# Dehydrogenation of a Combined $LiAlH_4/LiNH_2$ System

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Although there have been numerous materials systems studied as potential candidates for hydrogen storage applications, none of the materials known to date has demonstrated enough hydrogen capacity or efficiency at required operating temperature ranges. There are still considerable opportunities for discovery of new materials or material systems that could lead to advances in science as well as commercial technologies in this area. $LiAlH_4$ is one of the most promising materials owing to its high hydrogen content. In the present work, we investigated dehydrogenation properties of the combined system of $LiAlH_4$ and $LiNH_2$ under atmospheric argon. Thermogravimetric analysis (TGA) of $2LiAlH_4/LiNH_2$ mixtures without any catalysts indicated that a large amount of hydrogen (~8.1 wt %) can be released between 85 and 320 °C under a heating rate of 2 °C/min in three dehydrogenation reaction steps. It is found that $LiNH_2$ effectively destabilizes $LiAlH_4$ by reacting with LiH during the dehydrogenation process of $LiAlH_4$.

## 1. Introduction

As a promising clean fuel for vehicles, hydrogen can be used for propulsion, either directly or in fuel cells. In both cases, a suitable hydrogen-storage material is needed to make this source of energy economically viable. Although there have been numerous materials systems studied as potential candidates for hydrogen storage applications, none of the materials known to date have demonstrated sufficient hydrogen capacity or efficiency at required operating temperature ranges. There are still considerable opportunities for discovery of new materials or material systems that could lead to advances in science as well as commercial technologies in this area.

Following the break-through work on Ti-doped $NaAlH_4$ by Bogdanovic and Schwickardi in 1997,[1] alkali- and alkaline-earth-metal-based complex aluminum hydrides, such as $MAlH_4$ (M = Li,[2−6] Na,[7−14] K[15]), have been studied intensively as possible candidate materials for high-capacity reversible hydrogen storage. It has been generally found that alkali-based aluminum hydrides have great potential for storing hydrogen at moderate temperatures and pressures. Among them, $LiAlH_4$, which was first synthesized in 1947[16] and is used as a powerful reducing agent in organic chemisty,[17] is one of the materials having the highest inherent hydrogen capacity. Its total hydrogen content is approximately 10.6 wt %.

In addition to the inherent hydrogen storage capacity, critical requirements for any solid hydrogen storage materials include the reversibility of hydrogen release and uptake reactions and the kinetics of these reactions. During decomposition at elevated temperatures, lithium alanate, $LiAlH_4$, first reduces to intermediate compounds $Li_3AlH_6$ and then to LiH at around 160 to 210 °C, and liberates 5.3 and 2.6 wt % of hydrogen, respectively.[18−22] The dehydrogenation of LiH, however, occurs at much higher temperatures, around 720 °C,[23] liberating another 2.6 wt % of hydrogen. This temperature is too high, and hence the decomposition of LiH is not considered viable for practical purposes. Thus, the maximum potential hydrogen storage capacity of $LiAlH_4$ decreases to 7.9 wt % for $LiAlH_4$. Clearly, the difficulty of releasing $H_2$ from LiH limits the practical hydrogen capacity of lithium alanates. It is noted that the same problem also exists for the $NaAlH_4$ system.

Recently, Chen et al.[24] and Hu and Ruckenstein[25] investigated the potential of lithium nitride, $Li_3N$, as a promising hydrogen storage material, in which the hydrogenation and dehydrogenation are accomplished by the following two-step reversible reactions (R1 and R2):[26]

$$LiNH_2 + LiH \leftrightarrow Li_2NH + H_2 \quad (1)$$

$$Li_2NH + LiH \leftrightarrow Li_3N + H_2 \quad (2)$$

$LiNH_2$ and LiH are used as the starting materials, and the dehydrogenation temperature is around 200 to 430 °C in a vacuum, based on the literature.[24−26]

As mentioned earlier, the utility of $LiAlH_4$ is limited because the temperature for dehydrogenation of LiH is too high. However, reactions 1 and 2 suggest that the dehydrogenation temperature of LiH can be decreased dramatically when it is combined with $LiNH_2$.[24−26] It is therefore hypothesized that, if $LiAlH_4$ and $LiNH_2$ are combined, the LiH that forms as an intermediate product of the dehydrogenation of $LiAlH_4$ can then react with $LiNH_2$ to release $H_2$ at a low temperature. In other words, all the hydrogen contained in $LiAlH_4$ can be released, which could raise the effective hydrogen storage capacity of $LiAlH_4$. In the present work, the dehydrogenation reactions of $LiAlH_4$ were studied by combining it with $LiNH_2$. The new combined system ($2LiAlH_4/LiNH_2$) has a very high inherent hydrogen capacity—10.1 wt %, theoretically. The characteristics of dehydrogenation reactions of the combined system are compared with that of $LiAlH_4$ and $LiNH_2$/2LiH. The effects of doping on the combined reactions are also investigated.

