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# LiBH<sub>4</sub>·NH<sub>3</sub>BH<sub>3</sub>: A new lithium borohydride ammonia borane compound with a novel structure and favorable hydrogen storage properties

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#### ABSTRACT

Mechanically milling ammonia borane and lithium borohydride in equivalent molar ratio results in the formation of a new complex, LiBH<sub>4</sub>·NH<sub>3</sub>BH<sub>3</sub>. Its structure was successfully determined using combined X-ray diffraction and first-principles calculations. LiBH<sub>4</sub>·NH<sub>3</sub>BH<sub>3</sub> was carefully studied in terms of its decomposition behavior and reversible dehydrogenation property, particularly in comparison with the component phases. In parallel to the property examination, X-ray diffraction and Fourier transformation infrared spectroscopy techniques were employed to monitor the phase evolution and bonding structure changes in the reaction process. Our study found that LiBH<sub>4</sub>·NH<sub>3</sub>BH<sub>3</sub> first disproportionates into (LiBH<sub>4</sub>)<sub>2</sub>·NH<sub>3</sub>BH<sub>3</sub> and NH<sub>3</sub>BH<sub>3</sub>, and the resulting mixture exhibits a three-step decomposition behavior upon heating to 450 °C, totally yielding ~15.7 wt% hydrogen. Interestingly, it was found that *h*-BN was formed at such a moderate temperature. And owing to the *in situ* formation of *h*-BN, LiBH<sub>4</sub>·NH<sub>3</sub>BH<sub>3</sub> exhibits significantly improved reversible dehydrogenation properties in comparison with the LiBH<sub>4</sub> phase. Copyright © 2012, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights

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# 1. Introduction

The development of hydrogen-fueled vehicles and portable electronics requires advanced hydrogen storage materials that can store and deliver large amounts of hydrogen at moderate temperature with fast kinetics. Recently, ammonia borane ( $NH_3BH_3$ , AB for short) has received extensive attention as a promising hydrogen storage material [1–3]. This is a result of its many appealing attributes, such as high hydrogen content (19.6 wt%), moderate thermal stability, and satisfactory air-stability. But on the other hand, the  $H_2$  release from AB is severely kinetically restricted and is entangled by the concurrent evolution of diverse volatile byproducts. In the past decade, several strategies have been employed to improve the dehydrogenation properties of AB. Addition of selected metal catalysts [4–10] or acids [11,12] enables rapid  $H_2$  release from the solvolysis reactions of AB at ambient temperatures. Confinement of AB in nanoscaffolds [13–15] or

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addition of chemical promoters [16-21] has proved to be effective means for promoting solid-state thermolysis of AB. In particular, reacting AB with alkali or alkaline-earth metal hydrides (with an exception of MgH<sub>2</sub>) has been established as a general approach for preparation of mono- or mixed-metal amidoboranes, which exhibit favorable combination of high hydrogen capacity, fast hydrogen release rate and suppressed volatile byproducts [22–31]. This progress stimulated further investigations on the chemical modification of AB using complex anionic hydrides containing [NH<sub>2</sub>] or [BH<sub>4</sub>].

Lithium borohydride (LiBH<sub>4</sub>) is a salt-like ionic crystal containing a high density of hydrogen (18.4 wt%). Due to the thermodynamic and kinetic limitations that are imposed by the strong chemical bonds, LiBH<sub>4</sub> exhibits high temperature threshold (>400 °C) for H<sub>2</sub> release and poor reversibility even under rigorous temperature and pressure conditions [32,33]. A recent study by Wu et al. found that two H-rich materials, AB and LiBH<sub>4</sub>, can readily combine together to form a new layered borohydride ammonia borane complex (LiBH<sub>4</sub>)<sub>2</sub>·NH<sub>3</sub>BH<sub>3</sub> ((LiBH)<sub>2</sub>·AB for short) [34]. In comparison with the component phases (LiBH)<sub>2</sub> · AB exhibits small but significant improvement on the dehydrogenation properties. This material discovery, together with the recent findings of metal amidoborane ammoniates [35-39], offers new opportunities for developing a practical source for generating molecular hydrogen. In this paper, we report the synthesis, structure, and hydrogen storage properties of a new lithium borohydride ammonia borane compound, LiBH<sub>4</sub>·NH<sub>3</sub>BH<sub>3</sub> (LiBH·AB for short). In comparison with its analogue (LiBH)<sub>2</sub>·AB, the newly developed LiBH · AB adopts a completely different crystal structure and can deliver much more H<sub>2</sub> via a three-step decomposition reaction.

