

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

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Please submit a plain text version of your cover letter here.  <b>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.</b>	<p>Dear Professor Joern Ritterbusch,</p> <p>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".</p> <p>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.</p> <p>Here we demonstrate for the first time 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>)-1 which thermodynamically allows a dehydrogenation temperature at 1.0 bar H<sub>2</sub> 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 LiBH<sub>4</sub> 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 LiBH<sub>4</sub> 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.</p> <p>With the important findings and in-depth understanding we strongly believe that this paper will have significant impact on the materials research for hydrogen storage and enriches the energy-research community of HLEs, and thus, is very appropriate for "Advanced Energy Materials".</p> <p>No conflict of interest exists in this submission of the manuscript, and the content of this manuscript is approved by all authors for publication. On behalf of my co-authors I would like to declare that this work was described original research that has not been published previously, and not under consideration for other publications, in whole or in part. All the authors listed have approved that this manuscript is enclosed.</p> <p>We appreciate your consideration of our manuscript, and we are looking forward to receiving kind comments from you and the reviewers. If you have any queries, please contact me at the address below.</p> <p>Thank you and best regards</p> <p>Yours sincerely</p> <p>Ping Chen, Professor Division head, Hydrogen Energy and Advanced Materials, Dalian Institute of Chemical Physics (CAS)</p>

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<b>Abstract:</b>	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.

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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  $\text{LiBH}_4$ ,  $\text{Mg}(\text{NH}_2)_2$  and  $\text{LiH}$ , 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  $24 \text{ kJ (mol-H}_2\text{)}^{-1}$  which thermodynamically enables a dehydrogenation temperature at 1.0 bar  $\text{H}_2$  to be as low as 266 K. Characterization of this combination of HLEs shows that  $\text{LiBH}_4$  serves as a reagent complexing with intermediates and products of the dehydrogenation of  $\text{Mg}(\text{NH}_2)_2\text{-LiH}$ , and significantly alters the overall thermodynamic and kinetic parameters of the system.

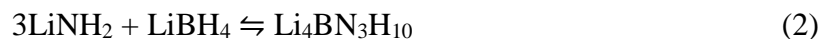
## 1. Introduction

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 LaNi<sub>5</sub> 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 LaNi<sub>5</sub> 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>



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. LiBH<sub>4</sub> 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<sub>4</sub>BN<sub>3</sub>H<sub>10</sub> 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

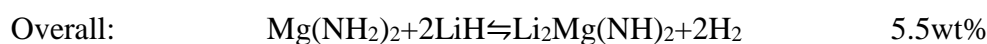
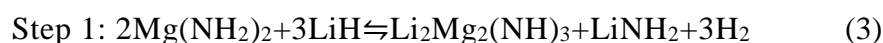
the  $2\text{LiNH}_2\text{-MgH}_2\text{-LiBH}_4$  and  $2\text{Mg}(\text{NH}_2)_2\text{-3LiH-1/3LiBH}_4$  composite systems.<sup>[22, 24]</sup> Our results also showed that a similar high-pressure dehydrogenation region appeared in the  $2\text{Mg}(\text{NH}_2)_2\text{-3LiH-LiBH}_4$  composition.<sup>[25]</sup> Because the interaction of  $\text{LiNH}_2$  and  $\text{LiBH}_4$  gives rise to a number of solid and liquid phases under different conditions and the  $\text{LiNH}_2$  to  $\text{LiBH}_4$  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  $2\text{Mg}(\text{NH}_2)_2\text{-3LiH-4LiBH}_4$ , which has a dehydrogenation enthalpy of  $24 \text{ kJ (mol-H}_2\text{)}^{-1}$  allowing hydrogen release under 1 bar  $\text{H}_2$  at a temperature as low as 266 K, from thermodynamic point of view. Our experimental data show that fully reversible  $\text{H}_2$  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  $\text{H}_2$ . A dehydrogenation pathway has been identified.  $\text{LiBH}_4$  exhibits “solvent”-like behavior that considerably stabilizes the dehydrogenation products, and thus, change the thermodynamics of dehydrogenation and re-hydrogenation.

## 2. Results and Discussion

### 2.1. Thermodynamic properties.

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



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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  $2\text{Mg}(\text{NH}_2)_2\text{-3LiH}$  composite. The Pressure-Composition curve of the  $2\text{Mg}(\text{NH}_2)_2\text{-3LiH}$  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  $\text{LiBH}_4$  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  $\text{LaNi}_5$  and Fe-Ti alloy, two of the typical metal alloys, and for  $\text{NaAlH}_4$ , the most investigated complex hydride, the equilibrium pressures at this temperature (460 K) are 120, 47 and 130 bar, respectively. [2, 5, 28]

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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.

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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  $\ln P_{\text{eq}}$  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-H<sub>2</sub>)<sup>-1</sup> 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 H<sub>2</sub> 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 NaAlH<sub>4</sub>. 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  $E_a$

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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  $\text{Li}_2\text{Mg}_2\text{N}_3\text{H}_3$  formation in the 2-3 sample,  $\text{MgNH}$ , the new phase ( $\text{Li}_2\text{NH-LiBH}_4$ ) and  $\text{Li}_4\text{BN}_3\text{H}_{10}$  are formed upon dehydrogenation of 2:3:4 composite.

