

Supporting Information

Ammine aluminum borohydrides: an appealing system releasing over 12 wt.% pure H₂ under moderate temperature

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1. Experimental

General considerations:

The source materials were obtained commercially, LiBH₄ 95% (Sigma-Aldrich, USA); AlCl₃ 99.999% and NH₃ (Alfa Aesar, China); Pb(NO₃)₂, hexamine, hydrochloric acid, trans-1,2-Diaminocyclohexane-N,N,N',N'-tetraacetic acid monohydrate (DCTA), xylenol orange and NaOH (analytical pure, Aladdin, China). NH₃ was purified by soda lime when using. Other reagents were used without further purification. All handling except ammonia related procedures were conducted under anaerobic and anhydrous condition by Schlenk techniques and glove box filled with argon.

Complexometric titration was used for the determination of Al content in the product.^{s1} Around 0.0300g precisely weighted product and 20mL aliquot of 0.02M DCTA solution were added into 250-mL Erlenmeyer flask. If any powder remains on the wall, wash it down with a small amount of demonized water. Then diluted hydrochloric acid was dripped into the solution until it didn't bubble. After standing for 0.5h, 10mL hexamine-hydrochloric acid buffer solution was added to the flask to get the sample solution. Then, the sample solution was back-titrated with standardized 0.02M lead solution using xylenol orange indicator. Repeated the titration twice. The Al content was calculated based on this volumetric analysis.

Thermal property measurements were performed by thermogravimetry (TG/ DTA, STA 409C) /mass spectrometer (MS, QMS 403) in argon glove box. Meanwhile, desorption properties for some samples were also evaluated using Sievert's volumetric methods with heating rate of 5 °C/min under argon with a pressure of 1 bar. Differential scanning calorimetry (DSC) was performed simultaneously on a Netzsch STA 409 PC, Germany, with highly pure Ar as the purge gas.

High-resolution X-ray powder diffraction data were collected on the Powder Diffraction Beamline, Australian Synchrotron by using a Mythen detector. For phase identification and structure determination, samples were loaded into pre-dried 0.7 mm glass capillary tubes inside the argon atmosphere glove box and sealed with vacuum grease for X-ray diffraction measurements.

FT-IR (Magna-IR 550 II, Nicolet) analyses were conducted to determine the chemical bond. Samples were pressed with KBr then loaded in sealed chamber filled with argon for the measurement.

Solid-state MAS NMR spectra were measured using a Bruker Avance 300 MHz spectrometer, employing a boron-free Bruker 4 mm CPMAS probe. The resonance frequency was 96.30 MHz for the ¹¹B nucleus. The powder samples collected after decomposition reaction was spun at 5 kHz, using 4mm ZrO₂ rotors filled up in purified argon atmosphere glove boxes. The one-dimensional (1D) ¹¹B MAS NMR spectra were acquired after a 1 μm single pulse.

The contents of H₂ and NH₃, or H₂ and B₂H₆ in the emission gas were determined using gravimetric and volumetric results. Firstly, the mass percent (W_p) and mole per gram (M_p) of gas released from the sample were calculated from the weights of the samples and volumetric results. For the product that mainly released H₂ and NH₃, the mole proportion of H₂ (C_{H2}) and NH₃ (C_{NH3}) can be calculated from equation (1) and (2). For the product that mainly released H₂ and B₂H₆ the mole proportion of H₂ (C_{H2}) and B₂H₆ (C_{B2H6}) can be calculated from equations (3) and (4).

$$C_{H_2} + C_{NH_3} = 1 \quad (1)$$

$$(C_{H_2} * 2.02 + C_{NH_3} * 17.03) * M_p = W_p \quad (2)$$

$$C_{H_2} + C_{B_2H_6} = 1 \quad (3)$$

$$(C_{H_2} * 2.02 + C_{B_2H_6} * 27.67) * M_p = W_p \quad (4)$$

Synthesis of ammonia complexes of LiBH₄ and their composites:

1) Synthesis of ammine aluminum borohydrides (Al(BH₄)₃·xNH₃, x = 5, 4, 3, 2)

The experimental set-up for the preparation of ammine aluminum borohydrides (Al(BH₄)₃·xNH₃, x = 5, 4, 3, 2) is schematically depicted in Fig. S1(a). The Al(BH₄)₃ source and the Al(BH₄)₃·6NH₃ are placed separately in the reaction tube. To produce Al(BH₄)₃·xNH₃, Al(BH₄)₃ emission was facilitated by heating its source to various temperatures (normally 20-40 °C), once it diffused to the Al(BH₄)₃·6NH₃. The increasing weight of the product was monitored by weighing reactor B shown in Fig. S1(a) during the experiment for process control, which gave the formation of the targeted ammine aluminum borohydrides with various NH₃ units. Ammine borohydrides with different coordination numbers were synthesized by allowing Al(BH₄)₃·6NH₃ to remain in contact with the Al(BH₄)₃ vapor until it reach the certain weight. Then, the product was mechanically milled for 60 min (planetary QM-1SP2) in argon using stainless steel spheres with a ball-to-powder ratio (BPR) of 30:1 to produce Al(BH₄)₃·xNH₃ with more uniform components. Furthermore, the Al contents of the products determined through complexometric titration just confirmed their coordination numbers calculated based on the weighing method, suggesting the feasibility of our process to produce Al(BH₄)₃·xNH₃, x < 6.

