Hydrogen Storage

Effects of Stoichiometry on the H₂-Storage Properties of Mg(NH₂)₂-LiH-LiBH₄ Tri-Component Systems

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Abstract: The hydrogen desorption pathways and storage properties of 2Mg(NH₂)₂-3LiH-xLiBH₄ samples (x=0, 1, 2, and 4) were investigated systematically by a combination of pressure composition isotherm (PCI), differential scanning calorimetric (DSC), and volumetric release methods. Experimental results showed that the desorption peak temperatures of 2Mg(NH₂)₂-3LiH-xLiBH₄ samples were approximately 10–15 °C lower than that of 2Mg(NH₂)₂-3LiH. The 2Mg(NH₂)₂-3LiH-4LiBH₄ composite in particular began to release hydrogen at 90 °C, thereby exhibiting superior dehydrogenation performance. All of the LiBH₄-doped samples could be fully dehydrogenated and re-hydrogenated at

a temperature of 143 °C. The high hydrogen pressure region (above 50 bar) of PCI curves for the LiBH₄-doped samples rose as the amount of LiBH₄ increased. LiBH₄ changed the desorption pathway of the 2Mg(NH₂)₂-3LiH sample under a hydrogen pressure of 50 bar, thereby resulting in the formation of MgNH and molten [LiNH₂-2LiBH₄]. That is different from the dehydrogenation pathway of 2Mg(NH₂)₂-3LiH sample without LiBH₄, which formed Li₂Mg₂N₃H₃ and LiNH₂, as reported previously. In addition, the results of DSC analyses showed that the doped samples exhibited two independent endothermic events, which might be related to two different desorption pathways.

Introduction

Recently, light-element metal hydrides, borohydrides, alanates, and amides have attracted widespread attention owing to their high volumetric energy densities.^[1] However, they are inadequate for onboard applications because of one or more limitations, such as unfavorable thermodynamics, sluggish kinetics, and the release of undesirable byproducts (ammonia or

diborane).^[2] To overcome these limitations, a combination of light-element metal hydrides, borohydrides, alanates, and amides as multicomponent systems has been proposed.^[2b] The hydrogen-storage properties of those multicomponent systems are significantly improved relative to single-component (i.e., LiNH₂ and LiH) systems. The LiNH₂-LiH system can reversibly store approximately 6.5 wt% of hydrogen by means of Reaction (1).

In comparison with single-component systems, the LiNH₂-LiH system exhibits improved thermodynamic properties, released hydrogen purity, and reversibility. However, some problems still exist that hinder the LiNH₂-LiH system from being suitable for H₂-storage applications. For example, the operating temperature at 1.0 bar H₂ pressure is above 250 °C. Further amide-based systems were proposed that might replace the LiNH₂ with Mg(NH₂)₂ or the LiH with MgH₂ in LiNH₂-LiH, Mg(NH₂)₂-2LiH, or 2LiNH₂-MgH₂. Relative to the LiNH₂-LiH system, Mg(NH₂)₂-2LiH (2LiNH₂-MgH₂) possesses some more attractive features, such as the approximately 5.5 wt% of reversible hydrogen obtainable at 200 °C. For this system, an operating temperature as low as 90 °C at 1 bar of H₂ pressure is thermodynamically expected. This reaction is described by Reaction (2).