## 2. Experimental Section

The starting materials, lithium aluminum hydride ($LiAlH_4$, 95%), lithium amide ($LiNH_2$, 95%), and $TiCl_3-{}^1/_3AlCl_3$, were

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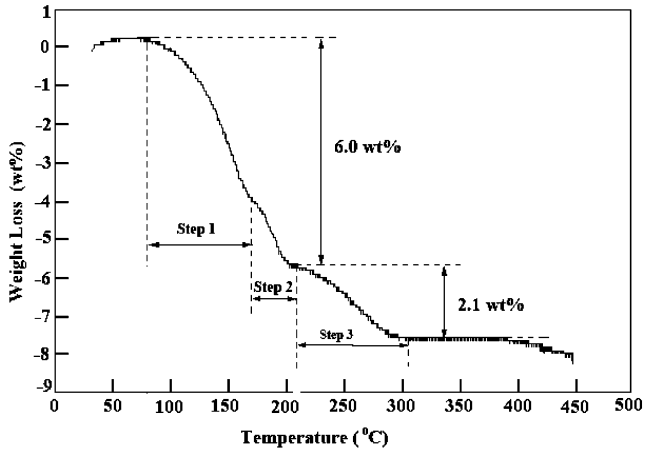


**Figure 1.** TGA curves of $2LiAlH_4 + LiNH_2$ (sample 1) under atmospheric argon and a heating rate of 2 °C/min.

purchased from Aldrich Chemical and used as received without any further purification. To prevent samples and raw materials from undergoing oxidation and/or hydroxide formation, they were stored and handled in a nitrogen-filled glovebox.

A mixture of $LiAlH_4$ and $LiNH_2$ with a molar ratio of 2:1 was ground by hand in a mortar for 10 min (designated as sample 1). Another mixture of $2LiAlH_4/LiNH_2/TiCl_3{-}^1/_3AlCl_3$ was obtained by further grinding the above mixture with 4 wt % of $TiCl_3{-}^1/_3AlCl_3$ for 5 min (designated as sample 2).

The thermal gas desorption properties of the mixtures were determined by thermogravimetry analyzer (TGA) (Shimadzu TGA50) upon heating to 450 °C at a heating rate of 2 °C/min. To avoid any exposure of the sample to air, this equipment was set inside the nitrogen-filled glovebox equipped with a recirculation system.

The identification of reactants and reaction products in the mixture before and after thermogravimetric analysis was carried out with a Siemens D5000 model X-ray diffractometer with Ni-filtered Cu K$\alpha$ radiation ($\lambda = 1.5406$ Å). A scanning rate of 0.02 deg/s was applied to record the patterns in the $2\theta$ range of 10° to 90°. In addition, it is noted that the amorphous-like background in the XRD patterns is attributed to the thin plastic films that were used to cover the powders.

## 3. Results and Discussion

**3.1. Desorption Properties of $2LiAlH_4/LiNH_2$.** Figure 1 shows the TGA result of the $2LiAlH_4/LiNH_2$ without catalyst (sample 1). The sample was run under argon atmosphere with a heating rate of 2 °C/min. Temperatures are held constant at time points when there is a definitive weight loss indicating a decomposition reaction until the reaction step is complete. Each reaction step is identified by the changes of the rate of the weight loss. It can be seen that a total of 8.1 wt % of hydrogen was released within the examined temperature range. The desorption process appears to consist of three steps: The first two steps are in the temperature range of 85 to 200 °C. A total of 6.0 wt % of hydrogen was released within these two steps. These two weight-loss steps can best be described by the following reactions (R3 and R4):

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

$$Li_3AlH_6 \rightarrow 3LiH + Al + {}^3/_2H_2 \quad (4)$$

The third step occurs at above 210 °C. Another 2.1 wt % of hydrogen was desorbed during the third step, which corresponds