Fig. S1(b) shows the average coordination number of the product during the experiment at various temperatures. Higher operating temperature resulted in faster reduction of the coordination number, since the formation of Al(BH₄)₃ was accelerated and its vapor concentration was therefore increased. However, a temperature higher than 60 °C can not be used because a layer of sticky ammine borohydride with low coordination number will form due to a rapid reaction of Al(BH₄)₃ with the surface of the Al(BH₄)₃·6NH₃, making it difficult to handle in the following ball-milling step. The Al(BH₄)₃·xNH₃, x = 5, 4, 3, 2 products were all white powdery solids. High-resolution synchrotron X-ray diffraction revealed that the diffraction patterns of Al(BH₄)₃·xNH₃, x = 5, 4, 3, 2 are different from those of their starting material, as well as from each other, thereby confirming the reaction of Al(BH₄)₃ with Al(BH₄)₃·6NH₃ (Fig. S1(c)). Among these synthesized Al(BH₄)₃·xNH₃ compounds, the Al(BH₄)₃·4NH₃ phase is very consistent with previously reported results (Table S1),^{S2} clearly suggesting the feasibility of the process, which may be a general strategy for synthesis of coordination complexes, especially unstable ones with different coordination numbers. With respect to Al(BH₄)₃·5NH₃ and Al(BH₄)₃·3NH₃, it is suggested that they might be the mixtures of Al(BH₄)₃·xNH₃ (x = 6, 4 and 2), as suggested in a previous report.

2) Preparation of Al(BH₄)₃·xNH₃-LiBH₄ composite

Approximately 0.5 g mixtures of Al(BH₄)₃·xNH₃-nLiBH₄ (x = 5, 4, 3 and n = 1, 2) were mechanically milled for 60 min (planetary QM-1SP2) in argon using stainless steel spheres with a ball-to-powder ratio (BPR) of 30:1 to produce Al(BH₄)₃·xNH₃/LiBH₄ composites. The milling process was carried out by alternating 6 min of milling and 6 min of rest in order to avoid increasing the temperature of the powders in the vial. High-resolution synchrotron X-ray diffraction revealed that the diffraction

patterns of AAB/LiBH₄ composites are different from those of their starting material, as well as from each other, thereby confirming the reaction of AAB with LiBH₄ to produce new compounds (Fig. S2).

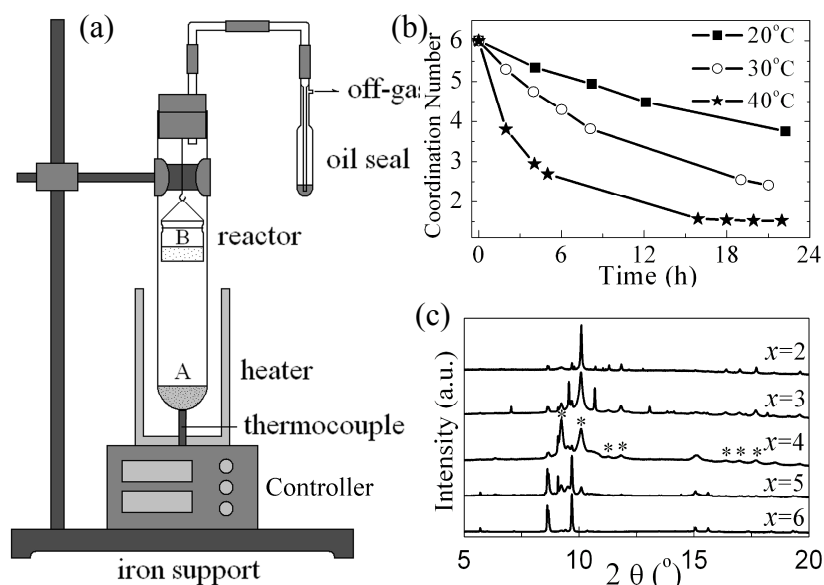
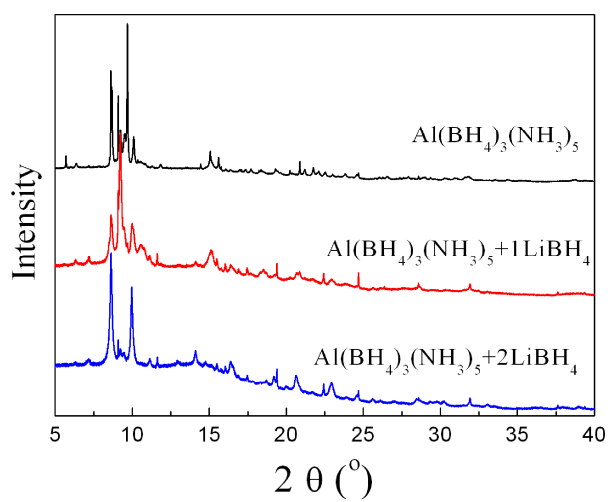