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Unfortunately, owing to the huge kinetic barriers, the rate of dehydrogenation of this composite is relatively low at temperatures below 180 °C.^[3] These kinetic barriers are likely to affect the interface reaction between Mg(NH₂)₂ and 2LiH. Although the newly developed ball-milling process assisted by dielectric-barrier discharge plasma influences both the kinetic and thermodynamic properties of hydrogen-storage materials, the introduction of additives seems to be more effective in changing the hydrogen-storage properties and the reaction mechanisms of the Mg(NH₂)₂-LiH composite.^[4] The addition of KH to the Mg(NH₂)₂-2LiH system has been reported to significantly lower the desorption temperature owing to the formation of three new K-containing intermediates: KH, K₂Mg(NH₂)₄, and Li₃K(NH₂)₄. For the KH-doped material, the lowest operating temperature at which it was possible to fully recharge the material was 107 °C.^[5] In 2008, a three-component composite based on 2LiNH₂-MgH₂-LiBH₄ was synthesized and characterized. It exhibited faster kinetics and lower desorption temperatures than those of the binary composites.^[6] The ternary system released hydrogen rapidly at 150 °C, which is 50–200 °C lower than those of the binary composites 2LiNH₂-LiBH₄, LiBH₄-MgH₂, and 2LiNH₂-MgH₂. The proposed reaction mechanism involves the reaction of LiNH₂ with LiBH₄ to form Li₄BN₃H₁₀ during ball milling and/or upon heating; then almost at the same time Li₄BN₃H₁₀ and MgH₂ partially convert to Mg(NH₂)₂, LiH, and LiBH₄. It was supposed that Li₄BN₃H₁₀ and melted LiNH₂-xLiBH₄ would be good Li-ion conductors, which might accelerate the transport of substances and improve the dehydrogenation kinetics of Li₄BN₃H₁₀-MgH₂ and/or Mg(NH₂)₂-LiH-iBH₄ systems.^[7] However, the dehydrogenation of 2LiNH₂-iBH₄-MgH₂ is reversible only if carried out below 230 °C. At temperatures above 230 °C, the Reactions (3) and (4) might take place, thereby resulting in a change in the dehydrogenation enthalpy from endothermic to mildly exothermic. Owing to the formation of stable desorption product Li₃BN₂, the dehydrogenation process becomes irreversible.^[8]

Hu et al. also discovered that the addition of LiBH₄ not only significantly enhanced the kinetics of the Mg(NH₂)₂-2LiH composite but also reduced the hydrogen desorption enthalpy.^[9] When 10 mol% LiBH₄ was added to the Mg(NH₂)₂-2LiH composite, 5 wt% of hydrogen could be reversibly desorbed at 140 °C and reabsorbed at 100 °C; and the desorption enthalpy was reduced from approximately 44 to 36.5 kJ mol⁻¹ H₂.^[10] Following these studies, other borohydrides such as Ca(BH₄)₂ and Mg(BH₄)₂ were also investigated;^[11] they showed similar effects to LiBH₄ because metathesis reactions take place between Ca(BH₄)₂/Mg(BH₄)₂ and LiH to form LiBH₄ and CaH₂/MgH₂ during ball milling or upon heat treatment.

The previous investigations focused mainly on the molar ratio of Mg/Li (1:2) to lower the hydrogen-desorption temperature and suppress the release of ammonia in the Mg(NH₂)₂-2LiH and 2LiNH₂-MgH₂ systems. The desorption reaction of

Mg(NH₂)₂-2LiH during pressure composition isotherm (PCI) measurement (250 °C) involves two main steps, and the optimal proportion of Mg(NH₂)₂ and LiH was determined to be 2 to 3, as depicted in Reaction (5).^[12]

When introducing LiI, LiBr, and LiBH₄ into the 2Mg(NH₂)₂-3LiH system, the reaction enthalpy of the 2Mg(NH₂)₂-3LiH system decreases to 33.3, 31.9, and 35.8 kJ mol⁻¹ H₂, respectively. The thermodynamic improvement is due to the formation of more stable products, that is, Li₃(NH₂)₂I, Li₂NH₂Br, and Li₄BN₃H₁₀. Furthermore, an additional high-pressure sloping region is observed in the PCI dehydrogenation of 2LiNH₂-MgH₂-LiBH₄ and 2Mg(NH₂)₂-3LiH-1/3LiBH₄.^[13] In our early work, the PCI curve of the 2Mg(NH₂)₂-3LiH-4LiBH₄ composite showed an extended high-pressure region with a dehydrogenation enthalpy of 24 kJ mol⁻¹ H₂. Reversible H₂ absorption and desorption from 2Mg(NH₂)₂-3LiH-4LiBH₄ was achieved at 53 and 98 °C, respectively. A better reaction pathway is involved in the high-pressure region. LiBH₄ exhibits solvent-like behavior that considerably stabilizes the dehydrogenation intermediates and products and thus changes the thermodynamics and kinetics of dehydrogenation and re-hydrogenation.^[14]

The stoichiometry of the Mg(NH₂)₂-LiH-LiBH₄ composites might have significant influence on both the thermodynamic and kinetic properties, similar to that of other hydrogen-storage alloys.^[15] In this work, Mg(NH₂)₂-LiH-LiBH₄ systems in molar ratios of 2:3:1, 2:3:2, and 2:3:4 were systematically investigated. The dehydrogenation behaviors of the 2Mg(NH₂)₂-3LiH-xLiBH₄ composites were studied by means of PCI and volumetric release measurements. A novel desorption pathway to form MgNH and an eutectic melting solution of LiBH₄ and LiNH₂ with a molar ratio of 1:2 at elevated temperatures is then proposed.