#### 2. Experimental

AB (97% purity), LiBH<sub>4</sub> (90% purity) and sodium borohydride (NaBH<sub>4</sub>, 98% purity) powders from Sigma–Aldrich [40] were used as received. The xLiBH<sub>4</sub>/AB mixtures in varied molar ratios (x = 0.5-2) were mechanically milled under an argon (99.999% purity) atmosphere using a Fritsch 7 Planetary mill at 200 rpm for 3 h. In the control experiment, the 1:1 NaBH<sub>4</sub>/AB was milled under identical conditions. All sample handlings were carried out in an argon (99.999% purity)-filled glovebox equipped with a circulative purification system, in which the H<sub>2</sub>O/O<sub>2</sub> levels were typically <0.1 ppm.

The decomposition behaviour of the post-milled xLiBH<sub>4</sub>/AB samples was examined by synchronous thermogravimetry, differential scanning calorimetry, mass spectroscopy (TG, DSC, MS, Netzsch 449C Jupiter/QMS 403C) and volumetric method. In the thermal analyses, the samples with a typical amount of ~2 mg were heated to 450 °C at a ramping rate of  $2 \,^{\circ}$ C min<sup>-1</sup> under a flowing argon (99.999% purity) atmosphere. The temperature-programmed desorption (TPD) and isothermal measurements were carried out in a carefully calibrated Sievert's type apparatus under an initial pressure <100 Pa. In a typical TPD run, the sample with an amount of ~100 mg was heated to 450 °C at a ramping rate of  $2 \,^{\circ}$ C min<sup>-1</sup> and held at this temperature until hydrogen desorption completed. In an isothermal measurement, data collection

started from the moment when the sample chamber was pushed into the preheated furnace. The solid residuals at different decomposition stages were collected after heating the sample to preset temperatures and then fan-cooling to room temperature. Rehydrogenation of the sample was conducted at 400 °C under an initial hydrogen pressure of 10 MPa for 12 h.

The post-milled xLiBH<sub>4</sub>/AB and the relevant neat AB and LiBH<sub>4</sub> samples at varied states were characterized by XRD (Rigaku D/max 2500, Cu K $\alpha$  radiation), Fourier transformation infrared (FTIR) spectroscopy (Bruker TENSOR 27, 4 cm<sup>-1</sup> resolution). Special measures were taken to minimize H<sub>2</sub>O/O<sub>2</sub> contamination during the sample transfer process. In the routine XRD analysis, the powder samples were protected by a polymeric tape to minimize the air- and moisture-contamination. In the study of crystal structure, the sample was sealed inside a 1 mm quartz glass capillary and analyzed in a continuous scan mode for over 12 h in the 20 range of 5–70° with a step size of 0.02°. FTIR spectra of the samples were collected using the KBr-pellets method, and the obtained spectra were normalized using OPUS 6.5 software.

First-principles calculations based on density-functional theory (DFT) were performed by using the PWSCF package [41]. We used a Vanderbilt-type ultrasoft potential with Perdew-Burke-Ernzerhof exchange correlation. A cutoff energy of 544 eV was found to be enough for the total energy to converge within 0.5 meV/atom. Car-Parrinello molecular dynamics simulations [42] were used to help in searching for the most likely crystal structures. The conventional unit cells were used, with the cell dimensions fixed at the experimental values. The initial system temperature was set to 600 K. The system was first allowed to evolve and equilibrate for 20 ps, and then the system temperature was slowly decreased to 0 K in a period of 20 ps. Structure optimizations on the resulting candidate structures at 0 K were further performed with respect to atomic positions. This information was used in combination with XRD pattern matching to derive the best crystal structure solution of LiBH·AB.