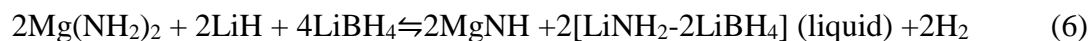
FT-IR measurements (**Figure 3(b)**) show absorption peaks at  $3273\text{ cm}^{-1}$  and  $3326\text{ cm}^{-1}$  in the as-milled 2:3:4 sample that are assigned to the symmetrical and asymmetrical vibrations of N-H bonds in  $\text{Mg}(\text{NH}_2)_2$ .<sup>[17, 30]</sup> The dehydrogenated 2:3 sample contains two typical peaks at  $3196\text{ cm}^{-1}$  and  $3164\text{ cm}^{-1}$  belonging to the N-H vibrations of  $\text{Li}_2\text{Mg}_2(\text{NH})_3$ .<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  $\text{Li}_2\text{Mg}_2(\text{NH})_3$  were not observed, instead, a broad peak centered at  $3192\text{ cm}^{-1}$  possibly assignable to the N-H stretch of  $\text{MgNH}$  was detected.<sup>[31]</sup> The absorption peaks at  $3243$  and  $3301\text{ cm}^{-1}$  are the characteristic N-H vibration in  $\text{Li}_4\text{BN}_3\text{H}_{10}$ .<sup>[14, 16]</sup> Moreover, the peaks intensities of  $\text{Mg}(\text{NH}_2)_2$  decreased dramatically. When the back pressure reduced to 80 bar (**Figure 3(a)-III**), the vibrations of  $\text{Mg}(\text{NH}_2)_2$  are barely detectable, which is in good agreement with the results of PXD patterns. There is a broad vibration centered at  $3168\text{ cm}^{-1}$  in the fully dehydrogenated 2:3:4 sample, (**Figure 3(b)-IV**) which is similar to IR absorption of the new phase composed of  $\text{Li}_2\text{NH-LiBH}_4$  (**Figure S3** in Supporting Information).

The formation of  $\text{MgNH}$  and  $\text{Li}_4\text{BN}_3\text{H}_{10}$  rather than  $\text{Li}_2\text{Mg}_2(\text{NH})_3$  and  $\text{LiNH}_2$  in the higher plateau region provides evidence of the change in dehydrogenation pathway upon the addition of substantial amount of  $\text{LiBH}_4$  in the  $\text{Mg}(\text{NH}_2)_2\text{-LiH}$  composite. Except for forming stoichiometric  $\text{Li}_4\text{BN}_3\text{H}_{10}$  phases;  $\text{LiNH}_2$  and  $\text{LiBH}_4$  in a wide range of compositions becomes liquid solution at elevated temperatures, with the lowest melting point at 368K when the  $\text{LiNH}_2$  to  $\text{LiBH}_4$  ratio is 1:2 according to the  $\text{LiNH}_2\text{-LiBH}_4$  phase diagram.<sup>[15]</sup> In other words, the liquid  $\text{LiNH}_2\text{-(LiBH}_4)_x$  phase is thermodynamically more stable than solid phases of  $\text{Li}_2\text{BNH}_6$ ,  $\text{Li}_4\text{BN}_3\text{H}_{10}$  and their mixtures with  $\text{LiBH}_4$  in a certain temperature range and  $\text{LiNH}_2/\text{LiBH}_4$  ratio, which may partially, if not conclusively, explain the significantly

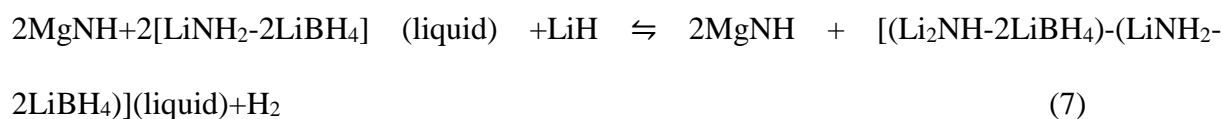
improved thermodynamics during hydrogen release. The formation of the liquid phase with dehydrogenation (Temperature > 460K) is strongly supported by the absence of any LiBH<sub>4</sub>-related phases (not only just phases composed of LiNH<sub>2</sub>-xLiBH<sub>4</sub>, but also Li<sub>2</sub>NH-yLiBH<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



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



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

1 due to the establishment of  $H^+ \cdots H^-$  dihydrogen bonding.<sup>[13, 14, 32]</sup> It is not a surprise that  
2  $LiBH_4$  and  $Li_2NH$  will have similar interaction to form a stable bi-anionic hydride. Unlike the  
3  
4  $LiBH_4$ - $MgH_2$  reactive composite,  $LiBH_4$  in the 2:3:4 composite does not decompose to  $H_2$  but  
5  
6 rather tunes the reaction pathway by forming stable compounds with intermediates and final  
7  
8 products. Such a role is similar to Si on LiH or  $MgH_2$ ,<sup>[33]</sup> while  $LiBH_4$  is certainly more  
9  
10 chemical-rich and may exhibit versatile functionalities to other hydrides upon proper design  
11  
12 and development.  
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### 16 17 18 **3. Conclusion** 19