Results and Discussion

Kinetic Behavior

Four samples, namely, 2Mg(NH₂)₂-3LiH-xLiBH₄ with x=0.5, 1, 2, and 4, were prepared for investigation with temperature-programmed desorption mass spectrometry (TPD-MS) (Figure 1). For comparison, the TPD-MS curve of the pristine 2Mg(NH₂)₂-3LiH sample is also presented. TPD measurements revealed that the dehydrogenation onset temperature of the 2:3:4 sample is the lowest among the investigated systems, and its peak temperature is 15 °C lower than that of the pristine sample (189 °C; Figure 1a).

The TPD curve of the 2:3:4 sample is different from the others. It presents a weak desorption peak at 135 °C, a main dehydrogenation peak at 174 °C, and a shoulder peak at 189 °C. TPD curves of the 2:3:0.5, 2:3:1, as well as 2:3:2 samples are almost the same, since only the main dehydrogenation peaks can be observed. The TPD curves of the 2:3:0.5 and 2:3:1 samples almost overlap with each other, and their peak temperature is 179 °C. Compared to the pristine sample, all of

Figure 1. TPD-MS curves of $2\text{Mg}(\text{NH}_2)_2\text{-}3\text{LiH-xLiBH}_4$ mixtures ($x=0, 0.5, 1, 2$ and 4 ; based on the ratio of $\text{Mg}(\text{NH}_2)_2/\text{LiH}/\text{LiBH}_4$, they are also denoted as $2:3, 2:3:0.5, 2:3:1, 2:3:2$, and $2:3:4$). Samples heated from 50 to 250°C at a heating rate of 2°C min^{-1} .

the LiBH_4 -doped samples not only desorb hydrogen over narrower temperature ranges but also have a descending trend in their onset and peak temperatures. Moreover, the amount of ammonia released from LiBH_4 -doped samples is much lower than that of the pristine sample, and it only can be observed above 210°C for the $2:3:0.5$ and $2:3:1$ samples, which reveals that the addition of LiBH_4 effectively suppresses the evolution of this undesired side product (Figure 1b).

The dehydrogenation activation energies (E_a) of the $2\text{Mg}(\text{NH}_2)_2\text{-}3\text{LiH-xLiBH}_4$ and the pristine systems were calculated by means of Kissinger's method [Eq. (6)]:

$$\ln(\beta/T_m^2) = -E_a/(RT_m) + C \quad (6)$$

Here, T_m is the peak temperature at which the maximum reaction rate is attained, β the heating rate, E_a the activation energy, and R the gas constant. The TPD method was applied to collect the maximum reaction rate temperatures at various heating rates (Figure 2). As shown in Figure 2a, a good linear dependency of $\ln(\beta/T_m^2)$ upon $1/T_m$ exists for both samples. The slope of the fitted line is used to determine the value of E_a/R . The dehydrogenation activation energies of the $2\text{Mg}(\text{NH}_2)_2\text{-}3\text{LiH-xLiBH}_4$ samples dropped from 109 to 76 kJ mol^{-1} , respectively (Table 1), when the amount of LiBH_4 in the $2\text{Mg}(\text{NH}_2)_2\text{-}3\text{LiH-xLiBH}_4$ samples was increased from 1 to

Figure 2. a) Kissinger's plots of samples of $2:3, 2:3:1, 2:3:2, 2:3:4$. H_2 -TPD profiles collected at different ramping rates for b) $2:3:2$ and c) $2:3:4$ samples.