## 3. Results and discussion

#### 3.1. Synthesis and structure of LiBH<sub>4</sub>·NH<sub>3</sub>BH<sub>3</sub>

A systematic study of the series of xLiBH<sub>4</sub>/AB samples (x = 0.5-2) found that different lithium borohydride ammonia borane complexes might be formed upon changing the molar ratio of the component phases. As shown in Fig. 1, mechanical milling the mixtures of x = 2 molar ratio produces (LiBH)<sub>2</sub>·AB, which agrees well with the early finding [34]. But for the 1:1 LiBH<sub>4</sub>/AB sample, milling-induced solid-phase reaction produces a new crystalline phase. Here, the nearly complete consumption of the starting materials suggests its formula of LiBH·AB. When 1 < x < 2 applied, the post-milled sample for 3 h is a mixture of (LiBH)<sub>2</sub>·AB and LiBH·AB phases. To gain insight into the formation of the new LiBH AB phase, we further examined the phase evolution in the milling process of the 1:1 LiBH<sub>4</sub>/AB sample. As shown in Fig. 2, the XRD pattern of the post-milled LiBH<sub>4</sub>/AB sample for 0.5 h showed the formation of (LiBH)<sub>2</sub>·AB, instead of the expected LiBH·AB



Fig. 1 – XRD patterns of the post-milled xLiBH<sub>4</sub>/AB samples (x = 0.5-2).

phase. But after 1 h milling, the LiBH·AB phase was clearly detected and meanwhile the peak intensity of the 2LiBH·AB and AB phases became weakened. Upon extending the milling time to 3 h, the sample was predominantly composed of the LiBH·AB phase together with a small amount of AB residual. These observations clearly indicate that the formation of LiBH·AB undergoes a stepwise phase transition process, wherein the (LiBH)<sub>2</sub>·AB phase serves as an intermediate.

Major peaks in the XRD pattern of 1:1 LiBH<sub>4</sub>/AB can be indexed using a monoclinic unit cell (P2<sub>1</sub>, No. 4) with lattice parameters of a = 14.3131 (11) Å, b = 4.3634 (5) Å, c = 15.3500(13) Å, and  $\beta = 90.325(11)^\circ$ . The crystal structure was first partially solved using the direct space method. Due to the relatively large unit cell and the uncertain H and Li positions from laboratory X-ray data, First-principles molecular dynamics simulated annealing were then performed to help determine the BH<sub>4</sub> and NH<sub>3</sub>BH<sub>3</sub> configurations with the lowest energy and the positions of light-weight Li atoms. The



Fig. 2 – XRD patterns of the post-milled 1:1 LiBH<sub>4</sub>/AB sample for a period ranging from 0.5 to 3 h.

stoichiometry derived from the determined crystal structure is LiBH<sub>4</sub>·NH<sub>3</sub>BH<sub>3</sub>. Detailed crystallographic data are listed in Table S1 in the Supporting Information, and the Rietveld fit to the XRD pattern on the DFT optimized structural model is shown in Figure S1 in the Supporting Information. The reasonably good fit to the data with agreement factors of  $R_{wp} = 0.0665$  and  $R_p = 0.0449$  strongly supported the validity of our determined structure model. The fully relaxed structure of LiBH·AB is illustrated in Fig. 3 and is used in the bond length discussion below.

A noticeable feature of the new LiBH AB structure is that LiBH<sub>4</sub> components gather into columns running along b direction (Fig. 3). This is remarkably different from the previous reported (LiBH)<sub>2</sub>·AB and CaBH·2AB, where the borohydride components were sandwiched by AB component layers. Both borohydrides and AB spread out in twodimensional (2D) layers, and retain certain structural similarities to the particular planes of the bulk parent materials [34]. However, in LiBH·AB, columns of LiBH<sub>4</sub> component are separated by AB molecules, and thus loses its structural likeness to the bulk LiBH<sub>4</sub>. In such an arrangement, Li cation strongly deviates from the center of its usual coordination tetrahedron to the center of one of the triangular faces, and adopts trigonal-planar coordination. Each Li is surrounded either by 3BH<sub>4</sub><sup>-</sup> or 2BH<sub>4</sub><sup>-</sup>/1NH<sub>3</sub>BH<sub>3</sub> groups. Such distortion in Li coordination causes notable changes in its interactions with nearby anions. The distances between Li and B are 2.22–2.81Å (see Table S2, Supporting information), within the range of those in other Li-complex hydrides. While the distances between Li and the hydridic H in NH<sub>3</sub>BH<sub>3</sub> group are 1.78-2.07 Å, significantly shorter than those in (LiBH)<sub>2</sub>·AB (2.08–2.32 Å) [34], indicating considerable interactions between Li<sup>+</sup> and AB molecules.

