Adsorption 11: 811–816, 2005

On the Reversibility of Hydrogen Storage in Novel Complex Hydrides

JUN WANG, ARMIN D. EBNER AND JAMES A. RITTER*
Department of Chemical Engineering, Swearingen Engineering Center, University of South Carolina, Columbia, South Carolina 29208, USA
ritter@engr.sc.edu

Abstract. A comparison of the hydrogen release and uptake (cycling) capability of Ti-doped $NaAlH_4$, $LiAlH_4$ and $Mg(AlH_4)_2$ as a function of Ti dopant concentration, temperature, pressure, and cycle number is reported. Temperature programmed desorption revealed hydrogen release capacities of around 3 wt% at 140°C, 3 wt% at 100°C and 6 wt% at 150°C, respectively for the Ti doped Na, Li and Mg alanates. In the same order, release capacities of 0.5, 2.0 and 1.5 wt% were obtained in 150, 6 and 150 min during constant temperature desorption at 90°C. Although all three alanates exhibit striking characteristics that make them potential hydrogen storage materials, it remains that only Ti-doped $NaAlH_4$ exhibits around 3 wt% reversibility under reasonable conditions.

Keywords: titanium chloride, hydrogen storage, sodium alanate, lithium alanate, magnesium alanate

Introduction

Hydrogen storage is proving to be one of the most important issues and potentially biggest roadblock, when it comes to implementing a hydrogen economy (Ritter et al., 2003). Of the three options that exist for storing hydrogen, i.e., in a solid, liquid or gaseous state, solid state hydrogen storage is becoming more and more accepted as the only method of having any expectation of meeting the gravimetric and volumetric densities of the recently announced FreedomCar goals. By 2005, for example, a hydrogen storage material must meet or exceed the following DOE/FredomCAR performance targets to be viable: 1.5 kWh/kg (4.5% hydrogen on a system basis or about 6.5 wt% on a material basis), 1.2 kWh/L and about $6.00/kWh. Of all the known hydrogen storage materials being studied today, including carbon nanotubes, various activated carbon structures, various zeolite structures, metal hydrides (still) and even metal organic framework compounds, complex hydrides are the only ones showing considerable promise of meeting these stringent goals (Ritter et al., 2003).

*To whom correspondence should be addressed.

It is also becoming quite clear that materials relying on physical adsorption alone may never realize such a large reversible hydrogen storage capacity at reasonable conditions. A material needs to interact quite strongly with hydrogen to increase its capacity, with the interaction energy essentially dictating reversible hydrogen uptake and release at reasonable temperatures and pressures. Metal hydrides, like $LaNi_5$, Pd and TiFe, are a good example, because they typically have phase change enthalpies of around 30 to 40 kJ/mol, and rely on interstitial and intermetallic interactions, not simple physical adsorption to achieve only about 1 to 2 wt% hydrogen at near ambient conditions (Sandrock and Thomas, 2001). This enthalpy is much higher than that typically associated with the physical adsorption of hydrogen on many different carbon adsorbents, which is generally 2 to 12 kJ/mol, depending on the carbon, and the temperature and pressure ranges (Valenzuela and Myers, 1989). At this time, however, it is not clear where the complex hydride materials fall within the realm of interaction energies; even so, the $NaAlH_4$ system is providing sufficient evidence to justify the continued study of complex hydride materials for reversible hydrogen storage.

For example, the $NaAlH_4$ system is proving to be a very attractive material for hydrogen storage because it contains a high concentration of useful hydrogen (5.6 wt%). At standard conditions, the dehydrogenation of $NaAlH_4$ is thermodynamically favorable, but it is kinetically slow and takes place at temperatures well above 200°C in a two-step process involving the following reactions (Bogdanovic and Schwickardi, 1997):