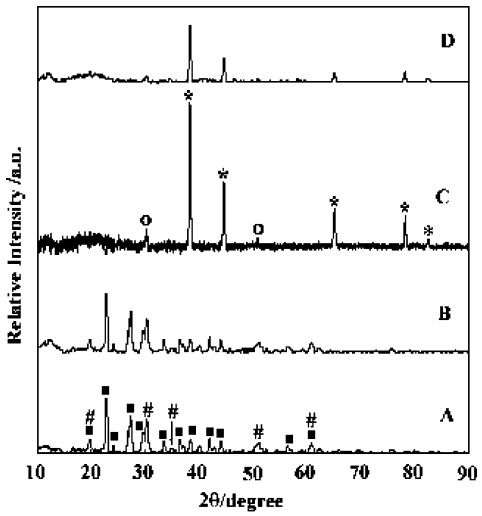


**Figure 2.** XRD patterns of (A) sample 1 before dehydrogenation, (B) sample 2 before dehydrogenation, (C) sample 1 after dehydrogenation, and (D) sample 2 after dehydrogenation.

to reaction 1. Thus, the overall reaction for the combined $LiAlH_4$ and $LiNH_2$ system can be given as (R5):

$$2LiAlH_4 + LiNH_2 \rightarrow 2Al + Li_2NH + LiH + 4H_2 \quad (5)$$

To verify these specific reaction steps, X-ray diffraction analysis was carried out on the raw materials as well as on the reaction products. Figure 2 shows the XRD patterns of selected samples before and after dehydrogenation. Crystalline phases are identified by comparing the experimental data with JCPDS files from the International Center for Diffraction Data. In Figure 2A, which shows the XRD pattern of sample 1 before dehydrogenation, the peaks marked with closed squares are attributed to the phase of monoclinic $LiAlH_4$, and those marked with hashes are attributed to the phase of tetragonal $LiNH_2$. Figure 2B shows the XRD pattern of sample 2 before dehydrogenation. No characteristic peaks of crystalline $TiCl_3$ or $AlCl_3$ are observed, which is possibly due to their low contents. Figures 2C and 2D show the XRD patterns of samples 1 and 2, respectively, after dehydrogenation. The XRD patterns clearly show that $LiAlH_4$ and $LiNH_2$ are absent in the samples, indicating that they are consumed by the decomposition and some new compounds formed. In these figures, the peaks that are marked with open circles are indexed to be the cubic phase of $Li_2NH$, and those marked with asterisks are indexed to be Al or Al + LiH (Al and LiH peaks overlap on the XRD patterns). However, because only $Li_2NH$, and not $Li_3N$, exists after dehydrogenation, these peaks are indexed to be the mixture of Al + LiH, based on the reaction between LiH and $LiNH_2$.[24,26]

Figure 2 confirms the overall dehydrogenation (R5) by identification of the final reaction products. However, it does not provide any information regarding the reaction path. To determine the reaction paths, i.e., the intermediate reactions, two approaches were taken. First, R3 and R4 are proposed as the intermediate reactions because the molar balance of these reactions matches with the weight loss reaction steps as indicated by the TGA curve in Figure 1. To further confirm each reaction step, the intermediate products after partial dehydrogenation at specific temperatures were analyzed with XRD. Figure 3A shows the XRD pattern of the product after dehydrogenation at 100 °C for 20 min, in which the peaks that are marked with open circles are indexed to be monoclinic $Li_3AlH_6$, those marked

**TABLE 1: The Dehydrogenation Temperature and Hydrogen Capacity for Different Systems**

| | $LiAlH_4$ | $LiAlH_4$ + 4 wt % $TiCl_3$−$AlCl_3$ | 2LiH + $LiNH_2$ | 2$LiAlH_4$ + $LiNH_2$ | 2$LiAlH_4$ + $LiNH_2$ + 4 wt % $TiCl_3$−$AlCl_3$ |
|---|---|---|---|---|---|
| step 1 (°C/wt %) | 170/4.4 | 140/4.4 | 220/6.0 | 85/4.0 | 95/3.8 |
| step 2 (°C/wt %) | 200/2.0 | 165/2.2 | | 165/2.0 | 140/2.1 |
| step 3 (°C/wt %) | | | | 200/2.1 | 205/2.2 |
| total wt % $H_2$ | 6.4 | 6.6 | 6.0 | 8.1 | 8.1 |