LiBH·AB contains oppositely charged  $H^{\delta-}$  (in  $BH_4^-$  and hydridic H in AB) and  $H^{\delta+}$  (protonic H in AB). It would be interesting to check for the presence of dihydrogen bonding as addressed in other B–N hydrogenous compounds. From the crystal structure, all protonic H's in AB have short separations, in a range of 1.85–2.31 Å, to the adjacent  $BH_4^-$ , indicating rather strong dihydrogen bonding between  $BH_4^-$  and AB. The BH<sup>...</sup>HN distances for constituting a dihydrogen bond are 1.86–2.39 Å between AB molecules. Therefore, in contrast to (LiBH)<sub>2</sub>·AB, where little dihydrogen bonding was observed in AB layers, strong BH<sup>...</sup>HN interactions are present throughout the entire LiBH·AB crystal structure. Such interatomic BH<sup>...</sup>HN dihydrogen bonding networks and the strong interactions between Li<sup>+</sup> and its surrounding ligands should play an important role in cohesion and structural stability.

#### 3.2. Decomposition behavior of LiBH<sub>4</sub>·NH<sub>3</sub>BH<sub>3</sub>

The TPD profile of the LiBH·AB sample, as given in Fig. 4, shows a distinct three-step decomposition feature. Ignoring the error arising upon the evolution of volatile byproducts, LiBH·AB totally released 4.1 equiv. of H<sub>2</sub>, corresponding to 15.7 wt%, upon heating to 450 °C. A parallel TG/DSC/MS analysis provides further information about the phase transition and decomposition behavior of the LiBH·AB sample. As shown in Fig. 5, the thermal decomposition of LiBH·AB is preceded by two endothermic events which occur with no





Fig. 3 – a) Crystal structure of LiBH AB viewed in (010) direction. Li, B, N, and H atoms are represented by yellow, green, blue, and white spheres, respectively. The  $BH_4^-$  ions are shown in green tetrahedra. b) Trigonal-planar coordination arrangements of Li atoms in LiBH AB. c) Schematic arrangement of LiBH<sub>4</sub> and AB components in the crystal structure (viewed in (010) direction): LiBH<sub>4</sub> components gather into columns along b direction (highlighted in light blue regions) separated by the surrounding AB molecules (highlighted in orange/black dash lines). Black rectangle indicates the unit cell of LiBH AB. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

appreciable weight loss. The XRD (Fig. 6A) and FTIR (Fig. 7A) results together with the designed experiment (Figure S2, Supporting information) suggest that the endothermic event at 54 °C corresponds to the disproportionation reaction of LiBH·AB following Eq. (1), which results in the formation of (LiBH)<sub>2</sub>·AB and AB phases. Here, the invisibility of AB in the XRD analysis indicates its amorphous nature. Also, it should be noted that this transition may have largely ironed out the



Fig. 4 – TPD profiles of LiBH AB, AB and LiBH<sub>4</sub> samples. The ramping rate was 2  $^{\circ}$ C min<sup>-1</sup>. The temperature profile was given as a dash-dot line.

structure difference between LiBH·AB and (LiBH)<sub>2</sub>·AB phases, which may explain why the two lithium borohydride ammonia borane compounds exhibit similar dehydrogenation behaviors (see below). In an effort to ascertain the nature of the second endothermic peak at ~75 °C, we examined the post-heated sample at ~100 °C and found that the sample should have been molten. This finding suggests that a eutectic melting of (LiBH)<sub>2</sub>·AB and AB occurs at lower temperature than their melting points (85 °C for (LiBH)<sub>2</sub>·AB and 105 °C for AB, Figure S2).