$$3NaAlH_4 \rightarrow Na_3AlH_6 + 2Al + 3H_2 \quad (1)$$

$$Na_3AlH_6 \rightarrow 3NaH + Al + 3/2H_2 \quad (2)$$

The first reaction releases 3.7 wt% hydrogen, while the second reaction releases 1.8 wt%. Note that the theoretical hydrogen capacity of $NaAlH_4$ is 7.5 wt%, whereas its useful capacity is only 5.6 wt%. The difference is due to the formation of NaH in Eq. (2), the decomposition temperature of which is too high to be useful for hydrogen generation. $NaAlH_4$ is also only one of a few complex hydrides that are commercially available (Sandrock and Thomas, 2001). This fact has made it very popular to study as a hydrogen storage material, especially since Bogdanovic and Schwickardi (1997) showed that the dehydrogenation temperature, and hence the kinetics of dehydrogenation and also the rehydrogenation conditions, could be markedly improved by the addition of a dopant, such as titanium butoxide, to $NaAlH_4$. Much follow on work has been done with metal-doped $NaAlH_4$ (Zidan et al., 1999; Jensen et al., 1999; Bogdanovic et al., 2003), with state-of-the-art being about 3 wt% reversible hydrogen capacity at 110°C (Ritter et al., 2003). Nevertheless, this performance level makes it one of the highest capacity, hydride based, hydrogen storage materials known (Sandrock and Thomas, 2001). This very favorable result has also sparked considerable interest in other complex hydride materials, especially $LiAlH_4$ (Chen et al., 2001; Balema et al., 2000, 2001) and $Mg(AlH_4)_2$ (Fichtner and Fuhr, 2002).

To date, however, no one has undertaken a systematic analysis of the cyclability and stability of lithium aluminum hydride as a potential hydrogen storage material. Similar to Eqs. (1) and (2), the thermal decomposition of $LiAlH_4$ occurs in the following two steps:

$$3LiAlH_4 \rightarrow Li_3AlH_6 + 2Al + 3H_2 \quad (3)$$

$$Li_3AlH_6 \rightarrow 3LiH + Al + 3/2H_2 \quad (4)$$

The first reaction releases 5.4 wt% hydrogen, while the second reaction releases 2.5 wt%. With a useful hydrogen capacity of 7.9 wt% and a low decomposition temperature (Balema et al., 200), $LiAlH_4$ exhibits a strong potential as a hydrogen storage material. Note that the theoretical hydrogen capacity of $LiAlH_4$ is 10.5 wt%, whereas its useful capacity is only 7.9 wt%. Again, this difference is due to the formation of very stable LiH Eq. (4). Moreover, it has been reported that the ΔH° at 25°C for the decomposition of $LiAlH_4$ through Eq. (3) and $NaAlH_4$ through Eq. (1) are 28.5 and 56.5 kJ/mol, respectively (Bass and Smith, 1963). This indicates that thermal dissociation is more thermodynamically favorable for $LiAlH_4$ than for $NaAlH_4$. Additionally, it has been shown that the activation energy for the decomposition of Li_3AlH_6 is 54.8 kJ/mol H_2, while that for Na_3AlH_6 is 96.9 kJ/mol H_2 (Sandrock et al., 2002; Chen et al., 2001). Evidently, lithium alanate is less stable than sodium alanate; however, no conclusive studies have been done to show whether Eqs. (3) and (4) are reversible (i.e., cyclable) when doped with Ti. In fact, lithium alanate has been reported to completely decompose after 5 min of mechanochemical treatment with 3 mol% $TiCl_4$ (Belema et al., 2001). It has also been reported that doping lithium alanate with 2 mol% $TiCl_3$ through mechanochemical treatment does not cause it to decompose and yields a reversible compound according to Eq. (4) (Chen et al., 2001). These results are clearly contradictory.

Also, to date, no one has undertaken a systematic analysis of the cyclability and stability of magnesium aluminum hydride as a potential hydrogen storage material. Magnesium alanate may be a very promising candidate as an on-board hydrogen storage material because it readily decomposes below 200°C and contains 9.3 wt% hydrogen (Fichtner and Fuhr, 2002). The decomposition of $Mg(AlH_4)_2$ also follows a two step reaction:

$$Mg(AlH_4)_2 \rightarrow MgH_2 + 2Al + 3H_2 \quad (5)$$

$$MgH_2 \rightarrow Mg + H_2 \quad (6)$$

The first reaction releases 7.0 wt% hydrogen, while the second reaction releases 2.3 wt%. It is noteworthy that these reactions are somewhat different from the reactions associated with the decomposition of $NaAlH_4$ and $LiAlH_4$. $Mg(AlH_4)_2$ decomposes directly to MgH_2, which further and rather easily decomposes to Mg. Hence, $Mg(AlH_4)_2$ has the potential to deliver all of its theoretical hydrogen of 9.3 wt%. This amount of hydrogen just meets the 2005 Freedon CAR goals on a wt% material basis (Ritter et al., 2003). However,

this compound is not available commercially, which has hindered its study. Nevertheless, in recent work by Fichtner and Fuhr (2002), a systematic procedure for the synthesis of rather pure $Mg(AlH_4)_2$ was developed; some of this material was made available to the authors to study its reversibility when doped with Ti.