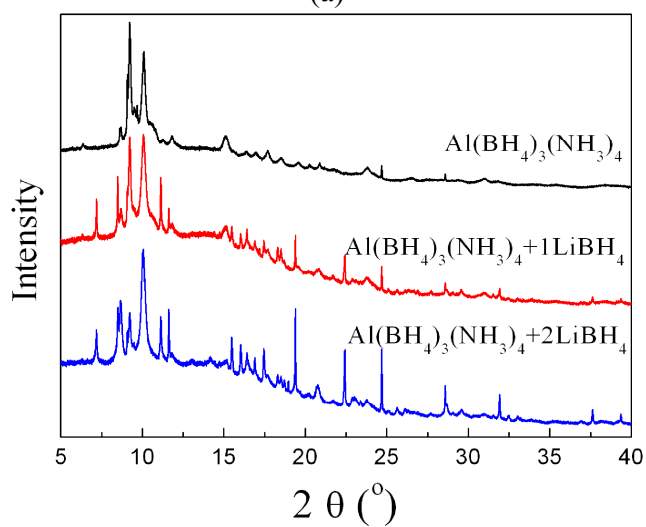
Figure S1 a) Apparatus for the preparation of ammine aluminum borohydrides: A, Al(BH₄)₃ source produced by a reaction of AlCl₃ with LiBH₄, B, solid Al(BH₄)₃·6NH₃; b) Calculated average coordination number of the product during the reaction; c) High-resolution synchrotron X-ray diffraction results for Al(BH₄)₃·xNH₃, x = 6, 5, 4, 3, 2 samples; asterisks (*) are peaks assigned to Al(BH₄)₃·4NH₃ phase from ref. s2.

Table S1. 2θ information of Al(BH₄)₃·4NH₃ from reference s2 and our study. The wavelength for the XRD data of Al(BH₄)₃·4NH₃ was changed to the same as reference s2 (1.5418 Å).

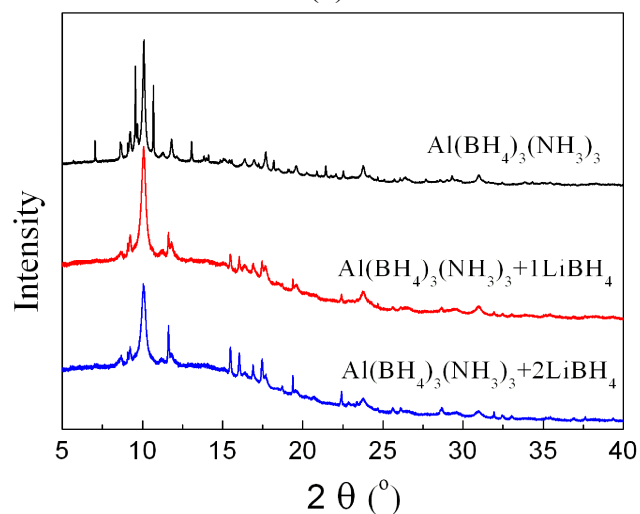
Al(BH ₄) ₃ (NH ₃) ₄	Our study / °	Reference ^[S2] / °
1	14.28	14.45
2	15.61	15.80
3	17.45	17.70
4	18.26	18.52
5	25.45	25.67
6	26.34	26.69
7	27.51	27.70
8	28.55	28.99
9	30.47	30.62
10	38.32	38.13
11	41.50	41.62



(a)



(b)



(c)

Figure S2. High-resolution synchrotron X-ray diffraction results for $\text{Al}(\text{BH}_4)_3 \cdot x\text{NH}_3 \cdot n\text{LiBH}_4$ ($x=5$ (a), 4 (b), 3(c) and $n=1, 2$) composites.