 $2\text{LiBH}_4 \cdot \text{NH}_3\text{BH}_3 \rightarrow (\text{LiBH}_4)_2 \cdot \text{NH}_3\text{BH}_3 + \text{NH}_3\text{BH}_3$ (1)

The first decomposition step of the LiBH·AB sample should be ascribed to the thermolysis of the AB component phase. This is not only supported by the observation that LiBH·AB releases several typical volatile byproducts of AB (i.e., NH<sub>3</sub>, B<sub>2</sub>H<sub>6</sub>, NH<sub>2</sub>BH<sub>2</sub>, c-(BHNH)<sub>3</sub>) (Fig. 5), but also evidenced by the phase/bonding



Fig. 5 – TG/DSC profiles and the synchronous MS results of the LiBH AB sample upon heating to 450 °C at a ramping rate of 2 °C min<sup>-1</sup>. Assignments of the MS signals: m/e = 2 (H<sub>2</sub>), m/e = 17 (NH<sub>3</sub>), m/e = 26 (B<sub>2</sub>H<sub>6</sub>), m/e = 29 (NH<sub>2</sub>BH<sub>2</sub>), m/ e = 80 (c- (NHBH)<sub>3</sub>).



Fig. 6 – XRD patterns of the LiBH AB samples that were collected at different stages: prior to H<sub>2</sub> release (A); after completing the first (B), the second (C), and the third dehydrogenation step (D). (A, B, C, and D as designated in Fig. 4). The two apparent humps at  $2\theta < 30^{\circ}$  come from the polymeric tape that was used for minimizing the H<sub>2</sub>O/O<sub>2</sub> contamination.

structure analyses results. As shown in Fig. 6B, XRD analysis of the decomposition products (collected at point B in Fig. 4) identified the formation of crystalline LiBH<sub>4</sub> phase. The parallel FTIR analysis (Fig. 7B) clearly showed the characteristic bands of LiBH<sub>4</sub> and polyborazylene (PB), a decomposition product of AB



Fig. 7 – FTIR spectra of the LiBH AB samples that were collected at different stages: prior to  $H_2$  release (A); after completing the first (B), the second (C), and the third dehydrogenation step (D) (A, B, C, and D as designated in Fig. 4) (E) After rehydrogenation. For comparison, the FTIR spectra of AB after dehydrogenation at 450 °C (PB) and LiBH<sub>4</sub> were also presented. The arrow-indicated bands should be assigned to O–H vibrations, which originate from the moisture contamination during the measurements.

after releasing over two equiv. of H<sub>2</sub> [43]. In line with this qualitative analysis, the TPD measurement determined a yield of 2.4 equiv. of H<sub>2</sub> upon heating the sample to 200 °C. On the basis of these results, the H<sub>2</sub> release at the first decomposition step can be described by Eq. (2).

 $(LiBH_4)_2 \cdot NH_3BH_3 + NH_3BH_3 \rightarrow 2LiBH_4 + 2BNH_{1.2} + 4.8H_2 \uparrow$  (2)