Therefore, the objective of this study was to analyze the dehydrogenation kinetics, cyclability and stability of the lithium and magnesium alanate systems when doped with titanium chloride through mechanochemical treatment. Temperature programmed desorption (TPD) and constant temperature desorption (CTD) experiments were carried out with just doped samples and after several rehydrogenation cycles of both alanates to determine their hydrogen release capacities and regenerability as a function of temperature and pressure. The results are compared to the state-of-the-art sodium alanate system prepared and tested under similar conditions.

Experimental

$TiCl_3$ (Aldrich, 99.99%, anhydrous), the catalyst precursor, was used as received. Crystalline $NaAlH_4$ (Fluka) was purified from a THF (Aldrich, 99.9%, anhydrous) solution and vacuum dried. The dried $NaAlH_4$ was mixed with $TiCl_3$ in THF to produce a doped sample containing up to 4 mol% Ti. The THF was evaporated while the $NaAlH_4$ and the catalyst were mixed manually for about 30 minutes using a mortar and pestle, or until the samples were completely dry. Crystalline $LiAlH_4$ in dry powder form (Aldrich, 95%) was also used as received. The $LiAlH_4$ was dry mixed with $TiCl_3$ to produce a doped sample containing up to 2 mol% Ti. Sufficiently pure $Mg(AlH_4)_2$, obtained from Fichtner and Fuhr (2002) was also used as received. The $Mg(AlH_4)_2$ was dry mixed with $TiCl_3$ to produce a doped sample containing up to 2 mol% Ti. These mixtures were then ball milled for the desired time using a SPEX 8000 high-energy mill. All procedures were carried out in a nitrogen glove box.

A thermogravimetric analyzer (TGA) located in a nitrogen glove box was used to determine the dehydrogenation kinetics at atmospheric pressure using TPD and CTD modes. For TPD runs, the samples were heated to 250°C at a ramping rate of 5°C/min under 1 atm of He, using an initial 1 min delay to ensure an environment of pure He. For CTD runs, a similar procedure was followed except that the samples were heated rapidly to the desired temperature and then held at this temperature for the desired time. Approximately 10 mg of sample were used in each TPD or CTD run.

A 3,000 psig Parr reactor, installed in an automated pressure and temperature cycling system, was used to evaluate sample rehydrogenation and cycling capabilities. The reactor conditions were continuously monitored and controlled with a computer. Samples were loaded into the reactor while in the glove box and then transferred to the cycling system. After completion of each rehydrogenation or cycling trial, the high pressure setting of hydrogen was maintained until the temperature was reduced to room temperature to prevent dehydrogenation. Then the pressure was released and the sample was removed in the glove box for TGA studies.

Rehydrogenation studies were carried out with $NaAlH_4$ doped with 2 mol% Ti and ball milled 120 min, $LiAlH_4$ doped with 2 mol% Ti and ball milled for 20 min, and $Mg(AlH_4)_2$ doped with 1 mol% Ti and ball milled 15 min. For all three alanates, a first rehydrogenation attempt was carried out in the Parr system at 125°C and 1,200 psig after being discharged of hydrogen at 125°C and 50 psig for 16 hrs; TPD was done afterwards. TPD was also done on all samples after carrying out 0 and 5 dehydrogenation (4 hrs) and rehydrogenation (8 hrs) cycles between 50 and 1,200 psig at 125°C for Na alanate, between 50 and 2,100 psig at 140°C for Li alanate, and between 50 and 1,500 psig at 150°C for Mg alanate in the Parr reactor system.