2. Results for ammine aluminum borohydrides and their composites

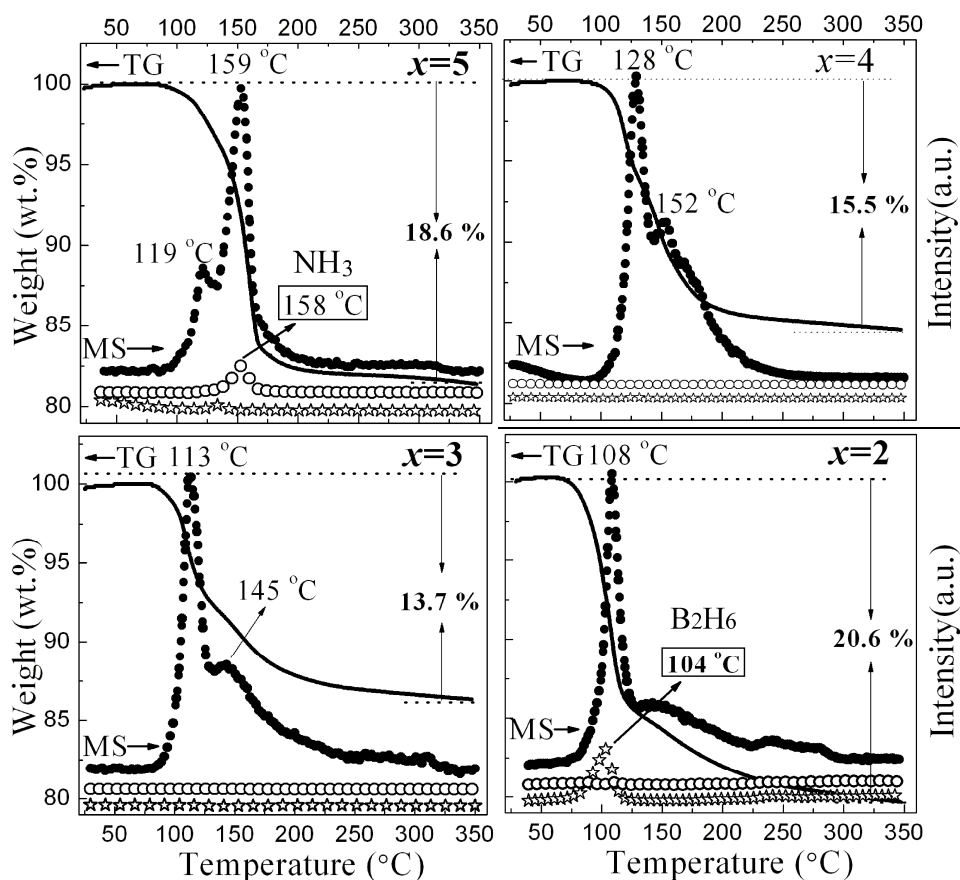


Figure S3 TG (solid line) and MS (symbols) profiles of $\text{Al}(\text{BH}_4)_3 \cdot x\text{NH}_3$ ($x = 5, 4, 3, 2$), with a heating rate of 5°C min^{-1} in argon. \bullet H_2 , $m/z = 2$, \circ NH_3 , $m/z = 16$, \star B_2H_6 , $m/z = 26$.

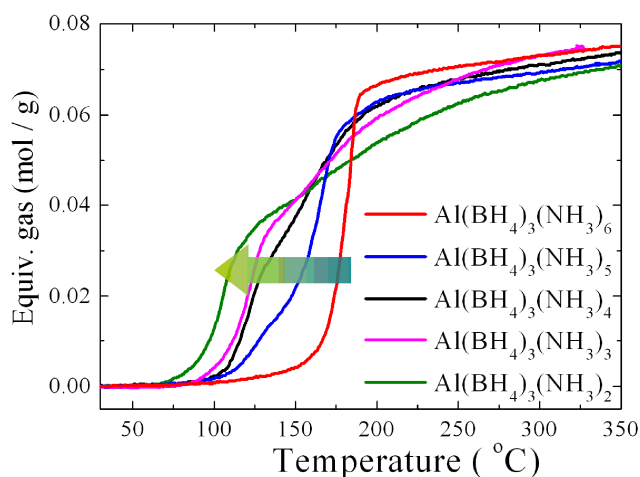


Figure S4. TPD profiles of $\text{Al}(\text{BH}_4)_3 \cdot x\text{NH}_3$ ($x = 6, 5, 4, 3, 2$) with a heating rate of 5°C min^{-1} in argon.

