A new dehydrogenation mechanism for reversible multicomponent borohydride systems—The role of Li–Mg alloys†

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A new dehydrogenation mechanism for $LiBH_4$–MgH_2 mixtures revealed that magnesium destabilised the $LiBH_4$ resulting in complete dehydrogenation of the borohydride phase and the formation of a Li–Mg alloy.

Using hydrogen as an energy carrier is an environment friendly approach that produces almost no local emission of pollutants from power generators such as fuel cells. However, for the last several decades the efficient and safe storage and transportation of hydrogen have been major concerns in the use of hydrogen as an energy carrier and there is significant interest in solid state hydrogen storage materials.[1,2] A design target for automobile fueling has been set by the U.S. Department of Energy at 6.5 wt%. Because it is unlikely that capacities of >6 wt% can be obtained in transition metal-based materials,[3–7] intense interest has developed in complex hydrides such as alanates (AlH_4^-), amides (NH_2^-), and borohydrides (BH_4^-).[8–14]

For $LiBH_4$, full decomposition to Li + B + $2H_2$ can yield 18.3 wt% hydrogen, exhibiting promising prospects for on-board applications. However, the main evolution of gas starts at 380 °C and only releases half the hydrogen below 600 °C.[15] Furthermore, to reverse the reaction is a significant challenge because of the extremely rigorous reaction conditions required (high pressure and high temperature). Züttel *et al.*[15] reported that SiO_2 may be used as a catalyst for the dehydrogenation of $LiBH_4$, lowering the temperature of hydrogen evolution to 300 °C. Pinkerton *et al.*[16] also reported that $LiBH_4$ could react with $LiNH_2$ to form $Li_3BN_2H_8$. This quaternary hydride released 10 wt% hydrogen above $\sim$250 °C. However, neither of the above reactions have been shown to be reversible. More recently, Vajo *et al.*[17] found that $LiBH_4$ may be reversibly dehydrogenated and rehydrogenated with a reduced reaction enthalpy by the addition of MgH_2. They thought that the formation of MgB_2 stabilized the dehydrogenated state and effectively destabilized the $LiBH_4$. According to the above hypothesis, the formation of MgB_2 should be accompanied with the decomposition of $LiBH_4$. However, our results presented here reveal that the decomposition of the borohydride resulted in the formation of a Li–Mg alloy, prior to the appearance of MgB_2.

The MS and TG profiles in Fig. 1 show the hydrogen desorption properties of ball milled $LiBH_4$–MgH_2 (mass ratio, 1 : 4). The first hydrogen desorption peak appeared at 354 °C, similar to the decomposition temperature of ball milled MgH_2. Further heating led to a second decomposition peak at 405 °C. This led to a region of steady hydrogen desorption in the temperature range of 430–580 °C. The TG results suggest that the weight loss of $LiBH_4$–MgH_2 mixture is in three steps. The first step is around 360 °C, corresponding to the first hydrogen desorption peak, with a weight loss of 5.7 wt%, which is comparable with the theoretical hydrogen capacity of MgH_2 in the mixture (5.8 wt%). The weight loss of the second and the third steps are 2.65 wt% and 0.85 wt%, respectively, this combined weight loss is in good agreement with the hydrogen capacity from the $LiBH_4$ (3.6 wt%). The total weight loss observed for the $LiBH_4$–MgH_2 mixture is equivalent to their theoretical hydrogen capacities, suggesting that all the hydrogen was released from the mixture below 600 °C. The TG data for the dehydrogenation of ball milled $LiBH_4$ is given in Fig. 1 for comparison and clearly shows that the dehydrogenation temperature for the borohydride has been significantly reduced.

The fact that the first weight loss is equivalent to the hydrogen capacity of MgH_2 in the $LiBH_4$–MgH_2 mixture is strongly indicative that the MgH_2 and $LiBH_4$ decomposed separately. Therefore, the improved dehydrogenation kinetics for the $LiBH_4$ was likely due to the Mg formed. To investigate the effect of Mg on the dehydrogenation of $LiBH_4$ a ball milled $LiBH_4$–Mg sample with a mass ratio of 1 : 4 was prepared. Fig. 2 shows the TG-MS results with a hydrogen desorption peak at 405 °C, which was the same temperature as that for the decomposition of $LiBH_4$ in the $LiBH_4$–MgH_2 samples, indicating that the Mg metal ball milled with $LiBH_4$ resulted in a similar effect on the decomposition of

