Near Ambient Condition Hydrogen Storage in a Synergized Tricomponent Hydride System

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# **Advanced Energy Materials** Near Ambient Condition Hydrogen Storage in a Synergized Tri-Component Hydride System --Manuscript Draft--

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Please submit a plain text version of your cover letter here. If you are submitting a revision of your manuscript, please do not overwrite your original cover letter. There is an opportunity for you to provide your responses to the reviewers later; please do not add them here.	Dear Professor Joern Ritterbusch, We would like to submit our enclosed manuscript entitled "Near ambient condition hydrogen storage in a synergized tri-component hydride system", an outcome of research collaboration from three institutes of DICP (CHINA), HZG (GERMANY) and INSTM (ITALY), which we hope to be considered as a full paper for publication in "Advanced Energy Materials". Tremendous efforts have been given to Hydrides of Light Elements (HLEs) because they are regarded as the most promising hydrogen storage materials; however, reversible hydrogen storage over HLEs under ambient condition is unattained albeit it has been pursued actively for nearly two decades. Here we demonstrate for the first time that the synergy among LiBH4, Mg(NH2)2 and LiH, three of the most-investigated HLEs, can lead to a fully reversible hydrogenation and dehydrogenation cycle at temperatures below 373 K. More importantly, the dehydrogenation enthalpy reaches 24 kJ(mol-H2)-1 which thermodynamically allows a dehydrogenation temperature at 1.0 bar H2 to be as low as 266 K, a highly encouraging result that is bringing HLEs a huge step closer to the practical application. The mechanism of this significant thermodynamic improvement has been well studied by in situ / ex situ PXRD and IR which disclose a "solvent" like behavior of LiBH4 in stabilizing the intermediate and products of hydrogen desorption reaction by forming different compounds including a new structure. Such an understanding of the role of LiBH4 will stimulate considerable research into the design and development of multi- component HLEs where all components collaborate with each other leading to favorable hydrogen storage properties to meet the practical requirement. With the important findings and in-depth understanding we storage and enriches the energy-research community of HLEs, and thus, is very appropriate for "Advanced Energy Materials". No conflict of interest exits in this submission of the manuscript, and the content of this manuscri

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# Near Ambient Condition Hydrogen Storage in a Synergized Tri-Component Hydride System

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Reversible hydrogen storage over hydrides of light elements (HLEs) under ambient condition has been pursued actively for nearly two decades. Limited progress has been made toward this end, however, because of unfavorable thermodynamics and/or severe kinetic barrier of HLEs. Here we demonstrate that the synergy among LiBH<sub>4</sub>, Mg(NH<sub>2</sub>)<sub>2</sub> and LiH, three of the most-investigated HLEs, can lead to a fully reversible hydrogenation and dehydrogenation cycle at temperatures below 373 K. More importantly, the dehydrogenation enthalpy reaches 24 kJ (mol-H<sub>2</sub>)<sup>-1</sup> which thermodynamically enables a dehydrogenation temperature at 1.0 bar H<sub>2</sub> to be as low as 266 K. Characterization of this combination of HLEs shows that LiBH<sub>4</sub> serves as a reagent complexing with intermediates and products of the dehydrogenation of Mg(NH<sub>2</sub>)<sub>2</sub>-LiH, and significantly alters the overall thermodynamic and kinetic parameters of the system.