Results and Discussion

The results shown in Fig. 1 provide the first comprehensive comparison of the effect of Ti as a dopant on the dehydrogenation of $NaAlH_4$, $LiAlH_4$ and $Mg(AlH_4)_2$ complex hydrides. Figure 1A displays the typical behavior of the dehydrogenation of $NaAlH_4$ doped with 1 to 4 mol% Ti during TPD, after being balled milled for 120 min. The first plateau region corresponds to hydrogen being released according to the decomposition reaction in Eq. (1), whereas the second plateau region corresponds to the decomposition reaction in Eq. (2). In the first case, about 3 wt% hydrogen is released and in the second case about 2 wt% hydrogen is released, with the total being about 5 wt% hydrogen. For the first reaction, the release rate is faster and occurs at a lower temperature with increasing Ti concentration. The Ti also has a more pronounced effect on the first reaction than the second reaction. Note that without the Ti dopant present, the decomposition reaction in Eq. (1) would not begin to yield any hydrogen until

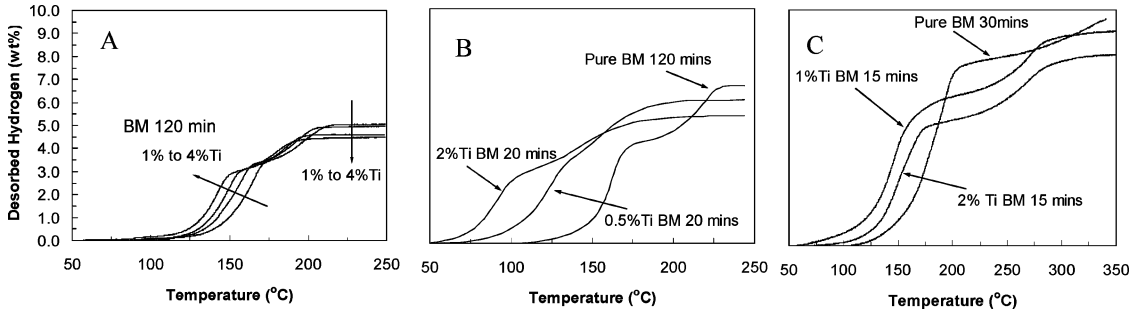

Figure 1. TPD (5°C/min) of the (A) $NaAlH_4$, (B) $LiAlH_4$, and (C) $Mg(AlH_4)_2$ systems when doped with Ti and ball milled.

about 230°C or so. This 3 wt% hydrogen release is essentially state-of-the-art for this system.

Figure 1(B) displays the behavior of the dehydrogenation of $LiAlH_4$ during TPD for an undoped sample ball milled for 120 min, and for two samples doped with 0.5 and 2 mol% Ti and each ball milled for 20 min. Again, the first plateau region corresponds to hydrogen being released according to the reaction in Eq. (3), whereas the second plateau region corresponds to the reaction in Eq. (4). In the first case, about 3 to 5 wt% hydrogen is released, and in the second case about 3 to 4 wt % hydrogen is released, both being dependent on the dopant level and ball milling time, with the total being 6 to 7 wt% hydrogen. The effect of the Ti dopant is very pronounced in this case. Increasing the dopant level causes hydrogen to be released at a much lower temperature, but also in smaller amounts. Doping with 0.5 mol% Ti consistently yields a marked decrease of around 50°C in the overall dehydrogenation temperature. Increasing the dopant level further to 2 mol% Ti yields an initial decomposition temperature similar to that obtained for the sample doped with 0.5 mol% Ti; however, the overall dehydrogenation temperature is lowered substantially by about 25°C. The Ti dopant also affects the first reaction more than the second reaction, similarly to the $NaAlH_4$ system. Contrary to information published in the literature (Balema et al., 2000, 2001), the stability of the $LiALH_4$ system, whether doped or not, does not seem to be a major issue. Note that when $LiAlH_4$ is doped with 2 mol% Ti, it releases 3 wt% hydrogen before 100°C is reached. The $NaAlH_4$ system, even when doped with 4 mol% Ti, does not begin to release hydrogen until about 100°C. Clearly, this makes the $LiAlH_4$ very attractive for hydrogen storage if it can be made to rehydrogenate.