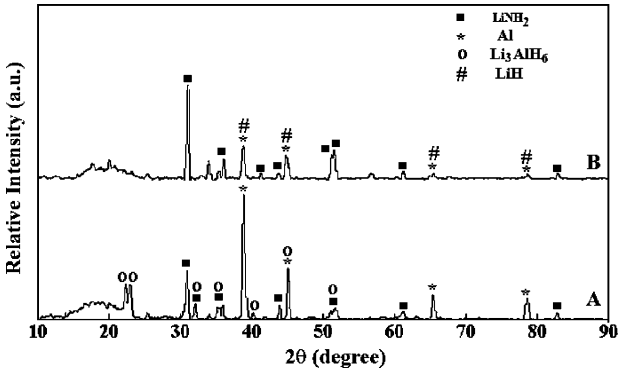


**Figure 3.** XRD patterns of (A) sample 1 after heating to 100 °C and (B) sample 1 after heating to 150 °C.

with asterisks are indexed to be cubic aluminum, and those marked with closed squares are indexed to be tetragonal $LiNH_2$. This confirms that the first dehydrogenation step corresponds to R3.

Figure 3B is the XRD pattern of the product after dehydrogenation at 150 °C for 20 min. It clearly shows that the sample contains $LiNH_2$ (marked with closed squares); however, $Li_3AlH_6$ is absent. The peaks that are marked with asterisks and hashes are indexed to be Al + LiH. This result confirms reaction 4. Therefore, the overall reaction path follows R3, R4, and R1.

**3.2. Comparison of the Current System to $LiAlH_4$ and 2LiH + $LiNH_2$.** To compare the kinetics of the dehydrogenation of the combined system (2$LiAlH_4$/$LiNH_2$) with that of the $LiAlH_4$ and $LiNH_2$/2LiH systems, TGA experiments were carried out with $LiAlH_4$, Ti-doped $LiAlH_4$, and $LiNH_2$/LiH under the same conditions as described for 2$LiAlH_4$/$LiNH_2$. Figure 4 shows the TGA results of Ti-doped $LiAlH_4$ and $LiNH_2$/2LiH. Primary characteristics of dehydrogenation processes include the temperature and the percentage of hydrogen released for each step of the process. Table 1 compares these characteristics among the Ti-doped $LiAlH_4$, $LiNH_2$/2LiH, and 2$LiAlH_4$/$LiNH_2$ systems. Table 1 shows that the dehydrogenation temperature of the 2$LiAlH_4$/$LiNH_2$ system is lower than that of either the Ti-doped $LiAlH_4$ or $LiNH_2$/2LiH systems. The percent of hydrogen released from the combined system is also higher than that from Ti-doped $LiAlH_4$ or $LiNH_2$/2LiH.

It is important to note that the current results for the $LiNH_2$/2LiH system differ from those reported by Chen et al.[24−26] The differences are attributed to the fact that the dehydrogenation experiments reported by Chen et al. were carried out in a vacuum, while the current study was carried out in atmospheric argon. Theoretically, the hydrogen storage capacity of the combined system is 10.1 wt % if the dehydrogenation is complete with a fourth reaction step as described in reaction 2. During Chen's experiment, reaction 2 was observed within the temperature range of 320 to 430 °C under vacuum. However, current results for the $LiNH_2$/2LiH system show that the percent of hydrogen decreases to 6.0% when the experiment is conducted under atmospheric pressure within the temperature range of room temperature to 450 °C. This suggests that the