20  
21 Although the overall hydrogen content of this tri-component hydride system falls short of  
22  
23 the practical requirement, the present investigation shows for the first time that an ambient  
24  
25 reversible hydrogen storage composite can be realized through the synergistic effect of three  
26  
27 component hydrides of LiH,  $Mg(NH_2)_2$  and  $LiBH_4$ . The hydrogen desorption enthalpy can be  
28  
29 reduced to  $24 \text{ kJ (mol-H}_2\text{)}^{-1}$ . The temperature for dehydrogenation and re-hydrogenation can  
30  
31 be remarkably reduced to 371 K and 326 K, which are close to the operation temperature of  
32  
33 proton-exchange-membrane fuel cell.  $LiBH_4$  serves as a reagent complexing with  
34  
35 intermediates and products of the dehydrogenation of  $Mg(NH_2)_2$ -LiH, and significantly alters  
36  
37 the overall thermodynamic and kinetic parameters of the system.  
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### 45 **4. Experimental Section**

#### 46 *Sample preparation* 47

48  
49  $Mg(NH_2)_2$  with a purity of  $\geq 95\%$  was synthesized by reacting metallic Mg power (99%,  
50  
51 Sigma-Adrich) with purified  $NH_3$  (about 8 bar) at 573 K for 2 weeks on a custom-made  
52  
53 autoclave reactor in our own laboratory (**Figure S4** in Supporting Information). The  
54  
55 synthesized  $Mg(NH_2)_2$ , LiH (98%, Alfa-Aesar) and  $LiBH_4$  (95%, Sigma Aldrich) were ball  
56  
57 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  
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2 h. All materials were stored inside a Mbraun glovebox filled with purified argon ( $O_2 < 5$  ppm,  
3  $H_2O < 0.1$  ppm) and directly used without further treatment.

4  
5 *Hydrogen storage properties measurement*

6  
7 Pressure-Composition-Temperature (PCT) dehydrogenation experiments were carried out  
8  
9 on an automatic Sieverts-type apparatus (Hy-Energy scientific instruments PCT Pro-2000)  
10  
11 with 300 mg of sample. The final pressure after the measurements in the sample chamber for  
12  
13 dehydrogenation experiments was 1 bar. The control precision of the sample temperature was  
14  
15  $\pm 1$  K. The equilibrium state was reached if the pressure variance ( $\Delta P$ ) was  $\leq 0.1$  bar for 24  
16  
17

18  
19 h. Isothermal dehydrogenation and re-hydrogenation experiments were carried out on an  
20  
21 automatic Sieverts-type apparatus (Advanced Materials Co.). The initial pressure in the  
22  
23 sample chamber for hydrogen desorption was 0.1 bar and for absorption was 60 bar.  
24  
25

26  
27  $NH_3$  concentration in gaseous products was monitored by using a conductivity meter (Thermo  
28  
29 Scientific) with an accuracy of  $0.1 \mu S/cm$ . 100 mL of diluted sulfuric acid ( $H_2SO_4$ ) solution  
30  
31 (0.0006 M) was used to absorb any  $NH_3$ . At the end of volumetric dehydrogenation  
32  
33 measurements, gaseous products accumulated in the sealed reactor chamber were bubbled  
34  
35 into the diluted  $H_2SO_4$  solution. The change in conductivity of the solution reflected the  
36  
37 amount of  $NH_3$  trapped by the solution and thus can be quantified to the amount of  $NH_3$   
38  
39 produced during the dehydrogenation. Temperature-programmed desorption (TPD) using  
40  
41 purified argon as the carrier gas was conducted in a custom-made reactor combined with an  
42  
43 online mass spectrometer (MS, Hiden, UK). In order to exclude the influence of  $H_2O$ ,  $m/z=15$   
44  
45 signal was monitored for  $NH_3$ . About 20 mg of sample was tested for each run at a given  
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51  
52 ramping rate.

53  
54 *Structure characterization*

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56 Structure identification was carried out on a Philips PANalytical X'pert diffractometer with  
57  
58 Cu  $K\alpha$  radiation at 40 kV, and 40 mA. Data were collected at room temperature with a step  
59  
60 size of  $0.05^\circ$ . N-H vibrations in the samples were identified by FTIR measurements conducted  
61  
62

1 on a Varian 3100 unit in DRIFT mode with a scan resolution of  $4 \text{ cm}^{-1}$  with an accumulation  
2 of 32 scans each time.  
3

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

31 Supporting Information is available from the Wiley Online Library or from the author.  
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42 the manuscript. Han Wang performed the experiments and wrote the manuscript. Hujun Cao,  
43 Claudio Pistidda, Anna-Lisa Chaudhary and Martin Dorheim contributed to the discussions  
44 and revisions. Sebastiano Garroni provided valuable help during high resolution powder X-  
45 ray diffraction (PXD) experiments at DESY (Deutsches Elektronen-Synchrotron), Germany,  
46 beamline P.02.1. All authors have given approval to the final version of the manuscript.  
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Figure 1(a)