Figure 1(C) displays the behavior of the dehydrogenation of $Mg(AlH_4)_2$ during TPD for an undoped sample ball milled for 30 min, and for two samples doped with 1 and 2 mol% Ti and each ball milled for 15 min. Again, the first plateau region corresponds to hydrogen being released according to the reaction in Eq. (5), whereas the second plateau region corresponds to the reaction in Eq. (6). In the first case, about 6 to 8 wt% hydrogen is released, and in the second case about 1 to 3 wt% hydrogen is released, both being dependent on the dopant level and ball milling time, with the total being 8 to 9 wt% hydrogen. The effect of the Ti dopant is again quite pronounced, but not as pronounced as the $LiAlH_4$ system. However, 1 mol% Ti does better than 2 mol%; this interesting effect has not been observed with either the $NaAlH_4$ or $LiAlH_4$ system. Nevertheless, at about 60°C, the doped samples begin to release hydrogen with significant amounts being released below 150°C. Hence, $Mg(AlH_4)_2$ doped with 1 mol% Ti and ball milled for 15 minutes exhibits the best dehydrogenation kinetics to date, releasing over 5 wt% hydrogen below 150°C. However, as exciting as these results may seem, the dehydrogenation temperature is still a bit too high for most practical applications, and reversibility is still questionable, as shown below.

Figure 2 shows the CTD curves obtained at 90°C for samples of $NaAlH_4$ ball milled for 120 min and doped with 4 mol% Ti, $LiAlH_4$ ball milled for 20 minutes and doped with 0.5 and 2 mol% Ti, and $Mg(AlH_4)_2$ ball milled for 15 min and doped with 1 mol% Ti. The relative hydrogen release rates of these doped complex hydride materials is quite clear. In 150 min, the sodium alanate releases less than 0.5 wt% hydrogen, and the magnesium alanate releases less than 1.5 wt% hydrogen, both being comparable and slow at this temperature. In contrast, the lithium alanate sample doped with 0.5 mol% Ti yields 3 wt% hydrogen within 30 min, while the sample doped with 2 mol% Ti yields 2 wt% hydrogen within 6 min, exceedingly fast rates

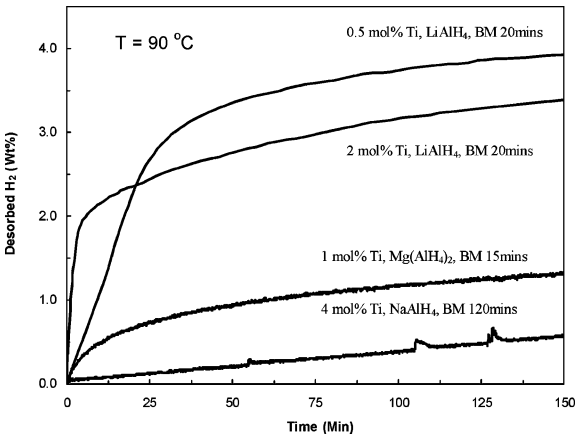

Figure 2. CTD (90°C) of the $NaAlH_4$, $LiAlH_4$, and $Mg(AlH_4)_2$ systems when ball milled and doped with Ti.

compared to the sodium and magnesium systems. Although the dehydrogenation rate of the $LiAlH_4$ sample doped with 2 mol% Ti is significantly greater than that associated with the $LiAlH_4$ sample doped with 0.5 mol% Ti, the latter has a greater yield of hydrogen due to the lower dopant level. For hydrogen storage, these results make the $LiAlH_4$ system look very attractive and the $Mg(AlH_4)_2$ system look somewhat attractive compared to the $NaAlH_4$ system.