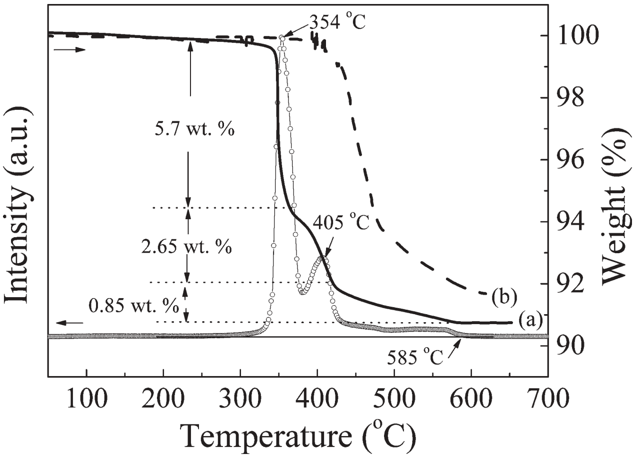

Fig. 1 (a) TG and MS results for the evolution of H_2 from $LiBH_4$–MgH_2 milled for 1 h. (b) TG results for $LiBH_4$. Both experiments used a heating rate of 10 °C min^{-1}.

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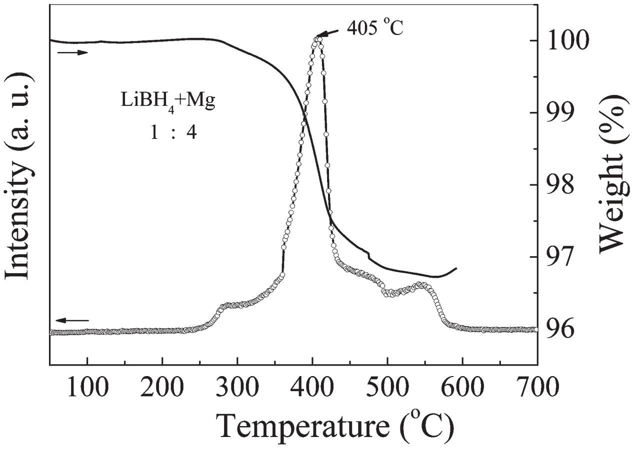

Fig. 2 TG and MS results for the evolution of H_2 from $LiBH_4$–Mg milled for 1 h. Heating rate was 10 °C min^{-1}.

$LiBH_4$ as did MgH_2. The hydrogen released by 600 °C gave a total weight loss of 3.35 wt%, lower than the 3.66 wt% expected from the $LiBH_4$ fraction of the sample. The lower wt% of hydrogen released is likely to be due to partial decomposition of $LiBH_4$ during ball milling. The strong correlation of the effect of Mg on the decomposition of $LiBH_4$ with that in the $LiBH_4$–MgH_2 samples shows that the main reaction in $LiBH_4$–MgH_2 includes two processes: one is the decomposition of MgH_2, and the other is the reaction of Mg with $LiBH_4$, which facilitates the hydrogen desorption from $LiBH_4$.

XRD results for the as prepared $LiBH_4$–MgH_2 and after heating to temperatures up to 600 °C are shown in Fig. 3. The XRD pattern for the as prepared sample only had a weak diffuse pattern corresponding to MgH_2. No pattern was detected for the borohydride phase because this was in much lower concentration and would also be nanocrystalline/disordered after the ball milling process. After heating to 360 °C the XRD pattern corresponds to Mg metal, suggesting that only MgH_2 decomposed forming Mg and H_2 during the first dehydrogenation step. There appears to be little change in the XRD pattern after heating to 405 °C, however, when heated to 440 °C and 500 °C, a shift to higher 2*θ* values can be observed in the position of the XRD reflections. The pattern at 500 °C matches the *d*-spacing for $Li_{0.184}Mg_{0.816}$.[18] The small amount of MgO was caused by oxidation during loading. No MgB_2 was formed, but after further heating to 600 °C, the XRD pattern can be seen to consist of $Li_{0.30}Mg_{0.70}$,[18] $Li_{0.184}Mg_{0.816}$, MgO, and MgB_2, showing that MgB_2 only formed at the higher temperature.[19] Table 1 presents the *d*-spacing data comparing the experimental results with the reference data for Mg, $Li_{0.184}Mg_{0.816}$, $Li_{0.30}Mg_{0.70}$ and Li.

