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Improved hydrogen storage of LiBH₄ catalyzed magnesium

Abstract

The effect of LiBH₄ on the hydrogen sorption performance of magnesium was investigated. It was found that the hydrogen storage properties of LiBH₄/Mg mixtures exhibit a dramatic improvement as compared to plain magnesium powder. For example, at 250 °C, a LiBH₄/Mg (mass ratio 1:4) composite can absorb 6.7 wt % hydrogen in 60 min, while only less than 1 wt % hydrogen was absorbed by pure magnesium in the same period under similar conditions. The hydrogen desorption properties of the composite at 350 °C were also improved significantly as compared to the plain magnesium powder. Furthermore, highly activated magnesium hydride was synthesized directly by ball milling LiBH₄/Mg mixtures under high hydrogen pressure. The synthesized magnesium hydride exhibits superior kinetics, absorbing 5.78 wt % hydrogen at the relatively low temperature of 200 °C within 100 min.

Keywords

Improved, hydrogen, storage, LiBH₄, catalyzed, magnesium

Disciplines

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Improved Hydrogen Storage of LiBH₄ Catalyzed Magnesium

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The effect of LiBH₄ on the hydrogen sorption performance of magnesium was investigated. It was found that the hydrogen storage properties of LiBH₄/Mg mixtures exhibit a dramatic improvement as compared to plain magnesium powder. For example, at 250 °C, a LiBH₄/Mg (mass ratio 1:4) composite can absorb 6.7 wt % hydrogen in 60 min, while only less than 1 wt % hydrogen was absorbed by pure magnesium in the same period under similar conditions. The hydrogen desorption properties of the composite at 350 °C were also improved significantly as compared to the plain magnesium powder. Furthermore, highly activated magnesium hydride was synthesized directly by ball milling LiBH₄/Mg mixtures under high hydrogen pressure. The synthesized magnesium hydride exhibits superior kinetics, absorbing 5.78 wt % hydrogen at the relatively low temperature of 200 °C within 100 min.

Introduction

Developing new practical hydrogen storage materials with high volumetric and gravimetric hydrogen densities is necessary to implement fuel cell technology for transportation applications,¹ for which a capacity of 6.5 wt % is regarded as the target by the U.S. Department of Energy.² Magnesium, due to its high theoretical hydrogen storage capacity (7.6 wt %), abundance, and low cost, has excellent potential for hydrogen-related applications.³ However, hydrogenation/dehydrogenation occurs only at high temperatures (>300 °C), and the reaction rate is too slow to form the practical basis for a hydrogen store. Various attempts have been undertaken to overcome the kinetic limitations. Among them, mechanical milling has been used by many researchers for preparing composites of magnesium with various additives, including transition metals,^{4–7} H-storage alloys,⁸ metal oxides,^{9–11} metal hydrides,¹² and graphite,^{13–15} resulting in improved kinetics. For example, Liang et al. reported⁴ the catalytic effect of transition metals (Ti, V, Mn, Fe, and Ni) on hydrogen sorption of MgH₂ after 20 h of milling under argon. The composites containing Ti exhibited rapid absorption kinetics in the temperature range of 29–200 °C, which reportedly can absorb 4.6 wt % hydrogen in 20 s, 4.9 wt % in 200 s, and 5.0 wt % in 1000 s at 200 °C. Oelerich et al. reported⁷ the catalytic effects of V, V₂O₅, VN, and VC on the hydrogen sorption of MgH₂ powder after 120 h of milling under argon. The maximum storage capacity is typically reached after 1 min, and MgH₂/(VN)_{0.05} can absorb 5.2 wt % hydrogen after 1 min at 300 °C. Zinsou et al. studied¹¹ the effect of MgO on the (de)hydrogenation properties of Mg. MgH₂ was milled with or without 10 wt % MgO under Ar atmosphere. Pure MgH₂ milled for 100 h has

good kinetics at 300 °C. Hydrogen can be absorbed or desorbed in 2000 s. Nevertheless, when MgH₂ is milled with MgO, absorption or desorption of hydrogen takes place in less than 150 s. Obviously, long ball milling times are necessary (typically >20 h) to form a nanocrystalline microstructure. This is energy consuming, especially for batch milling of large quantities of materials.