Figure 3(A) compares the $NaAlH_4$, $LiAlH_4$ and $Mg(AlH_4)_2$ systems during the first rehydrogenation cycle carried out in the Parr cycling system at 125°C and 1,200 pisg after being discharged of hydrogen at 125°C and 50 psig for 16 hrs. The uptake of hydrogen for the Na alanate system is evident by the pressure decreasing with time in this closed system. However, no pressure changes are observed with the Li and Mg alanate systems, indicating no uptake of hydrogen after one discharge and charge cycle at these conditions. TPD runs after 0 and 5 dehydrogenation/rehydrogenation cycles with the Na, Li and Mg alanate systems are shown in Fig. 3B. The Na system is clearly reversible with the typical loss in capacity of about 1 wt% observed after several cycles. In contrast, the Li alanate system shows no uptake of hydrogen even after five cycles; and although the Mg alanate system shows some release of hydrogen at about 250°C after 5 cycles, this release is primarily from the second reaction in Eq. (6), which is never fully dehydrogenated at the cycling temperature employed here. Hence, neither Li nor Mg exhibit any reversibility under conditions that cause the Na system to easily rehydrogenate, even after 5 cycles. It is noteworthy that the Li system appears to be stable when doped and ball milled, which is somewhat contrary to that reported elsewhere (Balema et al., 2000, 2001). The Li system is also not reversible at the conditions where reversibility was thought to occur, but probably did not (Chen et al., 2001).

Conclusions

A study of the hydrogen release and uptake capability of Ti-doped $NaAlH_4$, $LiAlH_4$ and $Mg(AlH_4)_2$ as a function of Ti concentration, temperature, pressure,

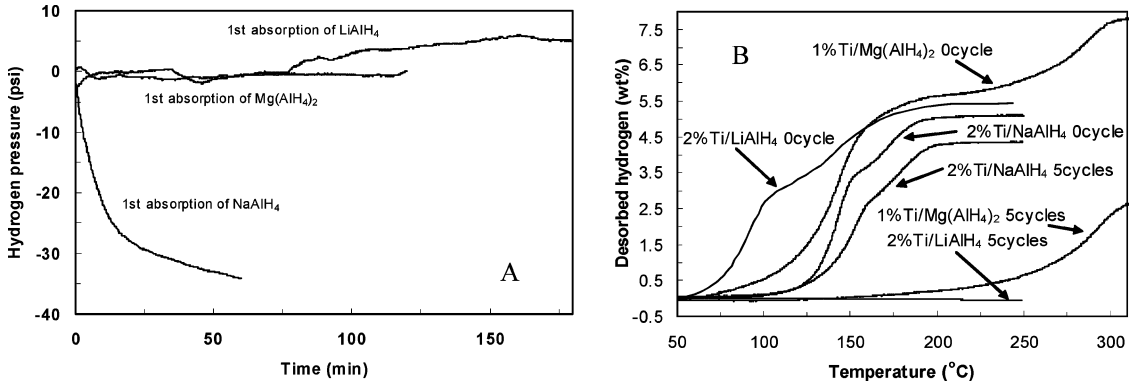

Figure 3. (A) Comparison of the $NaAlH_4$, $LiAlH_4$, and $Mg(AlH_4)_2$ systems during the first rehydrogenation cycle carried out in the Parr system at 125°C and 1,200 pisg after being discharged of hydrogen at 125°C and 50 psig for 16 hrs; and (B) TPD (5°C/min) of the $NaAlH_4$, $LiAlH_4$, and $Mg(AlH_4)_2$ systems after carrying out 0 and 5 discharge (4 hrs) and charge (8 hrs) cycles in the Parr system between 50 and 1,200 psig at 125°C for Na alanate ball milled 120 min, between 50 and 2,100 psig at 140°C for Li alanate ball milled for 20 min, and between 50 and 1,500 psig at 150°C for Mg alanate ball milled 15 min.

and cycle number was carried out. This was the first systematic study of the dehydrogenation kinetics and cyclability of Ti doped $LiAlH_4$. It was found that Li alanate can be dry doped with 2 mol% Ti and ball milled for up to 20 minutes with only minor hydrogen losses. $LiAlH_4$ doped with as little as 0.5 mol% Ti exhibited dehydrogenation rates at 90°C that were far superior to those exhibited by $NaAlH_4$ at 125°C, even when doped with 4 mol% Ti. However, Ti doped $LiAlH_4$ was found to be irreversible at conditions where Ti doped $NaAlH_4$ is easily rehydrogenated, i.e., at 125°C and 1,200 psig. Nevertheless, research is continuing with the Li alanate system because its kinetics are too appealing to give up at this point. This was also the first ever study of the dehydrogenation kinetics of Ti doped $Mg(AlH_4)_2$. Both, ball milling and Ti as a catalyst increased the dehydrogenation kinetics of $Mg(AlH_4)_2$, with very high hydrogen capacities and reasonable dehydrogenation rates exhibited at 150°C. This dehydrogenation temperature is still too high, however, for most practical applications. Moreover, Ti doped $Mg(AlH_4)_2$ was found to be irreversible at conditions where Ti doped $NaAlH_4$ is easily rehydrogenated. Hence, other conditions and dopants must be explored, because these impressive hydrogen capacities and kinetics warrant further study of this rather hopeful material. In conclusion, although all three alanates exhibit striking characteristics that make them potential hydrogen storage materials, it remains that only Ti-doped $NaAlH_4$ exhibits around 3 wt% reversibility under reasonable conditions.