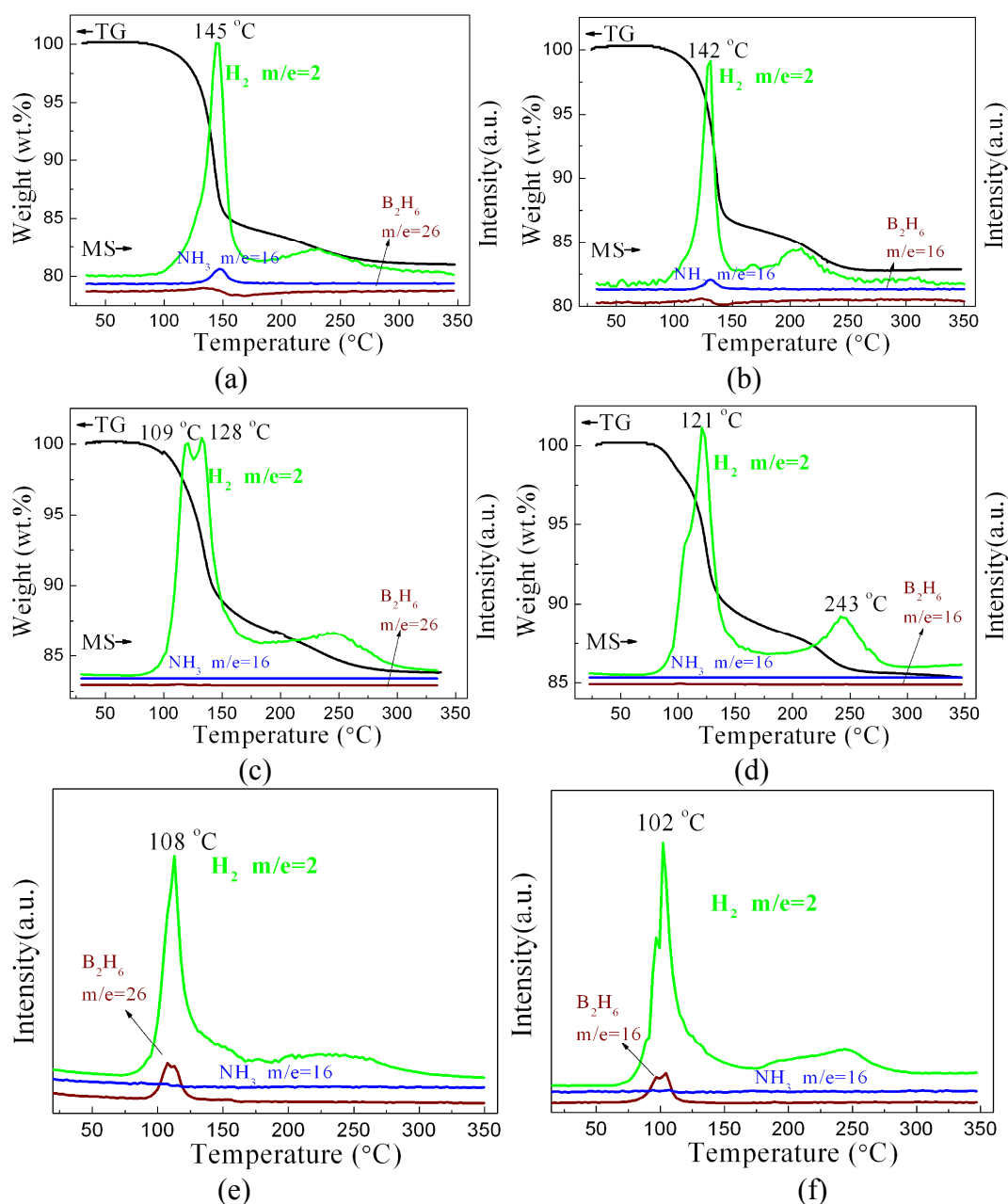


Figure S5. TG (black line) and MS (color line) profiles of $\text{Al}(\text{BH}_4)_3 \cdot 5\text{NH}_3 \cdot n\text{LiBH}_4$ composites ($n=1$ (a), $n=2$ (b)); $\text{Al}(\text{BH}_4)_3 \cdot 4\text{NH}_3 \cdot n\text{LiBH}_4$ composites ($n=1$ (c), $n=2$ (d)) and $\text{Al}(\text{BH}_4)_3 \cdot 3\text{NH}_3 \cdot n\text{LiBH}_4$ composites ($n=1$ (e), $n=2$ (f)) with a heating rate of $5\text{ }^\circ\text{C min}^{-1}$ in argon. Green line H_2 $m/z=2$, blue line NH_3 $m/z=16$, wine line B_2H_6 $m/z=26$.

Dehydrogenation improvements relative to that of the monometallic ammine borohydrides were observed for the $\text{Al}(\text{BH}_4)_3 \cdot x\text{NH}_3 \cdot n\text{LiBH}_4$ ($x=5, 4, 3$ and $n=1, 2$) composites. But for $\text{Al}(\text{BH}_4)_3 \cdot 3\text{NH}_3 \cdot n\text{LiBH}_4$ ($n=1, 2$) composites, two unexpected drawbacks were introduced besides the expected reduction of onset dehydrogenation temperature. The two composites were found foamed upon dehydrogenation, resulting in unsatisfied quality of the TG analysis which were not provided here. Meanwhile, borane impurity was also observed for the two composites.

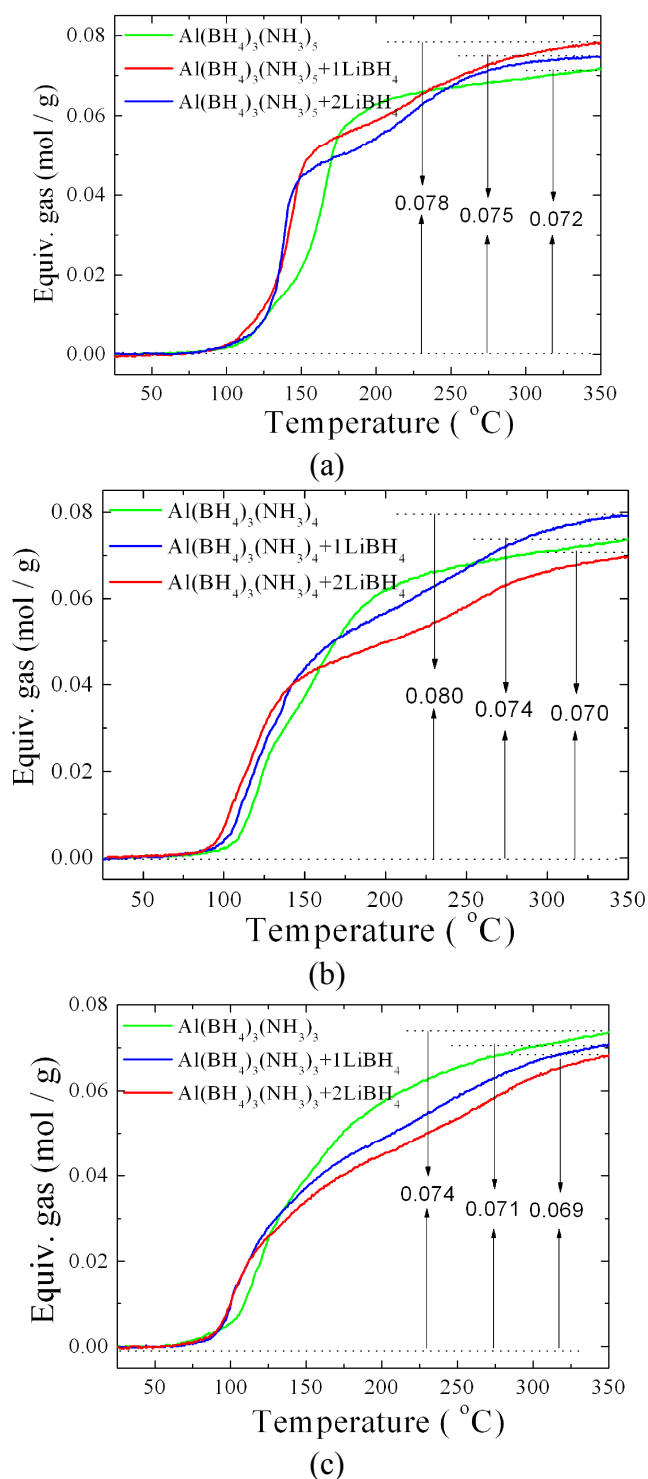


Figure S6. TPD profiles of $\text{Al}(\text{BH}_4)_3 \cdot x\text{NH}_3$ and their composites with LiBH_4 ((a), $x=5$; (b), $x=4$; (c), $x=3$) with a heating rate of $5\text{ }^\circ\text{C min}^{-1}$ in argon.