Recently, a number of new hydrogen storage systems has been proposed based on the interaction between MgH₂ and complex hydrides. Luo reported¹² that a 1:2 mixture of MgH₂ and LiNH₂ desorbed hydrogen reversibly at around 200 °C. Vajo et al.¹⁶ found that LiBH₄ may be reversibly dehydrogenated and rehydrogenated with a reduced reaction enthalpy upon addition of MgH₂. More recently, Johnson et al. reported¹⁷ an enhancement in the dehydrogenation/hydrogenation kinetics of MgH₂ through reaction with small amounts of LiBH₄ at 300 °C. However, the conditions for activation, heating at 300 °C for 12 h and five initial hydriding/dehydriding cycles, impact upon the practicalities and cost of operation. Here, we report a remarkable improvement on hydrogen absorption of Mg by short-time ball milling with a small amount of LiBH₄. The catalyzed Mg can absorb hydrogen at 200 °C without any activation. In addition, the highly activated magnesium hydride was directly synthesized by ball milling at a high hydrogen pressure (3 MPa).

Experimental Procedures

LiBH₄ (99%), LiH (95%), MgH₂ (98%), and Mg (99.8%, –300 mesh) were obtained commercially from Alfa Aesar and used without further purification. LiBH₄/Mg mixtures with a mass ratio of 1:4 and 1:10 and LiH/MgH₂ mixtures with a mass ratio of 1:9 were ball milled, respectively, in an argon atmosphere for 1 h. For comparison, pure magnesium was also examined. In addition, LiBH₄ and Mg with a mass ratio of 1:10 were ball milled in H₂ under 3 MPa for up to 40 h, and the

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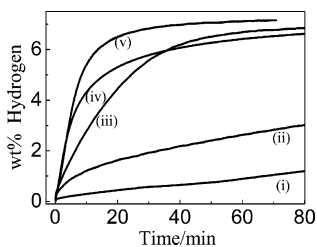


Figure 1. Hydrogen absorption of (i) ball milled Mg at 300 °C. Hydrogen absorption of LiBH₄/Mg (1:4) at 200 °C (ii), 250 °C (iii), 300 °C (v). Hydrogen absorption of LiBH₄/Mg (1:10) at 300 °C (iv) under 3 MPa H₂.

container was systematically refilled with hydrogen every 5 h to maintain the hydrogen pressure. The ball milling was undertaken in a planetary QM-1SP2 ball miller. The milling parameters were kept constant for all trials, and the ball-to-powder weight ratio was 30:1 at 580 rpm using stainless steel balls of 10 mm diameter. The milling was performed in special stainless steel vials, designed to operate in a pressure range of 0.1–10 MPa for various gases. All samples were handled in an Ar-filled glove box.

After milling, the vial was opened in an Ar-filled glove box, and ~1.5 g of the powder was placed in a small stainless steel container for hydrogen absorption/desorption in a gas reaction controller (Advanced Materials Corp.). The absorption kinetics measurements were performed at various temperatures with an initial pressure of 3 MPa, and the desorption properties were detected at 350 °C under 0.02 MPa hydrogen pressure and at 300 °C under argon with atmospheric pressure. The hydrogen capacity was calculated from the change in hydrogen pressure. Hydrogen capacity calculations were normalized to the magnesium content, aiding comparison between samples containing differing amounts of additive. The pressure–concentration isotherms (PCI) measurements were performed at 350 °C in the pressure range of 0.01 to ~3 MPa, and the equilibrium time for each point was 30 s. X-ray diffraction data were obtained with a Rigaku D/max 2400 using Cu K α radiation. Samples were mounted onto a 1 mm depth glass board in the Ar-filled glove box and sealed with a polyvinylchloride membrane to avoid oxidation during the XRD measurements.