The second decomposition step of the LiBH · AB sample occurs at a narrow temperature range of 260-280 °C, yielding ~0.6 equiv. of H<sub>2</sub> without undesired gaseous impurities. A combination of XRD (Fig. 6C) and FTIR (Fig. 7C) analyses indicates that the dehydrogenation should mainly arise from the thermolysis of PB. This is an interesting finding as the parallel TPD measurement clearly showed the stability of neat PB at temperatures up to 450 °C (Fig. 4). Evidently, the dramatically improved dehydrogenation property of PB should be ascribed to the presence of LiBH<sub>4</sub>. To gain insight into this phenomenon, we first conducted a control experiment on the relevant AB/NaBH<sub>4</sub> sample. No new phases were observed during the ball milling of AB/NaBH<sub>4</sub> mixture. However, it was found that NaBH<sub>4</sub> additive can also effectively promote H<sub>2</sub> release from PB (Figure S3, Supporting information). But in comparison with the PB/LiBH<sub>4</sub> mixture, the H<sub>2</sub> release from the PB/NaBH<sub>4</sub> sample occurs at higher temperature (320 °C) and shows less exothermicity. These findings suggest that both BH<sub>4</sub><sup>-</sup> and metal cations might have played crucial roles in promoting H<sub>2</sub> release from PB. In another control experiment, we remeasured the post-heated sample at 300 °C by DSC to determine the phase transition enthalpy of LiBH<sub>4</sub> and use it as a measure to evaluate the consumption of LiBH<sub>4</sub>. Our study found that, for the pure LiBH<sub>4</sub>, the slight decomposition upon melting causes a decreased phase transition enthalpy by around 9%. But in the post-heated PB/LiBH<sub>4</sub> sample at 300 °C, we observed a ~18% reduction of the phase transition enthalpy (Figure S4, Supporting information). The increased consumption of LiBH<sub>4</sub> is indicative of its partial participation in the second decomposition step. But fundamentally, the promoting effect of metals borohydrides might be understood from the provision of polar environment, wherein the hydridic H in  $BH_4^-$  may interact with the surrounding protonic H in PB and thereby causes its destabilization. In addition, the presence of metal cations may help to create lowbarrier pathways for hydrogen release from PB. In this regard, detailed study is still required to further the mechanistic understanding. Given the partial participation of LiBH<sub>4</sub>, the second dehydrogenation step should be expressed by Eq. (3). Here, the conservative assignment of the solid residue from PB as BNH<sub>v</sub> was made on the basis of the determined H<sub>2</sub> amount, and supported by the FTIR result that shows a broad band feature at 1380  $\text{cm}^{-1}$  (Fig. 7C).

 $LiBH_4 + BNH_{1.2} \rightarrow 0.82LiBH_4 + 0.18LiBH_{4-x} + BNH_y + 0.6H_2 \uparrow$  (3)

The third decomposition step of the LiBH·AB sample commences at ~400 °C, yielding ~1.1 equiv. of H<sub>2</sub>. According to the XRD (Fig. 6D) and FTIR (Fig. 7D) results, this step should be primarily ascribed to the dehydrogenation of LiBH<sub>4</sub> component phase, generating LiH and amorphous B as the major products. But the detection of weak B–H bands at 2418 and 2180 cm<sup>-1</sup> suggests that a small amount of H remains

trapped in the form of borohydride (donated as  $\text{LiBH}_{m}$ ). In addition, it was noticed that the B–N bands at 1380 and 800 cm<sup>-1</sup> become more strengthened, suggesting the liberation of the residual H from PB [44]. On the basis of these results, the third dehydrogenation step should be described by Eq. (4).

$$0.82\text{LiBH}_4 + 0.18\text{LiBH}_{4-x} + BNH_y \rightarrow (1-z)\text{LiH} + (1-z)B$$
  
+ zLiBH<sub>m</sub> + BN + 1.1H<sub>2</sub> \(\phi \) (4)

The aforementioned study has elucidated the phase transition and the stepwise decomposition behaviors of the new LiBH·AB compound. In a general view, the two component phases largely retain their intrinsic decomposition properties but with an important exception: LiBH<sub>4</sub> proved to be highly effective for promoting the release of the last residual hydrogen from AB, resulting in the formation of *h*-BN at relatively moderate temperatures. The formation of stable BN is not thermodynamically propitious for regeneration of the AB component, whereas it has favorable impact on the rehydrogenation of the LiBH<sub>4</sub> component phase.