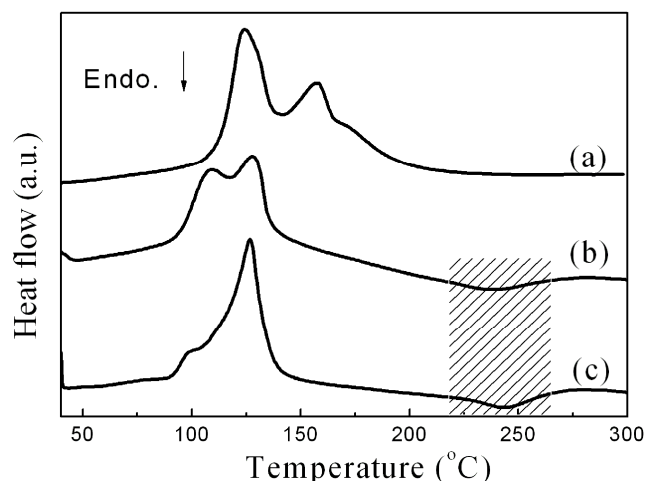


Figure S7. DSC curves from $\text{Al}(\text{BH}_4)_3 \cdot 4\text{NH}_3$ (a), $\text{Al}(\text{BH}_4)_3 \cdot 4\text{NH}_3 \cdot 1\text{LiBH}_4$ (b) and $\text{Al}(\text{BH}_4)_3 \cdot 4\text{NH}_3 \cdot 2\text{LiBH}_4$ (c) with a heating rate of $5\text{ }^\circ\text{C min}^{-1}$ in nitrogen.

The DSC curve indicates exothermic events below $200\text{ }^\circ\text{C}$ for all these samples, demonstrating that the main dehydrogenation steps of these samples are exothermic reactions, which is a big challenge for a direct rehydrogenation. However, interestingly, thermal effect reverse to endothermic was observed ranging from $220\text{--}260\text{ }^\circ\text{C}$ for $\text{Al}(\text{BH}_4)_3 \cdot 4\text{NH}_3/\text{LiBH}_4$ composites, indicating a thermodynamic feasibility for this step to a reversible hydrogen storage. Further investigation on the reversibility is on progress.

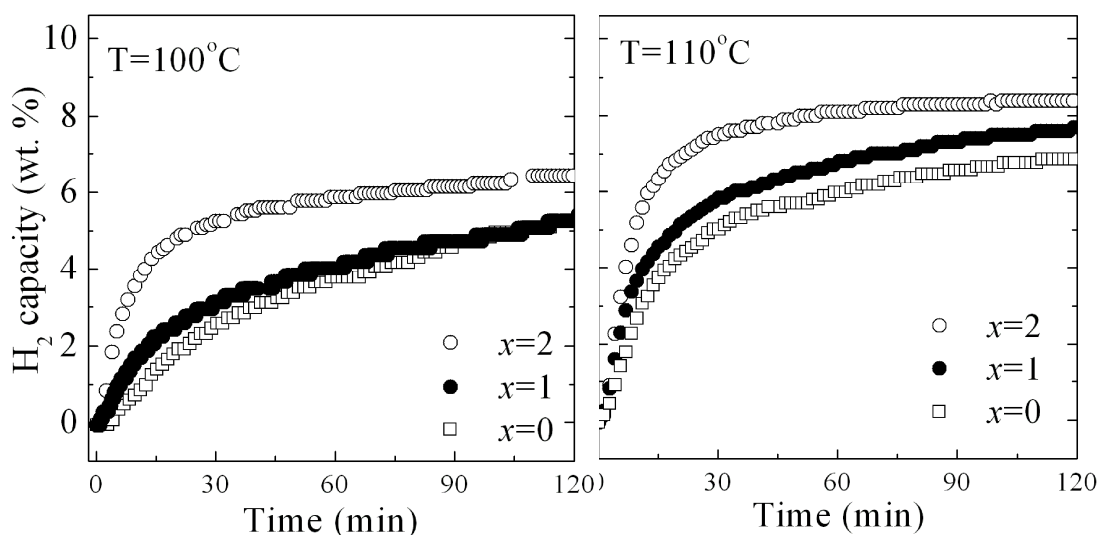


Figure S8 Isothermal TPD curves for the decomposition of $\text{Al}(\text{BH}_4)_3 \cdot 4\text{NH}_3 \cdot n\text{LiBH}_4$ ($n = 2, 1, 0$) within 2 h at 100 and 110 °C.