#### 1. Introduction

Storing hydrogen in a condensed-phase material with high volumetric and gravimetric hydrogen densities and favorable kinetic and thermodynamic properties is a technical challenge for the implementation of hydrogen energy.<sup>[1]</sup> Conventional metal hydrides, such as LaNi5 and Fe-Ti alloys, have excellent near-ambient operation and high volumetric hydrogen densities, but suffer from relatively low gravimetric densities (~1.4 wt% for LaNi5 and ~1.8 wt% for Fe-Ti alloy).<sup>[2, 3]</sup> Tremendous efforts have been devoted to hydrides of light elements (HLEs) (such as Al, B, N and C) in the past 2 decades.<sup>[4, 5, 6]</sup> These hydrides have high gravimetric hydrogen densities and tuneable composition that allows rational correlations of the composition, structure and performance;<sup>[7]</sup> however, there are pending issues about sluggish kinetics, unfavorable thermodynamic properties, reversibility, and side reactions that produce by-products of NH<sub>3</sub> or "boron sinks", such as stable B<sub>12</sub>H<sub>12</sub> complexes.<sup>[8]</sup> To date, none of the HLEs studied has been able to outperform conventional metal alloys under ambient conditions in terms of reversibility and capacity. The rich chemistry of HLEs, on the other hand, implies diversified possibilities in materials design and optimization. There are a number of strategies, such as compositing and complexing, which have been effectively employed in the thermodynamic alteration of HLEs.<sup>[9]</sup> LiBH<sub>4</sub>, an intensively investigated HLE, can release large amounts of hydrogen (13.6 wt%) endothermically (74 kJ (mol-H<sub>2</sub>)<sup>-1</sup>) at temperatures above 643 K.<sup>[6]</sup> When combined with MgH<sub>2</sub> or complexed with NH<sub>3</sub>, its dehydrogenation thermodynamics can be tuned to be mildly endothermic (46 kJ (mol-H<sub>2</sub>)<sup>-1</sup>) or exothermic.<sup>[10]</sup> Moreover, LiBH<sub>4</sub> can also be combined with LiNH<sub>2</sub>, however, during hydrogen release, the reaction is over-tuned to be mildly exothermic because of the formation of stable Li<sub>3</sub>BN<sub>2</sub>.<sup>[11]</sup> It is worth mentioning that distinct phases of Li<sub>2</sub>BNH<sub>6</sub> and Li<sub>4</sub>BN<sub>3</sub>H<sub>10</sub> can be formed from the mixture of LiBH<sub>4</sub> and

LiNH<sub>2</sub> in molar ratios of 1:1 and 1:3 through the exothermic reactions (1) and (2). <sup>[12, 13-15]</sup> Li<sub>4</sub>BN<sub>3</sub>H<sub>10</sub> and Li<sub>2</sub>BNH<sub>6</sub> exhibit superior lithium ionic conductions under mild conditions.<sup>[16]</sup>

$$LiNH_{2} + LiBH_{4} \rightleftharpoons Li_{2}BNH_{6}$$
(1)  
3LiNH\_{2} + LiBH\_{4} \leftrightharpoons Li\_{4}BN\_{2}H\_{10} (2)

$$3LiNH_2 + LiBH_4 \rightleftharpoons Li_4BN_3H_{10} \tag{2}$$

Similar research efforts have been given to the Mg(NH<sub>2</sub>)<sub>2</sub>-LiH composite material, which has an enthalpy of dehydrogenation reaction of 44 kJ (mol-H<sub>2</sub>)<sup>-1</sup> that allows H<sub>2</sub> release under 1 bar back pressure at 363 K but suffers from a severe dehydrogenation kinetic barrier of 102 kJ mol<sup>-1</sup>.<sup>[17, 18, 19]</sup> This composite, therefore, needs to be optimized from both kinetic and thermodynamic aspects. Among all the methods in the optimization of the Mg(NH<sub>2</sub>)<sub>2</sub>-LiH composite, the addition of LiBH<sub>4</sub> creates a number of possible interactions, thus altering its hydrogen storage properties. Yang et al. reported that the ternary composite, 2LiNH<sub>2</sub>-LiBH<sub>4</sub>-MgH<sub>2</sub>, exhibited faster dehydrogenation kinetics with desorption temperatures approximately 50 K lower than the pristine 2LiNH<sub>2</sub>-MgH<sub>2</sub> composite.<sup>[20]</sup> It should be noted that the 2LiNH<sub>2</sub>-MgH<sub>2</sub> composite is equivalent to Mg(NH<sub>2</sub>)<sub>2</sub>-2LiH.<sup>[17]</sup> With the addition of 10 mol % of LiBH<sub>4</sub>, ca. 5 wt% hydrogen can be reversibly desorbed at 413 K and re-absorbed at 373 K.<sup>[21]</sup> Cao et al. showed that the addition of LiBH<sub>4</sub> not only enhanced the reaction kinetics, but also noticeably improved the reaction thermodynamics, i.e., with the addition of 1/3 equiv. LiBH4 the thermodynamically allowed operating temperature at 1 bar H<sub>2</sub> back pressure drops from 363 K to 343 K, since it appears that LiBH<sub>4</sub> can stabilize one of the dehydrogenation products, LiNH<sub>2</sub>, by forming  $Li_4BN_3H_{10}$  via the reaction 2, i.e., the exothermic nature of reaction 2 leads to a reduced reaction enthalpy from 40 kJ (mol-H<sub>2</sub>)<sup>-1</sup> to 36 kJ (mol-H<sub>2</sub>)<sup>-1</sup>. <sup>[22]</sup> However, after more than 20 years' unremitting efforts, the lowest operating temperature of the "modified" Mg(NH<sub>2</sub>)<sub>2</sub>-LiH system for dehydrogenation/re-hydrogenation was still above 373 K, desorbing/re-absorbing hydrogen at near ambient temperature is yet to be achieved.<sup>[23]</sup>