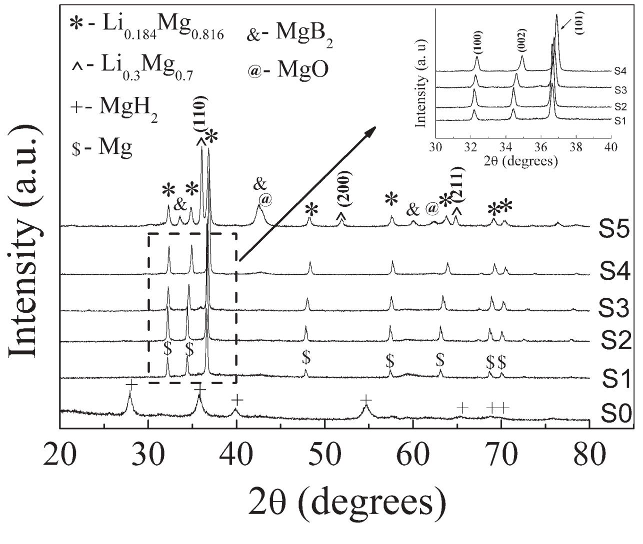

Fig. 3 XRD patterns for the $LiBH_4$–MgH_2 mixture before (S0) and after dehydrogenation to 360 °C (S1), 405 °C (S2), 440 °C (S3), 500 °C (S4) and 600 °C (S5).

Table 1 Comparison of *d*-spacings for $LiBH_4$–MgH_2 (mass ratio, 1 : 4) heated to 360 °C (S1), 405 °C (S2), 440 °C (S3), 500 °C (S4) and 600 °C (S5) with Mg, $Li_{0.184}Mg_{0.816}$ (ICSD: 104740), Li, $Li_{0.3}Mg_{0.7}$ (ICSD: 104741)

	d-Spacings (Å)					
Sample	(100)	(002)	(101)	(110)	(200)	(211)
Mg	2.779	2.606	2.452	—	—	—
$Li_{0.184}Mg_{0.816}$	2.764	2.566	2.434	—	—	—
S1	2.778	2.603	2.450	—	—	—
S2	2.777	2.603	2.451	—	—	—
S3	2.772	2.591	2.444	—	—	—
S4	2.765	2.566	2.434	—	—	—
Li	—	—	—	2.482	1.755	1.433
$Li_{0.3}Mg_{0.7}$	—	—	—	2.487	1.756	1.436
S5	2.768	2.572	2.438	2.488	1.757	1.437

The 1 : 4 $LiBH_4$–MgH_2 sample dehydrogenates in three steps. The first step is the dehydrogenation of the MgH_2 phase and results in the formation of Mg metal. The $LiBH_4$ phase dehydrogenates at 405 °C. Unfortunately because of the low content and poor crystallinity of this phase it was not possible to follow the loss of this phase by XRD. As there was no apparent change to the Mg phase during the 2nd dehydrogenation step, this indicates that the Mg acts as a catalyst. Assuming that the 2nd and 3rd dehydrogenation steps were due to the decompostion of the borohydride phase, the TG data shows that 76% of the hydrogen was produced during the 2nd dehydrogenation step and 24% during the 3rd. This corresponds well with the expected 3 : 1 ratio for hydrogen evolved from the dehydrogenation of $LiBH_4$ yielding LiH and B and the subsequent dehydrogenation of the LiH. LiH does not normally dehydrogenate until temperatures above 600 °C (ESI 1†), thus the presence of Mg also destabilises the LiH phase. At temperatures from 440 °C and higher the formation of Li–Mg alloy was evidenced in the XRD data. The Li–Mg alloy must be forming directly from the dehydrogenation of the LiH as this reaction is occuring at temperatures well above the vaporisation temperature of Li. The Li–Mg mole fraction for this system is 0.23 Li. This is within a two phase region consisting of a HCP α phase with Li content of 0.184 and BCC β phase with a Li content of 0.30.[20] Therefore as the LiH decomposes, an α phase with increasing Li content forms until saturation is reached whence the β phase forms. A solid state reaction between Mg and B has occured by 600 °C forming MgB_2, which will also deplete the available Mg for the Li–Mg system, resulting in further formation of the β alloy. This reaction mechanism was supported by the fact that the ratio of the 2nd and 3rd dehydrogenation steps remained the same for different ratios of $LiBH_4$–MgH_2 (ESI 2†) and that the