Table 1. Activation energies of the LiBH_4 -doped samples ($2:3:1, 2:3:2, 2:3:4$).			
Composite	$2:3:1$	$2:3:2$	$2:3:4$
R -squared	0.999	0.995	0.999
E_a [kJ mol^{-1}]	109 ± 4.0	86 ± 5.3	76 ± 3.5

4 . This result indicates that the addition of LiBH_4 can effectively reduce the activation energy of the $2\text{Mg}(\text{NH}_2)_2\text{-}3\text{LiH}$ composite (127 kJ mol^{-1}), which agrees well with the prior results.^[16]

To further investigate the differences between the $2:3:1$ and $2:3:4$ samples, thermogravimetric/differential thermal analysis (TG-DTA) experiments were carried out (Figure 3). The desorp-

Figure 3. TG-DTA curves of samples of $2:3:1$ and $2:3:4$. Samples heated from 50 to 250°C with a ramping rate of 2°C min^{-1} .

tion process of the $2:3:4$ sample started at 87°C , which is 48°C lower than that of the $2:3:1$ sample. After heating to 200°C , weight losses of 3.5 and 2.7% were found for $2:3:1$ and $2:3:4$ samples, respectively. Two endothermic signals can be observed in both cases. The first endothermic event relates to the low/high temperature transition phase of LiBH_4 . As the amount of LiBH_4 increases, this signal clearly becomes stronger. Apart from the phase transform event of LiBH_4 , only a single endothermic event at 176°C is visible. This means that the dehydrogenation process of the $2:3:1$ sample is a one-step reaction as described in a previous publication.^[17] Similar to the TPD-MS results, a shoulder peak can also be observed along with the major dehydrogenation peak in the DTA curve of the $2:3:4$ sample, which also indicates that the desorption pathway of the $2:3:4$ sample might be different.

Isothermal (143°C) dehydrogenation/re-hydrogenation measurements were carried out for the $2\text{Mg}(\text{NH}_2)_2\text{-}3\text{LiH-xLiBH}_4$ ($x=0, 1, 2, 4$) samples using a volumetric apparatus; the normalized data (hydrogen atoms/ $2\text{Mg}(\text{NH}_2)_2\text{-}3\text{LiH}$) are reported in Figure 4. The $2\text{Mg}(\text{NH}_2)_2\text{-}3\text{LiH}$ sample released 3.5 hydrogen atoms at 143°C after 250 minutes, which is significantly lower than the theoretical value (six atoms). However, the dehydrogenation kinetics of the $2\text{Mg}(\text{NH}_2)_2\text{-}3\text{LiH-xLiBH}_4$ samples were significantly improved by the addition of LiBH_4 , and a two-stage dehydrogenation process can be observed. For all

Figure 4. Volumetric isotherm at 143 °C a) dehydrogenation and b) re-hydrogenation curves of 2:3, 2:3:1, 2:3:2, and 2:3:4 under the H_2 backpressure of 0 and 60 bar for dehydrogenation and re-hydrogenation, respectively.

the investigated materials, the evolution of hydrogen rapidly reached 80% of the theoretical H_2 capacities and was complete after about 90, 70, and 170 min for the 2:3:1, 2:3:2, and 2:3:4 samples, respectively. The 2:3:2 sample exhibited the fastest desorption rate compared to the others. It should be pointed out that the dehydrogenation kinetics do not linearly follow the doping ratio of $LiBH_4$. The tangent slopes of the initial linear parts indicate that the dehydrogenation rate of the 2:3:2 sample is approximately 2.5 times faster than the pristine sample.

Unlike the isothermal dehydrogenation results, the isothermal absorption results show that the 2:3:1 sample had the fastest absorption rate, and it needed only 25 minutes to absorb more than 80% of the total hydrogen content. However, only 12% of hydrogen was absorbed by the 2:3 sample within the same time. During the first ten minutes, the 2:3:1 and 2:3:4 samples had the same absorption rates. The absorption rates of the 2:3:4 and 2:3 samples decelerated gradually, whereas the 2:3:1 sample maintained its fast absorption rate.^[17]

Thermodynamic Properties

For all the investigated systems the dehydrogenation properties were investigated by means of PCI methods at 187 °C (Figure 5). Figure 5a shows that the $2Mg(NH_2)_2-3LiH$ sample