A very intriguing but perhaps overlooked phenomenon is the appearance of a high-pressure sloping region in the Pressure-Composition-Temperature (PCT) during dehydrogenation of

the 2LiNH<sub>2</sub>-MgH<sub>2</sub>-LiBH<sub>4</sub> and 2Mg(NH<sub>2</sub>)<sub>2</sub>-3LiH-1/3LiBH<sub>4</sub> composite systems. <sup>[22, 24]</sup> Our results also showed that a similar high-pressure dehydrogenation region appeared in the 2Mg(NH<sub>2</sub>)<sub>2</sub>-3LiH-LiBH<sub>4</sub> composition.<sup>[25]</sup> Because the interaction of LiNH<sub>2</sub> and LiBH<sub>4</sub> gives rise to a number of solid and liquid phases under different conditions and the LiNH<sub>2</sub> to LiBH<sub>4</sub> molar ratios, <sup>[15, 26]</sup> it is possible that a Li-Mg-N-B-H material with better hydrogen storage properties can be developed by elucidating the chemistry involved in the sloping region.

Here we report the development of the first "ambient" HLE made up of  $2Mg(NH_2)_2$ -3LiH-4LiBH<sub>4</sub>, which has a dehydrogenation enthalpy of 24 kJ (mol-H<sub>2</sub>)<sup>-1</sup> allowing hydrogen release under 1 bar H<sub>2</sub> at a temperature as low as 266 K, from thermodynamic point of view. Our experimental data show that fully reversible H<sub>2</sub> absorption and desorption can be achieved at 326 K and 371 K; moreover, when temperature rises to 410 K, the dehydrogenation could occur with the backpressure of 70 bar H<sub>2</sub>. A dehydrogenation pathway has been identified. LiBH<sub>4</sub> exhibits "solvent"-like behavior that considerably stabilizes the dehydrogenation.

#### 2. Results and Discussion

#### 2.1. Thermodynamic properties.

Hydrogen absorption and desorption from  $Mg(NH_2)_2$ -LiH composite may be step-wise depending on the molar ratio of  $Mg(NH_2)_2$  and LiH. The following 2-step reactions describe the 1:2 ratio composite, i.e., the  $Mg(NH_2)_2$ -2LiH system.<sup>[27]</sup>

Step 1: 
$$2Mg(NH_2)_2+3LiH \rightleftharpoons Li_2Mg_2(NH)_3+LiNH_2+3H_2$$
 (3)

Step 2: 
$$Li_2Mg_2(NH)_3+LiNH_2+LiH \rightleftharpoons 2Li_2Mg(NH)_2+H_2$$
 (4)

Overall: 
$$Mg(NH_2)_2+2LiH \Rightarrow Li_2Mg(NH)_2+2H_2$$
 5.5wt%  
 $\Delta H = 44 \text{ kJ}(\text{mol-H}_2)^{-1}$  (5)

Step 1 accounts for hydrogen desorption in the pressure plateau of the P-C-T curve, and has better thermodynamic properties, therefore, our focus is given to the 2Mg(NH<sub>2</sub>)<sub>2</sub>-3LiH composite. The Pressure-Composition curve of the 2Mg(NH<sub>2</sub>)<sub>2</sub>-3LiH sample at 458 K is shown in **Figure 1** (a). Approximately 6 equiv. hydrogen atoms appear to be released through a rather flat pressure plateau with an average desorption pressure of 20 bar. We then introduce LiBH<sub>4</sub> to the composite with its content increasing from 1, 2 to 4 equivalents and prepared 3 samples for P-C-T measurements. The corresponding P-C isotherms are summarized in Figure S1 (Supporting Information). Clear composition-dependent isotherms are observed. Here, the 2:3:4 composite was selected for detailed investigation because of its distinct behavior among others. As shown in Figure 1 (a), its P-C isotherm at 460 K has two desorption events, i.e., a plateau and a sloping region, the amount of hydrogen released from the plateau is greater than that from the sloping region. The most distinct feature of the 2:3:4 composite from that of the 2:3 is the significantly uplifted desorption pressure, i.e., at 460 K its average plateau pressure reaches 97 bars, which is nearly 5 times that of the 2:3 sample. Noted that for LaNi<sub>5</sub> and Fe-Ti alloy, two of the typical metal alloys, and for NaAlH<sub>4</sub>, the most investigated complex hydride, the equilibrium pressures at this temperature (460 K) are 120, 47 and 130 bar, respectively. <sup>[2, 5, 28]</sup>

