

First principles investigations of the thermodynamics of complex metal hydrides

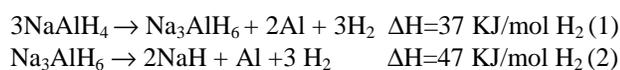
M.E. Arroyo y de Dompablo and G. Ceder.

Department of Material Science and Engineering
Massachusetts Institute of Technology, Cambridge,
Massachusetts 02139, US

The enormous potential of fuel cells has created a growing interest in metal hydrides as an efficient method of reversible hydrogen storage. We have recently investigated the factors that affect the stability of simple binary metal hydrides using first-principles modeling (1). Our analysis found that the hydride formation energy is determined by the cohesive energy of the metal and by its Fermi level. Such insight makes it possible to rationally engineer the stability of metal hydrides for any desired formation energy. In particular hydrides that are either marginally stable or unstable under normal conditions make be particularly interesting for hydrogen storage applications.

We have now also applied first principles computations to predict the behavior of substituted alkali metal aluminum hydrides, a very promising class of systems for reversible hydrogen storage (2-6).

In NaAlH₄ dehydrating takes place in a two step reaction:



The total theoretical reversible H₂ capacity is 5.6 %wt H. At atmospheric pressure the first reaction takes place at near-ambient temperature, while the second reaction occurs at ~110° C (4-6). The performance of this material could be greatly improved by removing the temperature difference between the reactions, preferably bringing both reactions to near the operating temperature of current proton membranes, and at similar pressure. Therefore, thermodynamic modifications are a key factor to enhance the performance of these materials. It would be desirable to selectively decrease the Na₃AlH₆ decomposition temperature, without increasing the NaAlH₄ plateau pressure. We investigate whether this improvement can be achieved by partial substitution of Na or Al. In addition, we investigate the thermodynamics of related compounds (such as analogous borohydrides) to search for new complex hydrides as reversible hydrogen storage systems.

We have performed a first principles investigation on complex hydrides of the type A(MH₄) and A₃(MH₆). The heat of formation, i.e., the amount of heat absorbed/liberated during hydrogen release/uptake, has been calculated using Density Functional Theory for hydrides with A= Li, Na, K and M = B, Al Ga. Mixed Li-Na alanates have also been investigated. In order to establish a comparison, this study has been restricted to the NaAlH₄, α-Na₃AlH₆ and β-Na₃AlH₆ structures.

We find that all of the AMH₄ compounds we investigated have negative heats of formation, except for LiGaH₄. Hence, all these compounds are stable and it should be possible to synthesize them. Borohydrides are much too stable, so hydrogen removal reaction will require very high temperatures. For hydrides less stable than NaAlH₄ the desorption will occur easily, but

absorption may require too high hydrogen pressures. Indeed this has been experimentally observed for LiAlH₄ (3). Our results suggest that partial substitution in the alkaline-metal site in NaAlH₄ by Li or K could provide an optimal material for the reaction in Eq. (1).

We also evaluated for which compounds the hydrogen removal reaction would occur through the intermediate compound A₃MH₆, as is the case for NaAlH₄ which reacts to Na₃AlH₆ before decomposing to NaH. We find that this intermediate will likely not occur for M = B, Ga in AMH₄. Hence for these materials dehydrating may occur in a single step as:



We have investigated in detail the miscibility of Li and Na on the alkali site of the alanates and metal hydride and find that Li may make for a useful substitution in NaAlH₄ and is likely to help optimize both the key reactions for alanates. The light weight of Li is consistent with the objective of maintaining a high gravimetric capacity.

References

- (1) H. Smithson, C.A. Marianetti, D. Morgan, A. Van der Ven, A. Predith, G. Ceder, *Phys. Rev. B* **66**, 144107 (2002)
- (2) B. Bogdanovic and M.J. Schwickardi, *J. Alloys Compd.* **253**, 1 (1997)
- (3) L. Zaluski, A. Zaluska, J.O. Strom-Olsen, *J. Alloys Compd.*, **290**, 71 (1999)
- (4) A. Zaluska, L. Zaluski, J.O. Strom-Olsen, *J. Alloys Compd.*, **298**, 123 (2000)
- (5) B. Bogdanovic, R.A. Brand, A. Marjanovic, M. schwickardi, and J. Tolle, *J. Alloys Compd.*, **302**, 36 (2000)
- (6) K. J. Gross, G.J. Thomas and C.M. Jensen, *J. Alloys Compd.*, **330-332**, 683 (2002)

Acknowledgments

MEAD acknowledges support from the Spanish MECD. GC acknowledges support from the Singapore/MIT alliance. NPACI resources were used for some of the computations in this work.