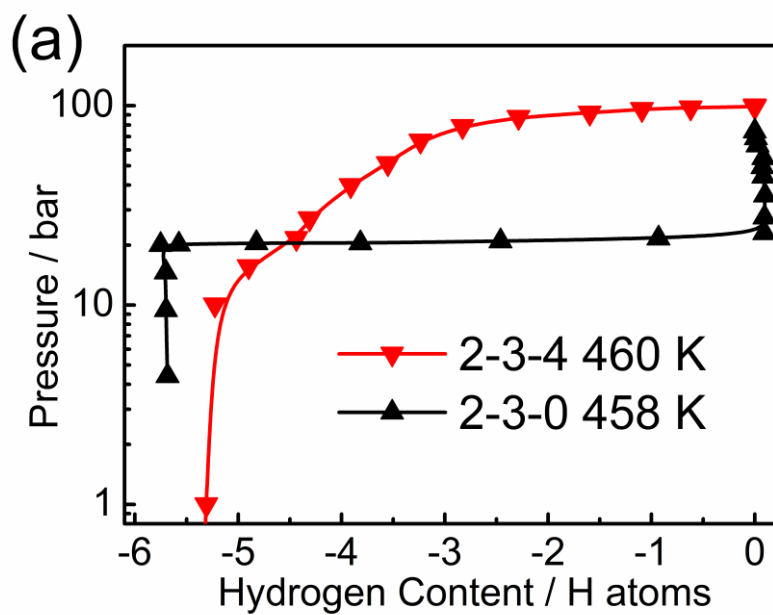


Figure 1(b)

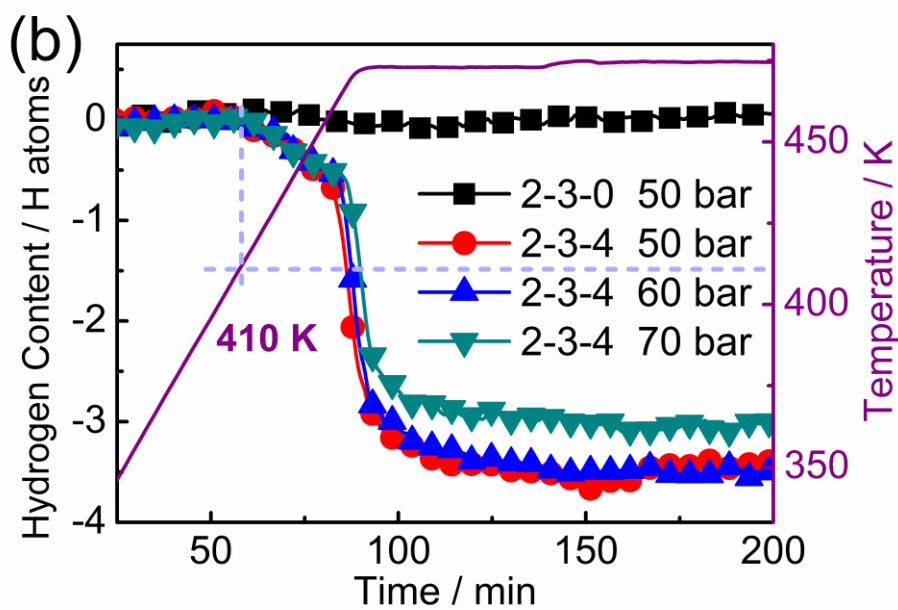


Figure 1(c)

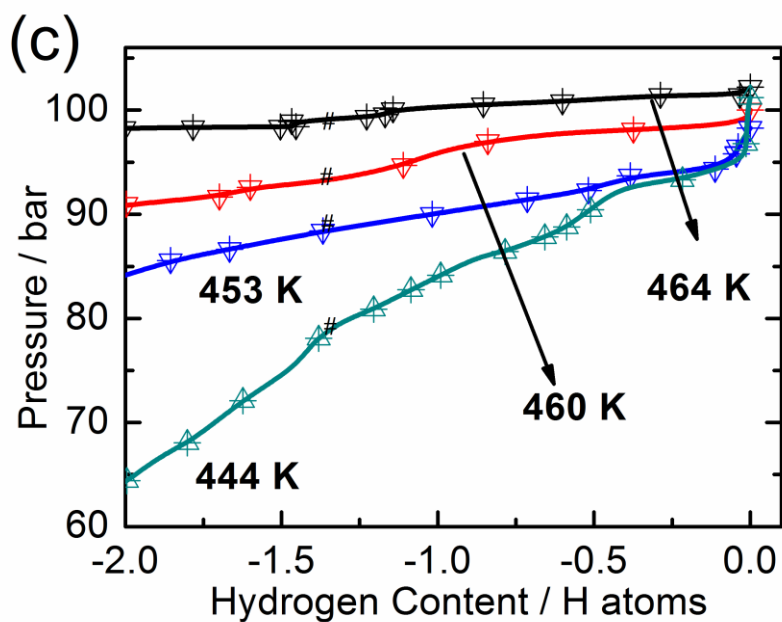
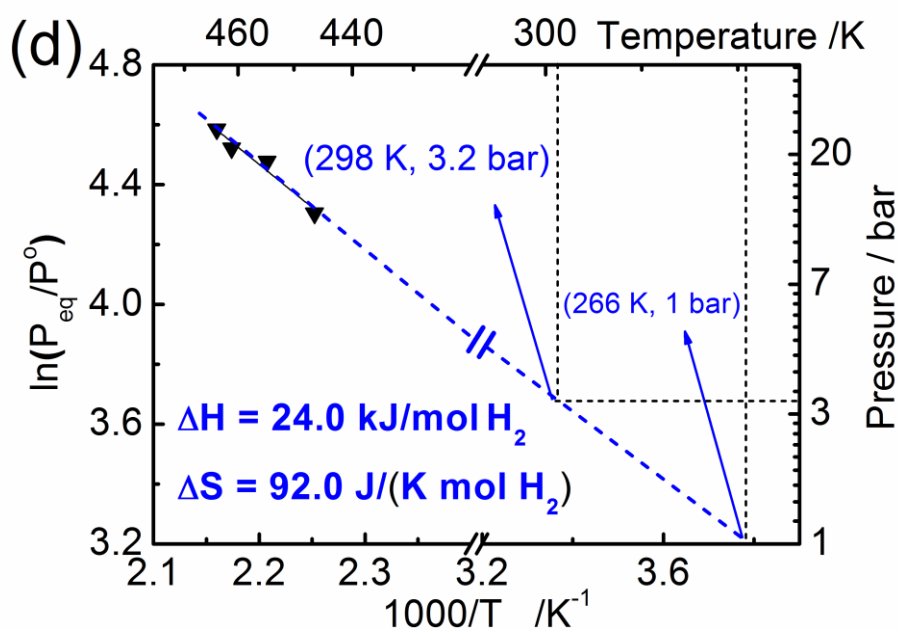


