shown as a solid line and the experimental heat capacities are shown as dots.

The predicted heats of mixing compare well to the heats of mixing predicted by density functional theory as shown in Figure 5.

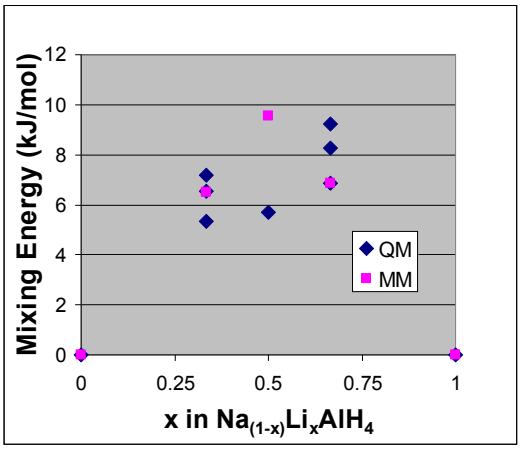

Figure 5. Comparison of Quantum Mechanical and Molecular Mechanics Estimates of the Heat of Mixing for $LiAlH_4$ and $NaAlH_4$

Simulated annealing (SA) was used to estimate the crystal structure of the mixed alanates. The SA procedure was implemented as a UNIX shell script which drives the programs GULP, DLPOLY and the UOP Cation Locator. Currently, this procedure requires 3 hours of CPU time to calculate the heat of mixing for a given composition. It is possible for us use this technique to scan a thousand phases per month on our eight processor system.

The heats of mixing calculated for mixtures of $NaAlH_4$, $LiAlH_4$ and $Mg(AlH_4)_2$ are shown in Figure 6. Note that two phases are predicted to have small heats of mixing. Neither of these phases is predicted to be stable with respect to dehydriding.

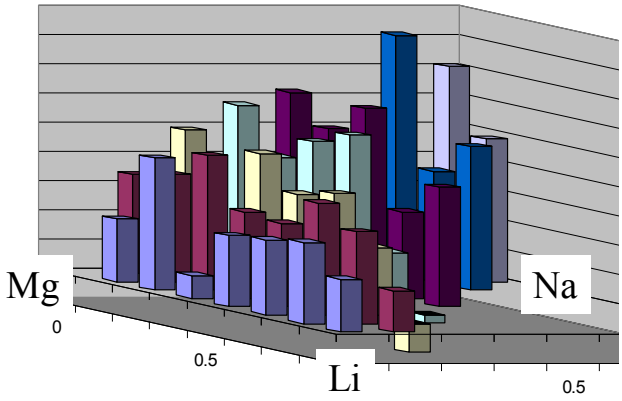

Figure 6. Estimated heats of mixing from molecular mechanics.

Conclusions

The medium throughput CSS approach has been demonstrated and validated for mixtures of alanates. The equipment for High Throughput CSS (HTCSS) is being built and tested. This equipment will allow the scanning of 48 phases simultaneously. VHTS is a validated approach to screening mixtures of alanates faster than HTCSS. These high throughput techniques will be used to explore new materials for hydrogen storage.

References

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