To highlight this thermodynamic improvement, temperature-programmed volumetric release measurements were also done on the 2:3:4 and 2:3 samples under hydrogen back pressures in the range of 50 to 70 bars. As shown in **Figure 1(b)**, the 2:3:4 sample starts to release hydrogen at ca. 410 K regardless of the back pressure applied, which indicates that the initial equilibrium desorption pressure is at least 70 bar at that temperature. This phenomenon also reflects the existence of certain kinetic barrier that defers hydrogen desorption rate at low temperatures, which will be discussed later in the following section. For the 2:3 sample, on the other hand, no desorption was observed under 50 bar back pressure till 473 K.

The reaction enthalpy ( $\Delta$ H) and entropy ( $\Delta$ S) for H<sub>2</sub> release in the high pressure plateau region of the 2Mg(NH<sub>2</sub>)<sub>2</sub>-3LiH-4LiBH<sub>4</sub> sample is determined by collecting the equilibrium pressures at 444, 453, 460 and 464 K upon releasing 2 equiv. hydrogen atoms, respectively (marked with # in **Figure 1(c)**). It is noted that the "plateau" is not fully flat, meaning that the thermodynamic parameters are of H content-dependence. Nonetheless, from the fairly linear correlation between In P<sub>eq</sub> and 1/T (**Figure 1(d)**), the reaction enthalpy  $\Delta$ H and entropy  $\Delta$ S in the temperature range of 444 to 464 K are calculated to be 24 kJ (mol-H2)-1 and 92 J (mol-H<sub>2</sub>.K)<sup>-1</sup>, respectively. If these data are valid in a wide temperature range, the equilibrium pressure would reach 3.2 bar at ambient temperature (298K). To achieve 1.0 bar equilibrium H2 desorption, the temperature could be as low as ca. 266K. (**Figure 1(d)**).

#### 2.2. Desorption and re-absorption kinetics

To investigate the kinetic properties of the 2:3:4 composite, we conducted isothermal dehydrogenation/re-hydrogenation at different temperatures. As shown in **Figure 2(a)** more than 80 % of the hydrogen can be released/re-absorbed within an hour at 416 K. Hydrogen desorption from this sample can also take place at a temperature as low as 371 K, a temperature domain comparable to that of NaAlH4. The re-hydrogenation of the composite at lower temperatures is more feasible than the dehydrogenation. As shown in **Figure 2(a)**, the majority of hydrogen can be re-absorbed in 6 hours at 371 K. Encouragingly, full re-hydrogenation can be achieved upon further reducing the temperature to 326 K, the lowest temperature reported to date for the Mg(NH<sub>2</sub>)<sub>2</sub>-LiH system.

The activation energy ( $E_a$ ) for the dehydrogenation is calculated using the Kissinger's method.<sup>[29]</sup> Shown in the insert of **Figure 2(b)** are the MS profiles of the composite which was heated with the ramping rates of 2, 4, 6, and 8 K min<sup>-1</sup>. The apparent activation energy  $E_a$ 

calculated is ca. 76.0 kJ mol<sup>-1</sup>, which is 25% lower than that of Mg(NH<sub>2</sub>)<sub>2</sub>-2LiH (~ 102 kJ mol<sup>-1</sup>). <sup>[19]</sup>

The concentration of NH<sub>3</sub> in the gaseous phase of dehydrogenation at 453 K is less than 20 ppm for the 2:3:4 sample and 220 ppm for the 2:3 sample. No other boron- and/or nitrogen-containing gaseous by-products were detected by Mass Spectrometry during the desorption process.