Figure 1(d)



**Figure 1.** (a) Desorption Pressure-Composition curves of the  $2\text{Mg}(\text{NH}_2)_2\text{-3LiH-4LiBH}_4$  and  $2\text{Mg}(\text{NH}_2)_2\text{-3LiH}$  composites at about 460 K. (b) Volumetric release curves of  $2\text{Mg}(\text{NH}_2)_2\text{-3LiH-4LiBH}_4$  and  $2\text{Mg}(\text{NH}_2)_2\text{-3LiH}$  composites under back hydrogen pressure. (c) Desorption Pressure-Composition curves of  $2\text{Mg}(\text{NH}_2)_2\text{-3LiH-4LiBH}_4$  composite at different temperatures. (d) van't Hoff plot of  $2\text{Mg}(\text{NH}_2)_2\text{-3LiH-4LiBH}_4$  composite.

Figure 2(a)

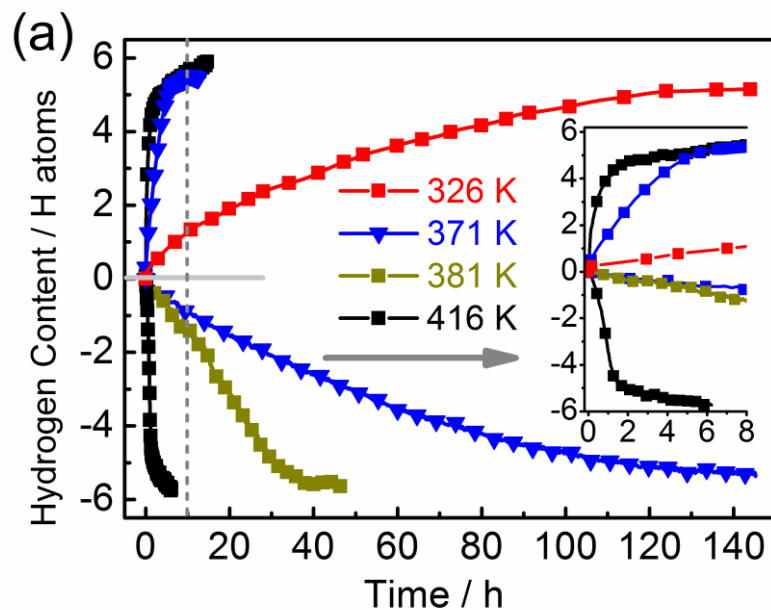
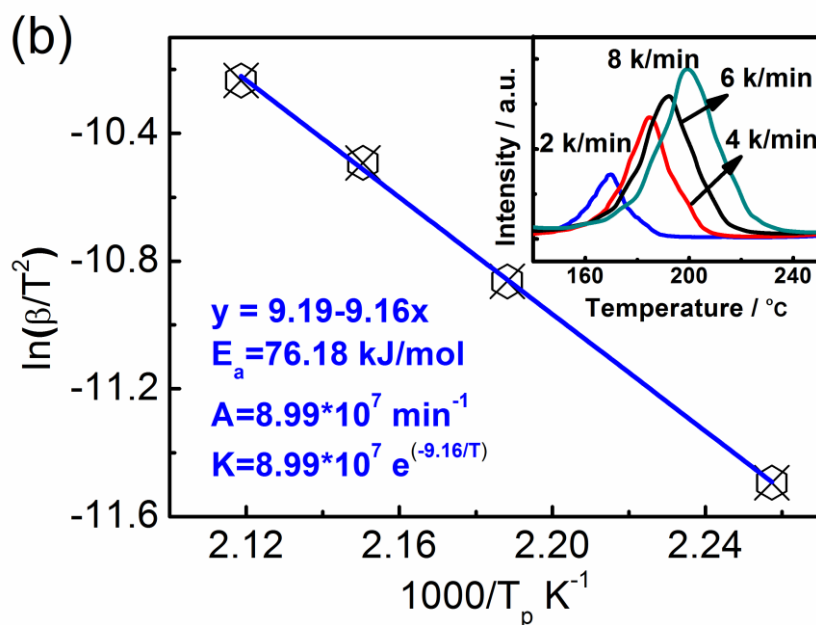


Figure 2(b)



**Figure 2.** (a) Volumetric hydrogen release and subsequent uptake of the  $2\text{Mg}(\text{NH}_2)_2\text{-}3\text{LiH-}4\text{LiBH}_4$  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  $2\text{Mg}(\text{NH}_2)_2\text{-}3\text{LiH-}4\text{LiBH}_4$  composite with heating rates of 2, 4, 6, 8 k/min. The insert contains TPD-MS results at various heating rates.