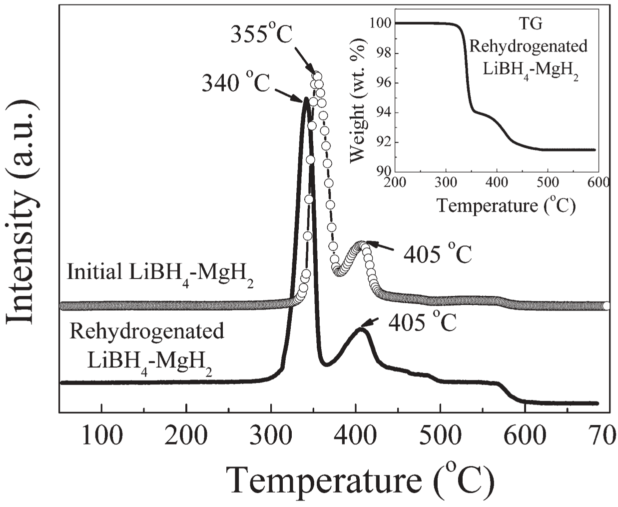

Fig. 4 MS and TG results (inserted) for initial and rehydrogenated $LiBH_4$–MgH_2 with a heating rate of 10 °C min^{-1}.

LiH phase in a ball milled control experiment of LiH–MgH_2 (mass ratio 1 : 9 corresponding to a mole fraction of 0.27 Li, also within the two phase region) started dehydrogention just above 400 °C and resulted in the same Li–Mg phases being formed (ESI 1†).

Based on the above analysis, the dehydrogenation for $LiBH_4$–MgH_2 mixture is postulated to be:

$$MgH_2 \xrightarrow{\sim 360\ ^\circ C} Mg + H_2 \tag{1}$$

$$0.30\ LiBH_4 \xrightarrow{\sim 405\ ^\circ C,\ Mg} 0.30\ LiH + 0.30\ B + 0.45\ H_2 \tag{2}$$

$$\begin{aligned} &Mg + 0.30\ LiH + 0.30\ B \xrightarrow{>420\ ^\circ C} \\ &0.37\ Li_{0.184}Mg_{0.816} + 0.15\ MgB_2 + 0.78\ Li_{0.30}Mg_{0.70} + 0.15\ H_2 \end{aligned} \tag{3}$$

The total reaction equation is:

$$\begin{aligned} &MgH_2 + 0.30\ LiBH_4 \xrightarrow{360\ ^\circ C - 600\ ^\circ C} \\ &0.37\ Li_{0.184}Mg_{0.816} + 0.15\ MgB_2 + 0.78\ Li_{0.30}Mg_{0.70} + 1.60\ H_2 \end{aligned}$$

In addition we have shown that the dehydrogenation $LiBH_4$–MgH_2 can be reversed without the formation of MgB_2. A $LiBH_4$–MgH_2 sample (mass ratio, 1 : 4) which had been dehydrogenated under a vacuum up to 400 °C (for which XRD results showed no MgB_2 phase (ESI 3†)) was rehydrogenated at 400 °C under 100 bar hydrogen pressure. Fig. 4 shows the TG-MS results for hydrogen evolution from the rehydrogenated $LiBH_4$–MgH_2 sample (the MS curve for an initial dehydrogenation is also shown for comparison). The first hydrogen desorption peak corresponds to the decomposition of MgH_2 located at 340 °C, which is slightly lower than that of the initial sample, suggesting that the dehydrogenation–rehydrogenation process has further improved the kinetics of MgH_2, potentially due to lattice defects from the presence of Li^+ in the MgH_2 lattice as postulated by Johnson *et al.*[21] The second hydrogen desorption peak at 405 °C, coinciding with that of the initial sample, corresponds to the hydrogen desorption from $LiBH_4$. The total weight loss for the rehydrogenated $LiBH_4$–MgH_2 sample was about 8.5 wt% (inserted TG curve, Fig. 4), comparing well with the first dehydrogenation cycle (9.2 wt%). The XRD results of the rehydrogenated sample also revealed the formation of $LiBH_4$ (ESI 3†). The effect of multiple cycles is currently being investigated.

In summary, it has been demonstrated that the hydrogen desorption in $LiBH_4$–MgH_2 mixtures include three steps: first, MgH_2 decomposes to Mg and H_2, then the Mg catalyses the dehydrogenation of $LiBH_4$ forming LiH and B, but the presence of Mg also expedites the dehydrogenation of LiH resulting in the formation of Li–Mg phases. MgB_2 was only formed about 500 °C. Dehydrogenated $LiBH_4$–MgH_2 mixture can be rehydrogenated at 100 bar hydrogen pressures and 400 °C and the reversibility of the reaction does not depend on the formation of MgB_2.

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