#### 2.3. The dehydrogenation pathway

The samples of the 2:3:4 composite before and after dehydrogenation were collected for ex situ PXD characterization at room temperature. As shown in Figure 3(a)-I, the as-milled 2:3:4 composite did show weak peaks belonging to Mg(NH<sub>2</sub>)<sub>2</sub>, LiH and LiBH<sub>4</sub>. While, only weak diffraction peaks of LiH can be detected in the as-milled 2:3 sample as shown in our previous publication. After dehydrogenation at ca. 460 K, the Li<sub>2</sub>Mg<sub>2</sub>(NH)<sub>3</sub> phase was observed in the 2:3 composite from the previous researches. <sup>[22]</sup> However, the characteristic peaks of Li<sub>2</sub>Mg<sub>2</sub>(NH)<sub>3</sub> are not present in the XRD patterns of the 2:3:4 samples of different degrees of dehydrogenation. As shown in Figure 3(a)-II, the sample upon dehydrogenation under 460K and 90 bar contains Mg(NH<sub>2</sub>)<sub>2</sub>, LiH, LiBH<sub>4</sub> phases with a near amorphous MgNH phase. At 80 bar of H<sub>2</sub> back pressure, it appears that more hydrogen has released according to the consumption of Mg(NH<sub>2</sub>)<sub>2</sub> and LiH. MgNH and Li<sub>4</sub>BN<sub>3</sub>H<sub>10</sub> phases can be clearly seen (Figure 3(a)-III). After full dehydrogenation the sample contains the characteristic diffraction peaks of MgNH, Li<sub>4</sub>BN<sub>3</sub>H<sub>10</sub> and a new phase having reflections at 16.7°, 23.1°, 25.6°, 32.1° etc. (Figure 3(a)-IV) Importantly, this new phase has identical diffraction pattern as the Li<sub>2</sub>NH-LiBH<sub>4</sub> mixture upon ball-milling and heat treatment at 423 K (Figure S2 in Supporting Information). Although the detailed structure and composition of the phase are still under investigation, it is most likely that the new phase presented in Figure 3(a)-VI is made of Li<sub>2</sub>NH and LiBH<sub>4</sub>. Therefore the most important information from the

PXD characterization is that, instead of  $Li_2Mg_2N_3H_3$  formation in the 2-3 sample, MgNH, the new phase ( $Li_2NH-LiBH_4$ ) and  $Li_4BN_3H_{10}$  are formed upon dehydrogenation of 2:3:4 composite.

FT-IR measurements (**Figure 3(b**)) show absorption peaks at 3273 cm<sup>-1</sup> and 3326 cm<sup>-1</sup> in the as-milled 2:3:4 sample that are assigned to the symmetrical and asymmetrical vibrations of N-H bonds in Mg(NH<sub>2</sub>)<sub>2</sub>.<sup>[17, 30]</sup> The dehydrogenated 2:3 sample contains two typical peaks at 3196 cm<sup>-1</sup> and 3164 cm<sup>-1</sup> belonging to the N-H vibrations of Li<sub>2</sub>Mg<sub>2</sub>(NH)<sub>3</sub>.<sup>[30]</sup> For the 2:3:4 sample dehydrogenated at 90 bar (**Figure 3(b)-II**), on the other hand, the typical –NH stretches of Li<sub>2</sub>Mg<sub>2</sub>(NH)<sub>3</sub> were not observed, instead, a broad peak centered at 3192 cm<sup>-1</sup> possibly assignable to the N-H stretch of MgNH was detected.<sup>[31]</sup> The absorption peaks at 3243 and 3301 cm<sup>-1</sup>are the characteristic N-H vibration in Li<sub>4</sub>BN<sub>3</sub>H<sub>10</sub>.<sup>[14, 16]</sup> Moreover, the peaks intensities of Mg(NH<sub>2</sub>)<sub>2</sub> decreased dramatically. When the back pressure reduced to 80 bar (**Figure 3(a)-III**), the vibrations of Mg(NH<sub>2</sub>)<sub>2</sub> are barely detectable, which is in good agreement with the results of PXD patterns. There is a board vibration centered at 3168 cm<sup>-1</sup> in the fully dehydrogenated 2:3:4 sample, (**Figure 3(b)-IV**) which is similar to IR absorption of the new phase composed of Li<sub>2</sub>NH-LiBH<sub>4</sub> (**Figure S3** in Supporting Information).