Figure 5. a) Pressure-composition isotherm (PCI) curves of samples of 2:3, 2:3:1, 2:3:2, and 2:3:4 at a temperature of 187 °C under H_2 backpressure dropped from 100 to 1 bar. b) Detailed analysis of the PCI results.

could only release hydrogen at or under 20 bar.^[12,18] In contrast to the $2Mg(NH_2)_2-3LiH$ sample, the $2Mg(NH_2)_2-3LiH-xLiBH_4$ samples started to release hydrogen at much higher H_2 pressures. As an example, the 2:3:4 sample released hydrogen at 100 bar of H_2 pressure. In checking these PCI curves carefully, they can be divided into three parts: a high-pressure plateau, a sloped region, and a low-pressure plateau. For the 2:3:4 sample, only the desorption slope and the high-pressure plateau are clearly visible. The different ratios of $LiBH_4$ lead to different amounts of H_2 being released in the slope segment of the PCI measurement as well as to different starting pressures. From Figure 5a, it can be observed that, during the release of the first hydrogen atom, the equilibrium pressures were 97, 89, 70, 40, and 20 bar for the 2:3:4, 2:3:2, 2:3:1, 2:3:0.5, and 2:3 samples, respectively. The dehydrogenation capacities (atoms) during the different steps are summarized in Figure 5b. It is clear that at high pressure it is possible to release more hydrogen in the high-pressure plateau region when increasing the amount of $LiBH_4$, whereas the amount of hydrogen released in the low-pressure (LP) plateau region gradually decreases or even disappears when the molar ratio of $LiBH_4$ is increased to 4.

In addition, $2Mg(NH_2)_2-3LiH-xLiBH_4$ samples ($x=0, 1, 2, 4$) were heated from room temperature to 200 °C under H_2 pressure at 50 bar (Figure 6). The $2Mg(NH_2)_2-3LiH$ sample could not release hydrogen at this temperature and pressure; interestingly, all the other samples could release hydrogen at a temperature of 140 °C under the sample hydrogen pressure, and the dehydrogenation content increased as the molar ratio of $LiBH_4$ in the $2Mg(NH_2)_2-3LiH-xLiBH_4$ sample increased. Finally, 3.6, 2.5, and 1.4 hydrogen atoms were released from the 2:3:4, 2:3:2, and 2:3:1 samples, respectively.

Figure 6. Volumetric release of ternary compositions 2:3, 2:3:1, 2:3:2, and 2:3:4 dehydrogenated upon dynamic heating ($2^{\circ}\text{C min}^{-1}$) up to 200°C with 50 bar of H_2 background pressure.

The Role of LiBH_4

To uncover the underlying reason that enables the $2\text{Mg}(\text{NH}_2)_2$ – 3LiH – $x\text{LiBH}_4$ samples to release H_2 under a hydrogen background pressure of 50 bar, dehydrogenation products of these samples were studied by means of XRD and FTIR techniques (Figure 7). XRD patterns show the diffraction peaks of

Figure 7. a) XRD patterns and b) FTIR spectrum of 2:3:1, 2:3:2, and 2:3:4 dehydrogenated upon 200°C with 50 bar of H_2 background pressure.

$\text{Mg}(\text{NH}_2)_2$ in the dehydrogenated 2:3:1 and 2:3:2 samples. In addition, several weak diffraction peaks of MgNH are also visible in the dehydrogenated 2:3:2 sample. Conversely, only the diffraction peaks of MgNH and Li_2BNH_6 are present in the dehydrogenated 2:3:4 sample. It is clear at this point that when the molar ratio of $\text{Mg}(\text{NH}_2)_2$ and LiBH_4 is higher than two the diffraction peaks of MgNH are present among the decomposition products. The presence of MgNH , rather than $\text{Li}_2\text{Mg}_2\text{N}_3\text{H}_3$, means that the dehydrogenation pathways of $2\text{Mg}(\text{NH}_2)_2$ – 3LiH system might be changed. To verify this possibility, the dehydrogenated $2\text{Mg}(\text{NH}_2)_2$ – 3LiH – $x\text{LiBH}_4$ composites were investigated by FTIR spectroscopy (Figure 7b). The FTIR results reveal that Li_2BNH_6 ($3298/3246\text{ cm}^{-1}$)^[17] or $\text{Li}_4\text{BN}_3\text{H}_{10}$ ($3301/3243\text{ cm}^{-1}$)^[17] are present during the dehydrogenation process under 50 bar hydrogen pressure. The N–H stretching at 3273 and 3327 cm^{-1} that belongs to $\text{Mg}(\text{NH}_2)_2$ gradually decreases,