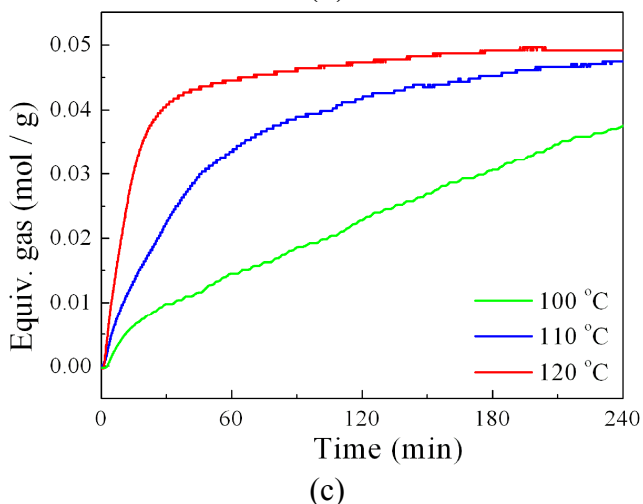
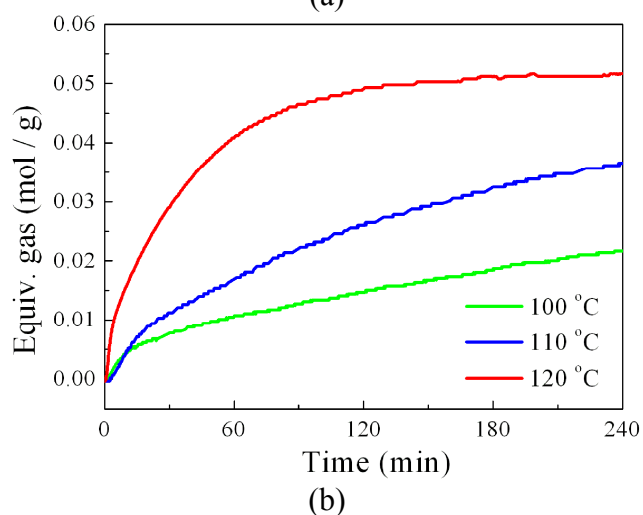
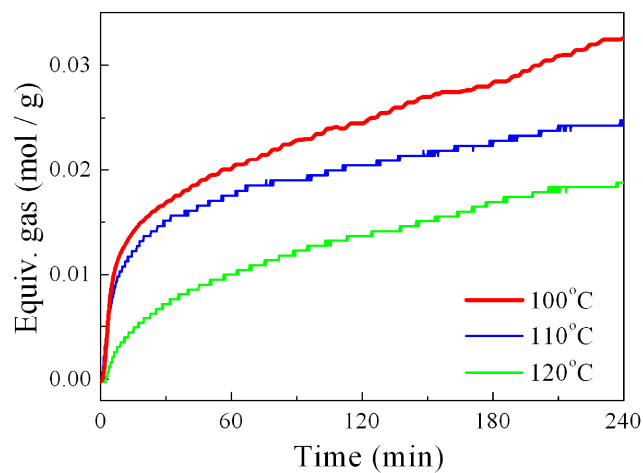
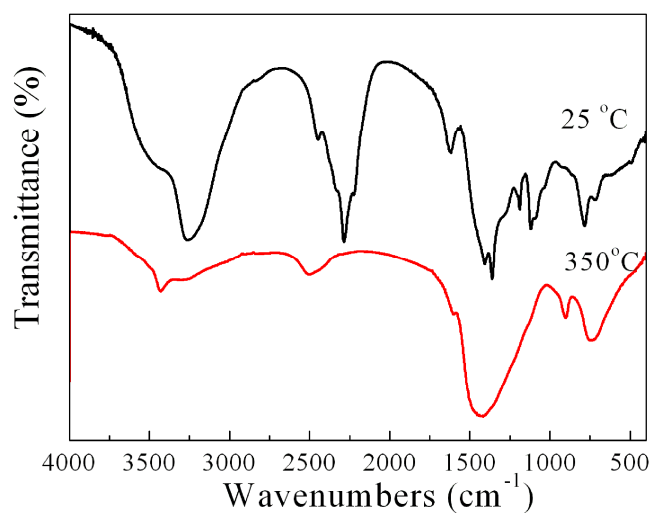
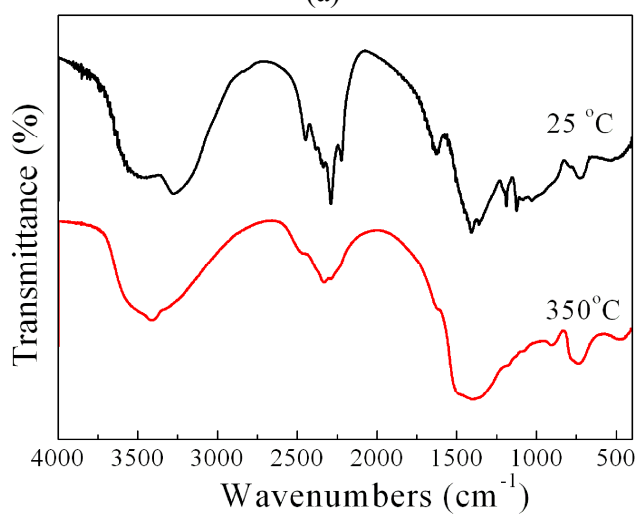


Figure S9. Isothermal TPD profiles of $\text{Al}(\text{BH}_4)_3 \cdot 5\text{NH}_3$ (a) and $\text{Al}(\text{BH}_4)_3 \cdot 5\text{NH}_3/\text{LiBH}_4$ composites with mole ratio of 1:1 (b) and 1:2 (c) in argon at 100, 110 and 120 °C.