The formation of MgNH and Li<sub>4</sub>BN<sub>3</sub>H<sub>10</sub> rather than Li<sub>2</sub>Mg<sub>2</sub>(NH)<sub>3</sub> and LiNH<sub>2</sub> in the higher plateau region provides evidence of the change in dehydrogenation pathway upon the addition of substantial amount of LiBH<sub>4</sub> in the Mg(NH<sub>2</sub>)<sub>2</sub>-LiH composite. Except for forming stoichiometric Li<sub>4</sub>BN<sub>3</sub>H<sub>10</sub> phases; LiNH<sub>2</sub> and LiBH<sub>4</sub> in a wide range of compositions becomes liquid solution at elevated temperatures, with the lowest melting point at 368K when the LiNH<sub>2</sub> to LiBH<sub>4</sub> ratio is 1:2 according to the LiNH<sub>2</sub>-LiBH<sub>4</sub> phase diagram.<sup>[15]</sup> In other words, the liquid LiNH<sub>2</sub>-(LiBH<sub>4</sub>)<sub>x</sub> phase is thermodynamically more stable than solid phases of Li<sub>2</sub>BNH<sub>6</sub>, Li<sub>4</sub>BN<sub>3</sub>H<sub>10</sub> and their mixtures with LiBH<sub>4</sub> in a certain temperature range and LiNH<sub>2</sub>/LiBH<sub>4</sub> ratio, which may partially, if not conclusively, explain the significantly improved thermodynamics during hydrogen release. The formation of the liquid phase with dehydrogenation (Temperature > 460K) is strongly supported by the absence of any LiBH<sub>4</sub>-related phases (not only just phases composed of LiNH<sub>2</sub>-xLiBH<sub>4</sub>, but also Li<sub>2</sub>NH-yLiBH<sub>4</sub>) during the in situ PXD measurement at elevated temperatures (**Figure 4**). As shown in the in situ PXD patterns, the diffraction peaks of Mg(NH<sub>2</sub>)<sub>2</sub> and LiBH<sub>4</sub> are gradually disappearing when the temperature is raised from 373 K to 453 K under a back hydrogen pressure of 50 bar. Only four extremely weak peaks which can be assigned to MgNH are observed at 473 K.

The disappearance of Mg(NH<sub>2</sub>)<sub>2</sub> may indicate the occurrence of dehydrogenation and the consumption of the reactant. The absence of the LiBH<sub>4</sub>-related phase, on the other hand, may reflect the molten state of the LiBH<sub>4</sub>-containing phases. Based on the in situ and ex situ PXD measurements, the following reactions (6) and (7) are proposed for the dehydrogenation of the 2:3:4 composite at elevated temperatures.

First Step: H<sub>2</sub> desorption in high pressure plateau

 $2Mg(NH_2)_2 + 2LiH + 4LiBH_4 \rightleftharpoons 2MgNH + 2[LiNH_2 - 2LiBH_4] (liquid) + 2H_2$ (6)

Second Step: H<sub>2</sub> desorption in slopping region

 $2MgNH+2[LiNH_2-2LiBH_4] (liquid) +LiH \rightleftharpoons 2MgNH + [(Li_2NH-2LiBH_4)-(LiNH_2-2LiBH_4)](liquid)+H_2$ (7)

It should be noted that the [LiNH<sub>2</sub>-2LiBH<sub>4</sub>] solidifies into Li<sub>4</sub>BN<sub>3</sub>H<sub>10</sub> and LiBH<sub>4</sub> phases at ambient temperature. The characterization results shown above demonstrate that the significantly improved dehydrogenation thermodynamics of Mg(NH<sub>2</sub>)<sub>2</sub>-LiH lies in the presence of a sufficient amount of LiBH<sub>4</sub> that can react with LiNH<sub>2</sub> and Li<sub>2</sub>NH to form LiNH<sub>2</sub>-2LiBH<sub>4</sub> and Li<sub>2</sub>NH-LiBH<sub>4</sub> species to stabilize the dehydrogenation products. Although the interesting phase diagram of LiBH<sub>4</sub>-LiNH<sub>2</sub>-Li<sub>2</sub>NH has yet to be developed, the compatibility of -BH<sub>4</sub> and -NH<sub>2</sub> within one phase has been well demonstrated, which is likely

due to the establishment of H<sup>+</sup>......H<sup>-</sup> dihydrogen bonding.<sup>[13, 14, 32]</sup> It is not a surprise that LiBH<sub>4</sub> and Li<sub>2</sub>NH will have similar interaction to form a stable bi-anionic hydride. Unlike the LiBH<sub>4</sub>-MgH<sub>2</sub> reactive composite, LiBH<sub>4</sub> in the 2:3:4 composite does not decompose to H<sub>2</sub> but rather tunes the reaction pathway by forming stable compounds with intermediates and final products. Such a role is similar to Si on LiH or MgH<sub>2</sub>,<sup>[33]</sup> while LiBH<sub>4</sub> is certainly more chemical-rich and may exhibit versatile functionalities to other hydrides upon proper design and development.