and the N–H stretching of MgNH at 3198 cm^{-1} emerges upon increasing the amount of LiBH_4 in the $2\text{Mg}(\text{NH}_2)_2$ – 3LiH – $x\text{LiBH}_4$ composite.^[19] This means that MgNH exists as a product as the dehydrogenation proceeds. As discussed above, it is clear that the addition of LiBH_4 changes the dehydrogenation pathway of the $2\text{Mg}(\text{NH}_2)_2$ – 3LiH sample under the hydrogen pressure of 50 bar, thus yielding the formation of MgNH and an eutectic that melts at elevated temperatures instead of forming $\text{Li}_2\text{Mg}_2\text{N}_3\text{H}_3$ and LiNH_2 . This is also confirmed by the disappearance of LiBH_4 reflections in the in situ XRD investigation of the 2:3:1 sample collected in a backpressure of hydrogen between 80 and 1 bar (see the Supporting Information). According to the phase diagram of LiNH_2 and LiBH_4 , the eutectic melt might be composed of LiNH_2 and LiBH_4 .^[7] LiNH_2 and LiBH_4 in a molar ratio of 1:2 has its lowest melting point at 95°C , which will be condensed into Li_2BNH_6 , $\text{Li}_4\text{BN}_3\text{H}_{10}$, and LiBH_4 when cooled under moderate conditions.

Calorimetric measurements of these samples under a closed system were carried out using a DSC-C80 instrument, and the results are reported in Figure 8. The pristine sample of

Figure 8. DSC-C80 (closed-system) measurements of ternary compositions $2\text{Mg}(\text{NH}_2)_2$ – 3LiH – $x\text{LiBH}_4$ ($x=0, 1, 2$, and 4) dehydrogenated upon dynamic heating ($0.2^{\circ}\text{C min}^{-1}$) up to 250°C under the 1 bar argon atmosphere.

$2\text{Mg}(\text{NH}_2)_2$ – 3LiH starts to release hydrogen at about 125°C and reaches its main peaks at 172 and 197°C , as also previously seen in the TPD-MS analysis in Figure 1. Moreover, a clear exothermic peak at 77°C is detected in the 2:3:4 sample, which is still under investigation. The endothermic event at approximately 110°C can be related to the phase transformation of LiBH_4 . The following two endothermic events at approximately 139 and 180°C are possibly related to two dehydrogenation reactions. With the increase in the LiBH_4 component, the low-temperature endothermic peak increases and the high-temperature endothermic peak decreases. The endothermic peak at 180°C even disappears in the 2:3:4 sample, and the main endothermic peak moves to 150°C , which confirms that the dehydrogenation pathway of $2\text{Mg}(\text{NH}_2)_2$ – 3LiH has completely changed by the addition of 4 mol LiBH_4 .

Conclusion

The effects of the stoichiometry of LiBH_4 in the $2\text{Mg}(\text{NH}_2)_2$ – 3LiH – $x\text{LiBH}_4$ ($x = 1, 2$, and 4) were investigated in detail in this work. Both the onset and peak temperatures were shifted to lower temperature with the help of LiBH_4 . The $2\text{Mg}(\text{NH}_2)_2$ – 3LiH – 4LiBH_4 sample in particular started to dehydrogenate at approximately 90°C . The $2\text{Mg}(\text{NH}_2)_2$ – 3LiH – $x\text{LiBH}_4$ composites exhibit significant low-temperature (143°C) reversibility, and their reversible hydrogen capacities are close to their theoretical value of six hydrogen atoms. The kinetic effect of LiBH_4 is also confirmed by their activation energies, which decrease from 127 kJ mol^{-1} in the $2\text{Mg}(\text{NH}_2)_2$ – 3LiH sample to 76 kJ mol^{-1} in the $2\text{Mg}(\text{NH}_2)_2$ – 3LiH – 4LiBH_4 sample. The PCI curves show a high-pressure plateau, a low-pressure plateau, and a slope in the LiBH_4 -doped samples, and the length of the high-pressure plateau depends on the amount of LiBH_4 . Moreover, the alteration of the thermodynamics corresponds to the new reaction pathway; for example, the desorption products of the ternary system of $2\text{Mg}(\text{NH}_2)_2$ – 3LiH – 4LiBH_4 under 50 bar of hydrogen background pressure are an eutectic melting solution of $[\text{LiNH}_2$ – $2\text{LiBH}_4]$ and MgNH , which are completely different from the products of the $2\text{Mg}(\text{NH}_2)_2$ – 3LiH system.