Figure 3(a)

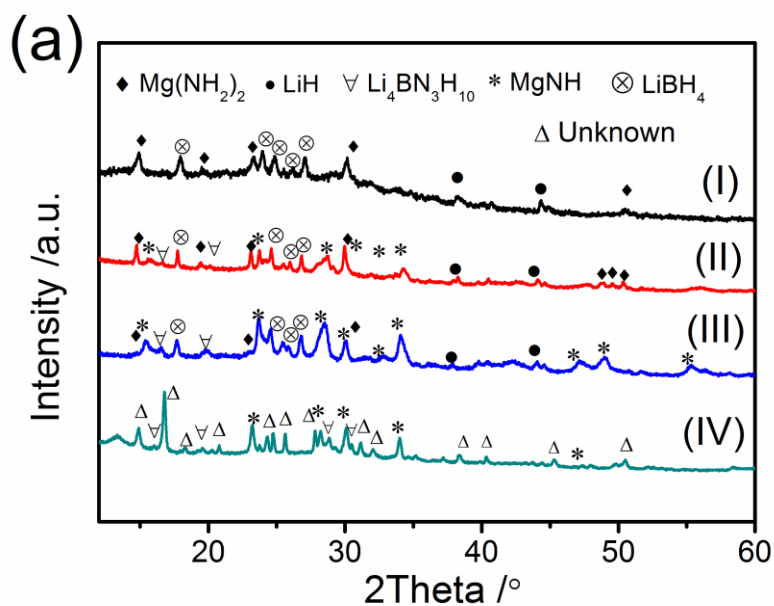
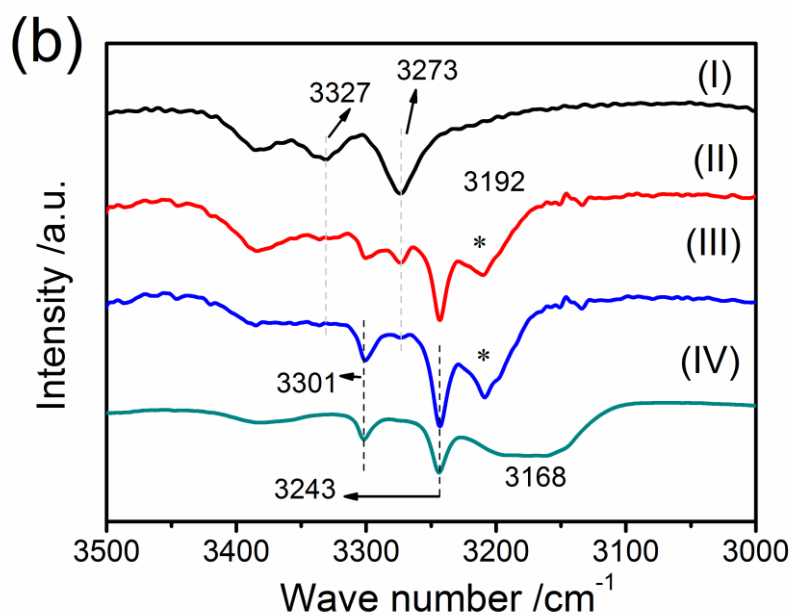
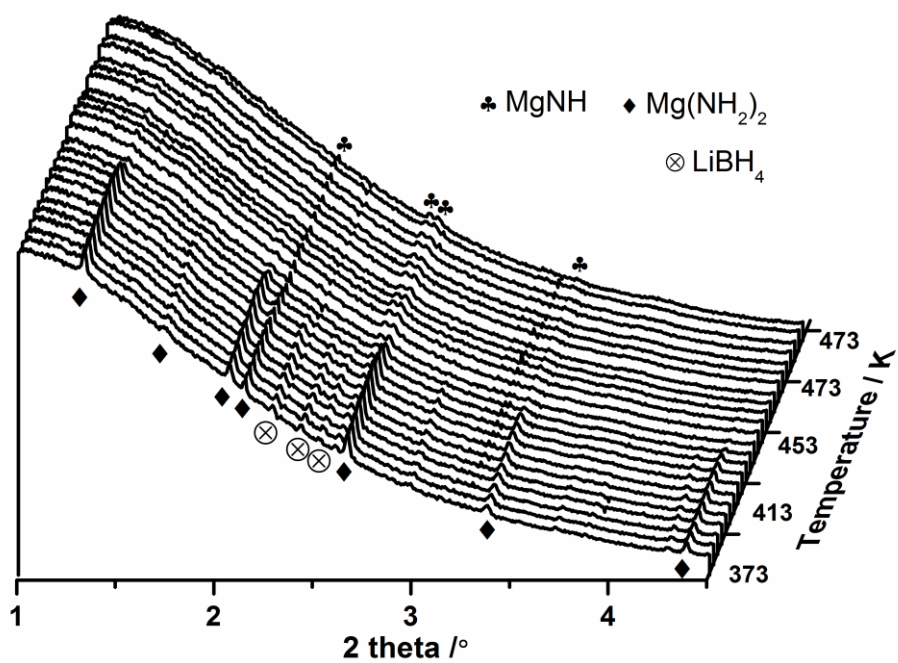


Figure 3(b)



**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  $2\text{Mg}(\text{NH}_2)_2\text{-}3\text{LiH-}4\text{LiBH}_4$  composite.