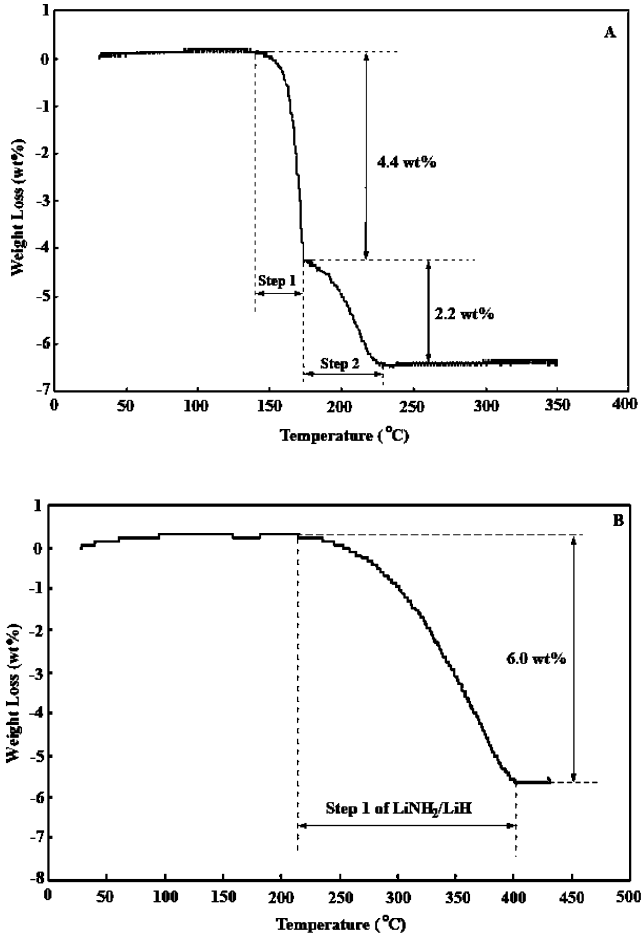


**Figure 4.** TGA curves of (A) $TiCl_3$−$^1/_3AlCl_3$ doped $LiAlH_4$ and (B) 2LiH + $LiNH_2$ under atmospheric argon and a heating rate of 2 °C/min.

fourth step, R2, does not occur in the combined system under the experimental conditions of this study, which explains why the total percent of hydrogen released is 8.1 wt %.

Although the percent of hydrogen released from the combined system is lower than its maximum potential within the temperature range used during this study, current results demonstrate that the kinetics of dehydrogenation of $LiAlH_4$ can be improved by combining it with $LiNH_2$. The effects of $LiNH_2$ are 2-fold. First, the temperature for dehydrogenation reaction 3 is lower than that of $LiAlH_4$ when it is heated alone. This suggests an interaction between light metal amide and alanate group (e.g. $AlH_4^-$) that changes the thermodynamics of the reactions by either lowering the enthalpy of the dehydrogenation reaction or tipping the balance of the reaction toward one direction. This is a fundamentally different reaction mechanism from the decomposition of alanates when they are heated alone. Second, the hydrogen combined in LiH can be liberated by reaction with $LiNH_2$, which increases the effective hydrogen capacity of $LiAlH_4$.

The thermodynamic effects of lithium amide on the overall reaction can be further understood by examining the reaction

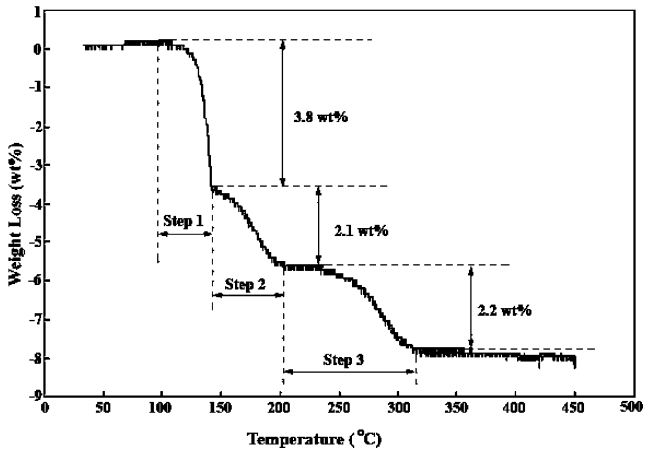


**Figure 5.** TGA curves of $TiCl_3-{}^1/_3AlCl_3$ doped $2LiAlH_4 + LiNH_2$ (sample 2) under atmospheric argon and a heating rate of 2 °C/min.

constant of R4. In general, the free energy of reaction can be described by the following expression

$$\Delta_r G_m = -RT \ln K^{\phi} + RT \ln Q \tag{6}$$

where $Q$ is the activity quotient and $K^{\phi}$ is the equilibrium constant. Specifically for R4,

$$K^{\phi} = \frac{(\alpha_{LiH}{}^2)_e \cdot (\alpha_{Al}{}^{2/3})_e \cdot (\rho_{H_2})_e}{(\alpha_{Li_3AlH_6}{}^{2/3})_e} \tag{7}$$

$$Q = \frac{(\alpha_{LiH}{}^2) \cdot (\alpha_{Al}{}^{2/3}) \cdot (\rho_{H_2})}{(\alpha_{Li_3AlH_6}{}^{2/3})} \tag{8}$$

when $Q < K^{\phi}$ and $\Delta_r G_m < 0$ the reaction moves toward the right spontaneously, $Q = K^{\phi}$ and $\Delta_r G_m = 0$ the reaction is at equilibrium, and $Q > K^{\phi}$ and $\Delta_r G_m > 0$ the reversible reaction occurs spontaneously.