### 3. Conclusion

Although the overall hydrogen content of this tri-component hydride system falls short of the practical requirement, the present investigation shows for the first time that an ambient reversible hydrogen storage composite can be realized through the synergistic effect of three component hydrides of LiH, Mg(NH<sub>2</sub>)<sub>2</sub> and LiBH<sub>4</sub>. The hydrogen desorption enthalpy can be reduced to 24 kJ (mol-H<sub>2</sub>)<sup>-1</sup>. The temperature for dehydrogenation and re-hydrogenation can be remarkably reduced to 371 K and 326 K, which are close to the operation temperature of proton-exchange-membrane fuel cell. LiBH<sub>4</sub> serves as a reagent complexing with intermediates and products of the dehydrogenation of Mg(NH<sub>2</sub>)<sub>2</sub>-LiH, and significantly alters the overall thermodynamic and kinetic parameters of the system.

#### 4. Experimental Section

#### Sample preparation

 $Mg(NH_2)_2$  with a purity of  $\ge 95\%$  was synthesized by reacting metallic Mg power (99%, Sigma-Adrich) with purified NH<sub>3</sub> (about 8 bar) at 573 K for 2 weeks on a custom-made autoclave reactor in our own laboratory (**Figure S4** in Supporting Information). The synthesized Mg(NH<sub>2</sub>)<sub>2</sub>, LiH (98%, Alfa-Aesar) and LiBH<sub>4</sub> (95%, Sigma Aldrich) were ball milled in the molar ratios of 2:3, 2:3:1, 2:3:2 and 2:3:4 on a Retsch PM400 at 200 rpm for 24

h. All materials were stored inside a Mbraun glovebox filled with purified argon ( $O_2 < 5$  ppm,  $H_2O < 0.1$  ppm) and directly used without further treatment.

#### Hydrogen storage properties measurement

Pressure-Composition-Temperature (PCT) dehydrogenation experiments were carried out on an automatic Sieverts-type apparatus (Hy-Energy scientific instruments PCT Pro-2000) with 300 mg of sample. The final pressure after the measurements in the sample chamber for dehydrogenation experiments was 1 bar. The control precision of the sample temperature was  $\pm 1$  K. The equilibrium state was reached if the pressure variance ( $\Delta P$ ) was  $\leq 0.1$  bar for 24 h. Isothermal dehydrogenation and re-hydrogenation experiments were carried out on an automatic Sieverts-type apparatus (Advanced Materials Co.). The initial pressure in the sample chamber for hydrogen desorption was 0.1 bar and for absorption was 60 bar. NH<sub>3</sub> concentration in gaseous products was monitored by using a conductivity meter (Thermo Scientific) with an accuracy of  $0.1 \,\mu\text{S}/\text{cm}$ . 100 mL of diluted sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) solution (0.0006 M) was used to absorb any NH<sub>3</sub>. At the end of volumetric dehydrogenation measurements, gaseous products accumulated in the sealed reactor chamber were bubbled into the diluted H<sub>2</sub>SO<sub>4</sub> solution. The change in conductivity of the solution reflected the amount of NH<sub>3</sub> trapped by the solution and thus can be quantified to the amount of NH<sub>3</sub> produced during the dehydrogenation. Temperature-programmed desorption (TPD) using purified argon as the carrier gas was conducted in a custom-made reactor combined with an online mass spectrometer (MS, Hiden, UK). In order to exclude the influence of H<sub>2</sub>O, m/z=15 signal was monitored for NH<sub>3</sub>. About 20 mg of sample was tested for each run at a given ramping rate.

#### Structure characterization

Structure identification was carried out on a Philips PANalytical X'pert diffractometer with Cu K $\alpha$  radiation at 40 kV, and 40 mA. Data were collected at room temperature with a step size of 0.05°. N-H vibrations in the samples were identified by FTIR measurements conducted

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on a Varian 3100 unit in DRIFT mode with a scan resolution of 4  $cm^{-1}$  with an accumulation of 32 scans each time.