Figure 4



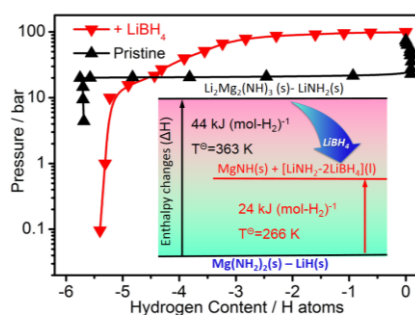
**Figure 4.** The *in-situ* PXD patterns of the  $2\text{Mg}(\text{NH}_2)_2\text{-}3\text{LiH}\text{-}4\text{LiBH}_4$  composites under 50 bar hydrogen pressure in the temperature range of 373 K-473 K.

**Table of Contents Entry:**

1 **Reversible hydrogen storage over Hydrides of Light Elements (HLEs) at ambient**  
 2 **condition is unattained albeit pursued actively for two decades.** The compositing and  
 3 complexing strategies, applied to three of the most investigated HLEs-- $\text{Mg}(\text{NH}_2)_2$ , LiH and  
 4  $\text{LiBH}_4$  may provide the possibility of the implementation of reversible hydrogen storage under  
 5 ambient condition.  
 6  
 7 .  
 8 .  
 9

**Keyword: Hydrogen storage**

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 14 Garroni, Martin Dornheim and Ping Chen\*  
 15

**Near Ambient Condition Hydrogen Storage in a Synergized Tri-Component Hydride System****Table of Contents Figure:**

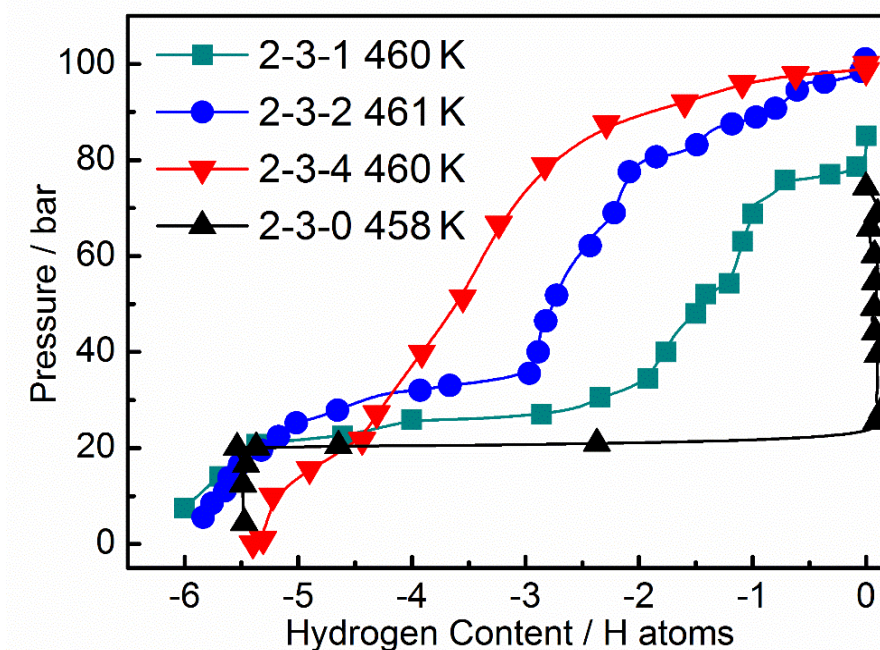
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## Supporting Information

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

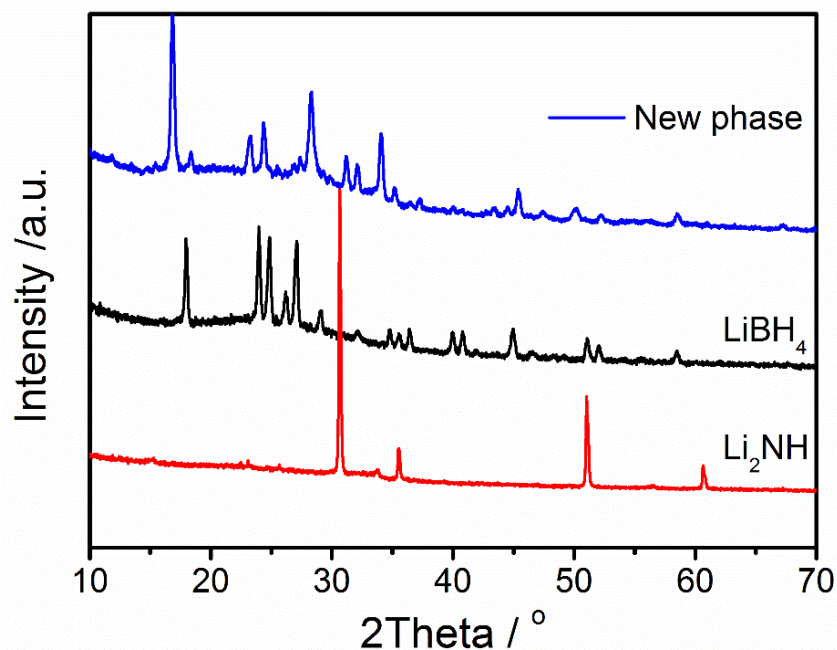
Han Wang, Guotao Wu\*, Hujun Cao, Claudio Pistidda, Anna-Lisa Chaudhary, Sebastiano Garroni, Martin Dornheim and Ping Chen\*