(a)



(b)

Figure S10. FTIR spectra for (a) $\text{Al}(\text{BH}_4)_3 \cdot 4\text{NH}_3$ and (b) $\text{Li}_2\text{Al}(\text{BH}_4)_5 \cdot 4\text{NH}_3$ composite before and after dehydrogenation at 350 °C.

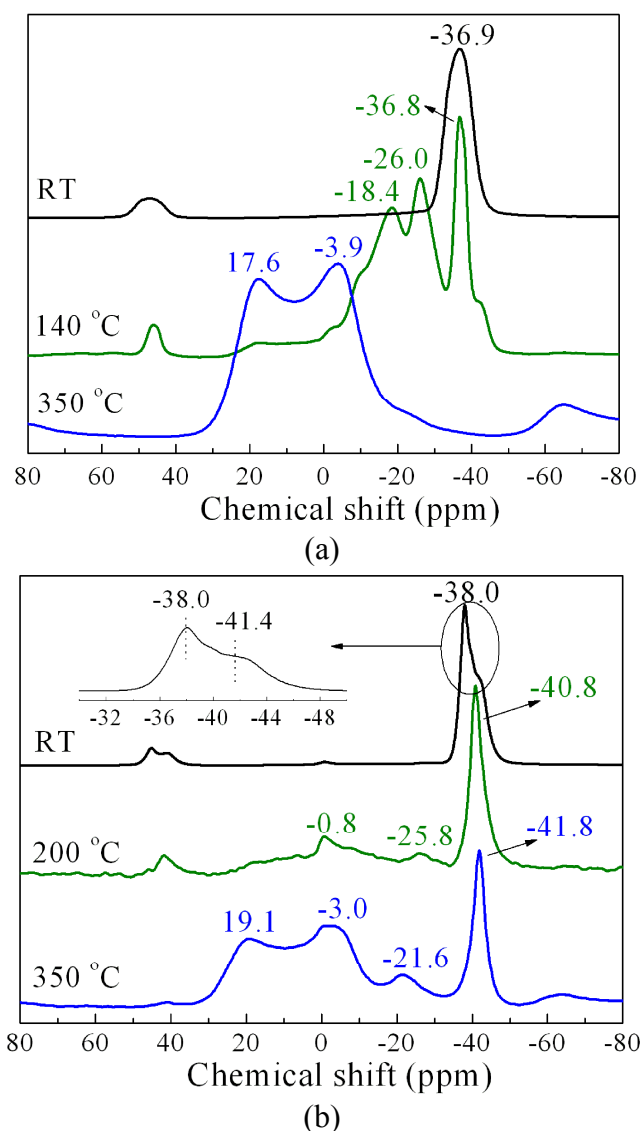


Figure S11. ^{11}B NMR results for (a) $\text{Al}(\text{BH}_4)_3 \cdot 4\text{NH}_3$ and (b) $\text{Li}_2\text{Al}(\text{BH}_4)_5 \cdot 4\text{NH}_3$ composite before and after heating to various temperatures.

$\text{Al}(\text{BH}_4)_3 \cdot 4\text{NH}_3$ has a similar single boron species at -36.9 ppm to that of $\text{Al}(\text{BH}_4)_3 \cdot 6\text{NH}_3$ (-36.7 ppm), indicating the assignment of this boron to the boron nucleus in the tetrahedral BH_4^- unit. On further heating $\text{Al}(\text{BH}_4)_3 \cdot 4\text{NH}_3$ to 140 °C, intensity reduction for the starting tetracoordinate B nucleus was observed and two other kinds of tetracoordinate B nucleus peaks at -18.4 and -26.0 ppm were present, suggesting partial consumption of $\text{Al}(\text{BH}_4)_3 \cdot 4\text{NH}_3$. After heat treatment at 350 °C, the disappearance of the peak ascribed to BH_4^- along with two ^{11}B resonances at 17.6 and -3.9 ppm was observed, suggesting the full involvement of BH_4^- in $\text{Al}(\text{BH}_4)_3 \cdot 4\text{NH}_3$ during the dehydrogenation, similar to that of $\text{Al}(\text{BH}_4)_3 \cdot 6\text{NH}_3$. In the case of $\text{Li}_2\text{Al}(\text{BH}_4)_5 \cdot 4\text{NH}_3$, an asymmetric resonance centered at -38.0 and -41.4 ppm were observed for the as-prepared sample, indicating two different B species as suggested in $\text{Li}_2\text{Al}(\text{BH}_4)_5 \cdot 6\text{NH}_3$. After heating to 300 °C, a tricoordinate B nucleus peaks at 19.1 and three kinds of tetracoordinate B nucleus peaks at -3.0 ppm, -21.6 and -41.8 ppm were observed,

suggesting partial involvement of the initial BH_4^- during the dehydrogenation, which may be due to the excessive supplement of BH_4^- as compared to the NH_3 groups.

References:

[s1] A. de Sousa, *Anal. Chim. Acta*, 1960, **22**, 522.

[s2] K. N. Semenenko, S. P. Shilkin and V. B. Polyakova, *Bulletin of the Academy of Sciences of the Ussr Division of Chemical Science*, 1978, **27**, 859.