When lithium amide is added to the system, $Q$ decreases as R1 and R2 proceed, which is in turn beneficial for dehydrogenation via R4. It should be noted that to further understand the destabilization effect of $LiNH_2$ on $LiAlH_4$, thermodynamic data including reaction enthalpies, entropies, and free energies of each reaction step are needed. These data can be determined either through experiments or modeling such as first-principle (FP) calculations, which is beyond the scope of the present study. As an example, the dehydrogenation of $NaAlH_4$, $Na_3AlH_6$, and NaH was investigated recently by Ke and Tanaka[27] using FP technique.

**3.3. Effect of $TiCl_3-{}^1/_3AlCl_3$ Doping.** It is well-known now that the potential of sodium alanate ($NaAlH_4$) for hydrogen storage applications is dependent upon doping $NaAlH_4$ with a Ti species. Ti doping improves the kinetics of the reversible hydrogen release and uptake reactions of $NaAlH_4$. To study any possible effects of doping on the dehydrogenation of the combined $2LiAlH_4/LiNH_2$ system, a mixture of $LiAlH_4$ and $LiNH_2$ doped with $TiCl_3-{}^1/_3AlCl_3$ (Sample 2) was analyzed by using TGA, as shown in Figure 5. It can be seen that, within the experimented temperature range, hydrogen desorbs from this mixture with rather similar behavior to that of sample 1, which is the same material without doping. Characteristic temperatures and percent of hydrogen release of doped $2LiAlH_4/LiNH_2$ are also listed in Table 1. It shows that the doping does not affect the kinetics of the combined $2LiAlH_4/LiNH_2$ system significantly, while $TiCl_3-{}^1/_3AlCl_3$ doping is very effective in reducing the dehydrogenation temperature of $LiAlH_4$ when used alone. The latter is in agreement with the literature.[3,4] In the current experiment, the dehydrogenation of $LiAlH_4$ from sample 1 takes place at almost same temperature as that of sample 2, which suggests that $LiNH_2$ acts as a destabilizer for decomposition of $LiAlH_4$. This is an important implication that could be useful for destabilizing other alkali aluminum hydride systems.

Finally, it is important to note that the reversibility of a solid hydride material is one of the most important properties of the material, determining its potential for practical applications. Although the current study did not address the reversibility issues directly, there are indications from the literature that the hydrogen release-and-uptake reactions of the combined $2LiAlH_4/LiNH_2$ system should be reversible.[3,24−26] However, it is obviously essential that the reversibility of the current system be demonstrated directly, which is a focus of the ongoing efforts of the present authors. In addition, although the current system shows great potential for hydrogen storage applications, the temperatures of dehydrogenation reactions of this system are still too high, particularly for the second and third steps. Further studies are needed to improve the kinetics of dehydrogenation reactions.

## 4. Summary

The dehydrogenation of a combined system of $LiAlH_4$ and $LiNH_2$ under atmospheric argon was studied.[28] Thermogravimetric analysis (TGA) of $LiAlH_4/LiNH_2$ mixtures without any catalysts indicated that a large amount of hydrogen (~8.1 wt %) can be released between 85 and 320 °C under a heating rate of 2 °C/min in three dehydrogenation reaction steps. The results also showed that the dehydrogenation temperature of the $LiAlH_4/LiNH_2$ system is lower than that of either Ti-doped $LiAlH_4$ or $LiNH_2/2LiH$. The percent of hydrogen released from the $2LiAlH_4/LiNH_2$ mixture is also higher than that from $LiAlH_4$ or $LiNH_2/LiH$. The results also show that $LiNH_2$ destabilizes $LiAlH_4$.

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(28) During the revision process of this paper, it came to our attention from one of the referees that a similar concept was presented during the 9th International Conference on Advanced Materials (ICAM, ICMAT, July 3−8, 2005, Singapore) by Zhitao Xiong, Guotao Wu, JianJiang Hu, and Ping Chen. It is noted that the present work and the work by Xiong et al. are independent of each other.