#### A. The thermodynamic investigations of $2\text{Mg}(\text{NH}_2)_2\text{-}3\text{LiH-xLiBH}_4$ composites --- the PCT curves

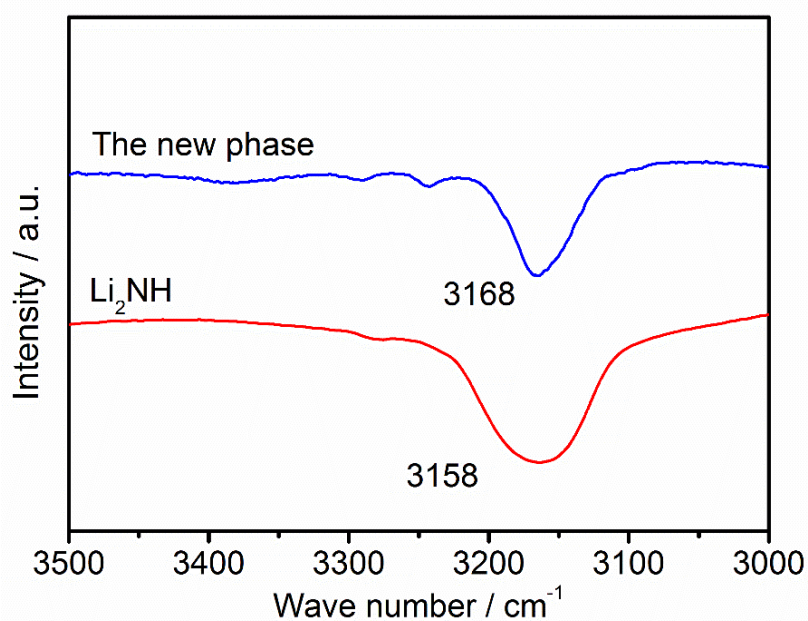


**Figure S1.** The Pressure-Composition-isotherm desorption curves of the  $2\text{Mg}(\text{NH}_2)_2\text{-}3\text{LiH-xLiBH}_4$  composites at about 460 K.

#### B. Characterization of the new phase composed of $\text{Li}_2\text{NH}$ and $\text{LiBH}_4$



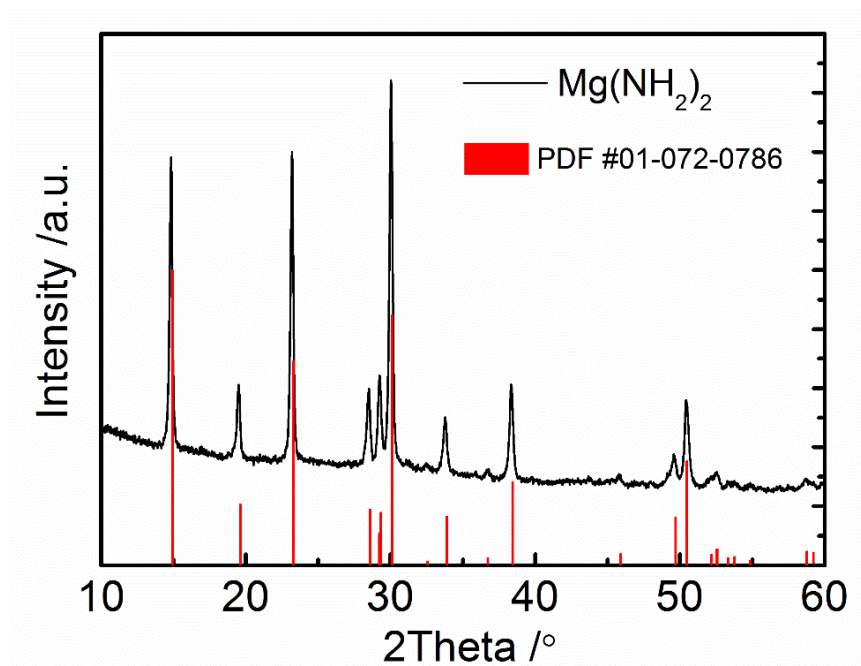
**Figure S2.** XRD patterns of the new phase, LiBH<sub>4</sub> and Li<sub>2</sub>NH.



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

### C. Characterization of self-made Mg(NH<sub>2</sub>)<sub>2</sub>

A complimentary study to confirm the phase of self-made chemical---Mg(NH<sub>2</sub>)<sub>2</sub> by the XRD pattern.



**Figure S4.** XRD pattern of self-made  $\text{Mg}(\text{NH}_2)_2$  and the reference.



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**Supporting Information**

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