Acknowledgments

The authors are grateful for the financial support provided in part by the US Army CECOM under Agreement Number DAAB07-03-3-K416, AMSEL-RD-C2-AP-ES-E (E1) at Ft Belvoir, VA, and in part by Mead-Westvaco and the Separations Research Program at the University of Texas at Austin. The authors also are grateful to M. Fichtner for supplying them with a sample of $Mg(AlH_4)_2$ for testing.

References

Balema, V., V. Pecharsky, and K. Dennis, "Solid State Phase Transformations in $LiAlH_4$ During High-Energy Ball-Milling," *J. Alloys Comp.*, **313**, 69–74 (2000).

Balema, V., J. Wiench, K. Dennis, M. Pruski, and V. Pecharsky, "Titanium Catalyzed Solid-State Transformations in $LiAlH_4$ During High-Energy Ball-Milling," *J. Alloys Comp.*, **329**, 108–114 (2001).

Bass, G. Jr. and M. Smith, "Heats and Free Energies of Formation of the Alkali Aluminum Hydrides and of Cesium Hydride," *J. Chem. Eng. Data.*, **8**, 342–346 (1963).

Bogdanovic, B. and M. Schwickardi, "Ti-Doped Alkali Metal Aluminum Hydrides as Potential Novel Reversible Hydrogen Storage Materials," *J. Alloys Comp.*, **253**, 1–9 (1997).

Bogdanovic, B. et al., "Investigation of Hydrogen Discharging and Recharging Processes of Ti-Doped $NaAlH_4$ by X-ray Diffraction Analysis (XRD) and Solid-State NMR Spectroscopy," *J. Alloys Comp.*, **350**, 246–255 (2003).

Chen, J., N. Kuriyama, Q. Zu, H. Takeshita, and T. Saki, "Reversible Hydrogen Storage via Titanium-Catalyzed $LiAlH_4$ and Li_3AlH_6,"*J. Phys. Chem. B.*, **105**, 11214–11220 (2001).

Fichtner, M. and O. Fuhr, "Synthesis and Structures of Magnesium Alanate and Two Solvent Adducts," *J. Alloys Comp.*, **345**, 286–296 (2002).

Jensen, C.M., R. Zidan, N. Mariels, A. Hee, and C. Hagen, "Advanced Titanium Doping of Sodium Aluminum Hydride: Segue to a Practical Hydrogen Storage Material," *Inter. J. Hydrogen Energy*, **24**, 461–465 (1999).

Ritter, J.A., A.D. Ebner, J. Wang, and R. Zidan, "Implementing a Hydrogen Economy," *Materials Today*, **9**, 18–23 (2003).

Sandrock, G., K.J. Gross, G. Thomas, C.M. Jensen, D. Meeker, and S. Takara, "Engineering Considerations in the Use of Catalyzed Sodium Alanates for Hydrogen Storage," *J. Alloys Comp.*, **330–332**, 696–701 (2002).

Sandrock, G. and G. Thomas, "The IEA/DOE/SNL On-Line Hydride Databases," *Appl. Phys. A: Mat. Sci. Proc.*,**72**, 153–155 (2001).

Valenzuela, D.P. and A.L. Myers, *Adsorption Equilibrium Data Handbook*, Prentice Hall (1989).

Zidan, R.A., S. Takara, A.G. Hee, and C.M. Jensen, "Hydrogen Cycling Behavior of Zirconium and Titanium-Zirconium-Doped Sodium Aluminum Hydride," *J Alloys Comp.*, **285**, 119–122 (1999).