#### 3.3. Reversible dehydrogenation of LiBH<sub>4</sub>·NH<sub>3</sub>BH<sub>3</sub>

The LiBH AB sample exhibits improved reversible dehydrogenation properties in comparison with the component phases. According to the TPD result, the dehydrogenated sample could reabsorb 3.4 wt% of hydrogen at 400 °C under an initial hydrogen pressure of 10 MPa. FTIR analysis of the recharged sample (Fig. 7E) clearly identified the characteristic bands of LiBH<sub>4</sub> and a new B–H band at 2478 cm<sup>-1</sup>, which might be assigned to the  $B_{12}H_{12}^{2-}$  species [45]. Meanwhile, the characteristic bands of h-BN at 1380 and 800 cm<sup>-1</sup> were observed to persist well and no N-H band was formed. These results indicate that only the LiBH<sub>4</sub> component in the LiBH · AB sample was restored, with a normalized capacity of 8.2 wt%. This value nearly doubles the recharged hydrogen amount in the neat LiBH<sub>4</sub> sample under identical rehydrogenation conditions. Furthermore, the restored LiBH<sub>4</sub> component in the LiBH AB sample shows improved dehydrogenation kinetics relative to neat LiBH<sub>4</sub>. As seen in Fig. 8, the recharged LiBH · AB sample starts to desorb hydrogen from  $\sim$  70 °C, which is over 200 °C lower than the threshold temperature for  $H_2$  release from the recharged LiBH<sub>4</sub> sample. Consistently, the isothermal volumetric measurements demonstrated the increased extent and rate of H<sub>2</sub> release from the recharged LiBH AB sample relative to the recharged LiBH<sub>4</sub> sample (Figure S5, Supporting information). Similar but less pronounced property improvements were observed for the LiBH<sub>4</sub> component phase in (LiBH)<sub>2</sub>·AB [34].

Presumably, the remarkable property improvements of the LiBH<sub>4</sub> component phase should be associated with the *in situ* formation of h-BN in the decomposition process of the LiBH·AB sample. According to the XRD result (Fig. 6B), LiBH<sub>4</sub> crystalline phase will precipitate from the LiBH·AB sample at the first dehydrogenation step. But the melting of LiBH<sub>4</sub> prior to its decomposition may offer chance for phase redistribution, resulting in a highly homogeneous mixing of the BN product into the molten LiBH<sub>4</sub>. After the final dehydrogenation step, the resulting LiH, B and LiBH<sub>m</sub> products will be



Fig. 8 – Comparison of the TPD profiles of the recharged LiBH AB sample (hydrogen capacity normalized to LiBH AB is denoted by red line and hydrogen capacity normalized to LiBH<sub>4</sub> by blue line), and the recharged pure LiBH<sub>4</sub> (black line). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

confined within the BN "network". As a consequence of the minimized composition segregation, reduced solid-state diffusion distance and prevented particle agglomeration/sintering, the LiBH<sub>4</sub> component in the LiBH·AB sample exhibits markedly improved reversible dehydrogenation property [46,47]. In this regard, the LiBH·AB sample may serve as a prototype for developing other novel nanoscaffolded hydrogen storage materials.

#### 4. Conclusions

A new lithium borohydride ammonia borane complex, LiBH<sub>4</sub>·NH<sub>3</sub>BH<sub>3</sub>, was synthesized using mechanochemical method and its structure was successfully determined using combined XRD and first-principles calculations. Differing from its analogues (LiBH<sub>4</sub>)<sub>2</sub>·NH<sub>3</sub>BH<sub>3</sub> and Ca(BH<sub>4</sub>)<sub>2</sub>·2NH<sub>3</sub>BH<sub>3</sub>, which adopt orthorhombic layered structures, LiBH<sub>4</sub>·NH<sub>3</sub>BH<sub>3</sub> crystallizes in a monoclinic structure, in which the LiBH<sub>4</sub> components gather into columns running along the b direction. LiBH<sub>4</sub>·NH<sub>3</sub>BH<sub>3</sub> undergoes a disproportionation reaction at ~54  $^{\circ}$ C and a distinct three-step decomposition at a temperature range of 100–450 °C, totally delivering  $\sim$  15.7 wt % of hydrogen. Due primarily to the weak interaction between the constituent molecules, LiBH<sub>4</sub>·NH<sub>3</sub>BH<sub>3</sub> shows essentially similar decomposition behaviors of the constituent phases. But meanwhile, our study clearly showed that LiBH<sub>4</sub> is highly effective for promoting the release of the last residual H from AB, resulting in the formation of *h*-BN at relatively moderate temperatures. Owing to the in situ formation of h-BN, the LiBH<sub>4</sub> component phase exhibits significant improvements on reversibility. Our study, in combination with the previous studies, shows the compositional and structural diversity of metal borohydride ammonia borane complexes. To develop these new compounds as promising hydrogen storage

materials, novel strategies for properly tuning the noncovalent interactions between component molecules are still required.

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# Appendix A. Supplementary material

Supplementary data related to this article can be found online at: doi:10.1016/j.ijhydene.2012.04.049.

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