Temperature-dependent high resolution powder X-ray diffraction (PXD) experiments were performed at the PETRA III Synchrotron facility at DESY (Deutsches Elektronen-Synchrtron), Germany, beamline P.02.1. The wavelength was fixed at  $\lambda = 0.13846$  Å and a PerkinElmer XRD1621 plate image detector (2048\*2048 pixel, each of size 200\*200 microns) was used to acquire the patterns, with a sample-to-detector distance of about 2360 mm. The sample was loaded in a sapphire capillary tube (0.8 mm ID) and placed in a custom made sample holder. The heating rate of the sample from 323 K to 473 K was 2 K min<sup>-1</sup>, and the measurement time at 473 K was approximately 30 min. The 2D images were then integrated using FIT2D software.

#### **Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

#### Acknowledgements

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**Figure 1.** (a) Desorption Pressure-Composition curves of the 2Mg(NH<sub>2</sub>)<sub>2</sub>-3LiH-4LiBH<sub>4</sub> and 2Mg(NH<sub>2</sub>)<sub>2</sub>-3LiH composites at about 460 K. (b) Volumetric release curves of 2Mg(NH<sub>2</sub>)<sub>2</sub>-3LiH-4LiBH<sub>4</sub> and 2Mg(NH<sub>2</sub>)<sub>2</sub>-3LiH composites under back hydrogen pressure. (c) Desorption Pressure-Composition curves of 2Mg(NH<sub>2</sub>)<sub>2</sub>-3LiH-4LiBH<sub>4</sub> composite at different temperatures. (d) van't Hoff plot of 2Mg(NH<sub>2</sub>)<sub>2</sub>-3LiH-4LiBH<sub>4</sub> composite.

### Figure 2(a)

б 





Figure 2. (a) Volumetric hydrogen release and subsequent uptake of the 2Mg(NH<sub>2</sub>)<sub>2</sub>-3LiH-4LiBH<sub>4</sub> composite at different temperatures. (Insert figure: Amplified region of the dehydrogenation in the time range of 0 to 8 h) (b) The Kissinger plots of hydrogen desorption from the 2Mg(NH<sub>2</sub>)<sub>2</sub>-3LiH-4LiBH<sub>4</sub> composite with heating rates of 2, 4, 6, 8k/min. The insert contains TPD-MS results at various heating rates.

#### Figure 3(a)



Figure 3(b)



**Figure 3.** (a) PXD patterns and (b) FT-IR spectra of (I) as-milled, dehydrogenation at 95 bar (II), 80 bar (III) and fully dehydrogenation samples (IV) of the 2Mg(NH<sub>2</sub>)<sub>2</sub>-3LiH-4LiBH<sub>4</sub> composite.





**Figure 4.** The *in-situ* PXD patterns of the 2Mg(NH<sub>2</sub>)<sub>2</sub>-3LiH-4LiBH<sub>4</sub> composites under 50 bar hydrogen pressure in the temperature range of 373 K-473 K.

### **Table of Contents Entry:**

**Reversible hydrogen storage over Hydrides of Light Elements (HLEs) at ambient condition is unattained albeit pursued actively for two decades.** The compositing and complexing strategies, applied to three of the most investigated HLEs--Mg(NH<sub>2</sub>)<sub>2</sub>, LiH and LiBH<sub>4</sub> may provide the possibility of the implementation of reversible hydrogen storage under ambient condition.

### Keyword: Hydrogen storage

Han Wang, Guotao Wu\*, Hujun Cao, Claudio Pistidda, Anna-Lisa Chaudhary, Sebastiano Garroni, Martin Dornheim and Ping Chen\*

# Near Ambient Condition Hydrogen Storage in a Synergized Tri-Component Hydride System

### **Table of Contents Figure:**



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### Supporting Information

# Near Ambient Condition Hydrogen Storage in a Synergized Tri-Component Hydride System

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#### A. The thermodynamic investigations of $2Mg(NH_2)_2-3LiH-xLiBH_4$ composites --- the

### PCT curves



**Figure S1.** The Pressure-Composition-isotherm desorption curves of the 2Mg(NH<sub>2</sub>)<sub>2</sub>-3LiHxLiBH<sub>4</sub> composites at about 460 K.

### B. Characterization of the new phase composed of Li<sub>2</sub>NH and LiBH<sub>4</sub>



Figure S2. XRD patterns of the new phase, LiBH<sub>4</sub> and Li<sub>2</sub>NH.



Figure S3. FT-IR spectra of the new phase and Li<sub>2</sub>NH.

### C. Characterization of self-made $Mg(NH_2)_2$

A complimentary study to confirm the phase of self-made chemical---Mg(NH $_2$ ) $_2$  by the XRD pattern.



Figure S4. XRD pattern of self-made  $Mg(NH_2)_2$  and the reference.

Supporting Information

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