Experimental Section

Sample Preparation

LiH and LiBH_4 were purchased from Alfa-Aesar and Sigma-Aldrich with purities of 98 and 95%, respectively. $\text{Mg}(\text{NH}_2)_2$ was a self-synthesized product with a purity of $\geq 95\%$, and its synthesis procedure was described in a previous publication.^[17] The $2\text{Mg}(\text{NH}_2)_2$ – 3LiH – $x\text{LiBH}_4$ mixtures, in which $x = 0, 0.5, 1, 2$, and 4 (for convenience, the samples were denoted as 2:3, 2:3:0.5, 2:3:1, 2:3:2, and 2:3:4 according to their LiBH_4 content), were ball milled using a Retsch PM400 planetary mill at 200 rpm for 24 hours. The ball-to-sample weight ratio was 60:1. To prevent degradation of the material owing to the heat developed during milling, the mill was set to revolve for 2 min in one direction and pause for 15 s, and then revolve in the opposite direction. To avoid air contamination, all handling of the materials was performed in a MBRAUN glovebox filled with purified argon gas (O_2 : $\delta < 5\text{ ppm}$; H_2O : $\delta < 0.1\text{ ppm}$).

Analysis of Hydrogen-Storage properties

A homemade temperature-programmed desorption (TPD) system coupled with a mass spectrometer (MS) (Hiden QIC-20) was used to check the evolving gases hydrogen ($m/z = 2$) and ammonia ($m/z = 15$). In each test, the sample was loaded and heated at a rate of 2°C min^{-1} up to 400°C . A thermocouple was used to measure the sample temperature by inserting it into the center of samples. Activation energies were calculated by Kissinger's method, and the fastest reaction rates were monitored by TPD techniques.

Thermogravimetry coupled with differential thermal analysis (TG-DTA) measurements were conducted using a STA-449C (Netzsch, Germany) installed in a glovebox. The measurements were performed in dynamic flow of argon (30 mL min^{-1}), and the heating rate was set to 2°C min^{-1} (open system). A C80 calorimeter (Setaram, France) was used for differential scanning calorimetric (DSC) measurements under static conditions.

The thermodynamic properties of the investigated materials were further investigated by means of a pressure-composition isotherm (PCI) in an automatic Sieverts-type apparatus (Hy-Energy scientific instruments PCT pro-2000). Samples of about 200 Mg were used each time. Initial and ending pressures in the sample chamber for dehydrogenation experiments were 100 and 1 bar. The control precision of the sample temperature was $\pm 0.5^\circ\text{C}$. For these experiments the equilibrium state points were acquired each time that the pressure variance (ΔP) was $< 0.1\text{ bar}$ for 24 h.

The hydrogen desorption and absorption capacities were measured using an automatic Sieverts-type apparatus (Advanced Materials Co.). The initial H_2 pressures were assigned as 0.01 bar and 60 bar for desorption/absorption, respectively.

Structural Characterization

The identification of the phases contained in the samples was performed by using a Philips PANalytical X'pert diffractometer with $\text{Cu}_{\text{K}\alpha}$ radiation at 40 kV and 40 mA. XRD patterns were collected in the 2θ range of 10 – 80° with a step increment of 5° min^{-1} . N–H vibrations in the samples were identified by means of an FTIR spectrometer on a Varian 3100 Unite in DRIFT mode; 32 scans were accumulated, and the scan resolution was 4 cm^{-1} .

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Conflict of Interest

The authors declare no conflict of interest.

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