Results and Discussion

Figure 1 shows the hydrogen absorption curves of the Mg, LiBH₄/Mg (1:4), and LiBH₄/Mg (1:10) samples, prepared by ball milling in an argon atmosphere for 1 h. Evidently, the LiBH₄/Mg mixture exhibits superior hydrogen absorption properties than just ball milled Mg. In the case of the LiBH₄/Mg (1:4) sample, a hydrogen absorption capacity of 7.2 wt % was reached at 300 °C in 60 min. Furthermore, the sample can absorb within 1 h 6.7 wt % hydrogen at 250 °C and 2.6 wt % hydrogen at 200 °C. In contrast, the ball milled Mg absorbed less than 1 wt % hydrogen at 300 °C even after 70 min. Further studies revealed that a smaller LiBH₄ addition showed similar results to the LiBH₄/Mg (1:4) sample. Comparing the uptake curves for the 1:4 and 1:10 samples at 300 °C, it can be seen that the initial rate is similar but that the curves diverge above 3.1 wt % hydrogen uptake. The 1:10 sample absorbed 6.42 wt % hydrogen after 60 min, 0.3 wt % lower than that of the LiBH₄/Mg (1:4) sample. The previous results suggest that LiBH₄ plays an important role in improving the kinetic properties of magnesium.

Figure 2 shows the cycling properties of LiBH₄/Mg (1:4) at 300 °C under 3 MPa H₂. It is clear that the hydrogen absorption

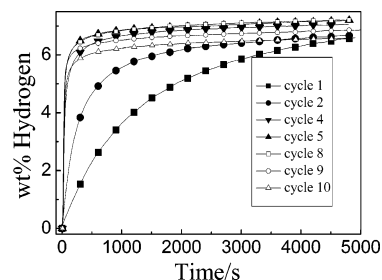


Figure 2. Hydrogen absorption cycle curves for milled LiBH₄/Mg (1:4) at 300 °C under 3 MPa H₂.

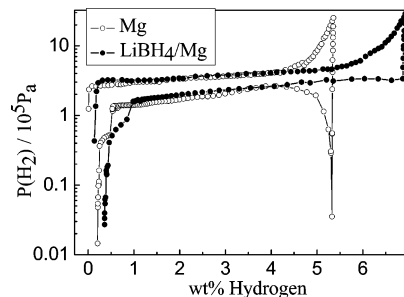


Figure 3. PCI for 1 h milled LiBH₄/Mg (1:10) mixture and pure Mg, both at 350 °C.

rate and hydrogen capacity increase with the initial cycle times and become stable after four cycles with a hydrogen capacity of 7.1 wt %. However, after eight cycles, the hydrogen capacity is deteriorated to 6.6 wt % in the 10th cycle, which might be due to the oxidation during the cycles.

To characterize the thermodynamic properties and dehydrogenation behavior, PC isotherms of the LiBH₄/Mg (1:10) mixture and pure Mg were measured at 350 °C as shown in Figure 3. It can be seen that LiBH₄/Mg and Mg showed similar desorption plateau pressures at 0.25 MPa, suggesting similar thermodynamic properties. The fact that adding LiBH₄ does not change the thermodynamic properties of magnesium hydride implies that LiBH₄ does not react with Mg during the dehydrogenation but plays the role of a catalyst.

The isotherm also shows that LiBH₄/Mg has a longer plateau and a higher capacity than that of pure Mg. As is seen in Figure 3, the isotherm of LiBH₄/Mg shows a stable plateau from 0.95 to 6.01 wt % with a capacity of 6.9 wt %, while Mg on its own just has a plateau from 0.56 to 4.66 wt % with a capacity of 5.43 wt %. The decrease of hydrogen capacity for the Mg sample could result from contamination during ball milling (e.g., from air and/or moisture).¹⁸ However, no apparent decrease was observed in the LiBH₄/Mg sample, suggesting that the presence of LiBH₄ may play an important role in counteracting the effect of contamination.¹⁹

The hydrogen desorption kinetic curves of Mg and LiBH₄/Mg (1:4) after hydrogen absorption at 350 °C are shown in Figure 4. LiBH₄/Mg desorbed hydrogen significantly faster than the pure Mg. The LiBH₄/Mg sample desorbed 6.0 wt % hydrogen after 25 min. However, pure Mg only desorbed 0.5 wt % hydrogen after 25 min, and 118 min was required to release 6.0 wt % hydrogen. These results suggest that LiBH₄ also has an important effect on improving the hydrogen desorption kinetic properties of MgH₂.

It is reported that MgH₂ can be formed by ball milling magnesium under high hydrogen pressure with or without any catalyst addition.^{20,21} However, the hydrogen absorption/desorption kinetics of the synthesized MgH₂ are still not satisfactory. Here, the highly activated magnesium hydride was directly

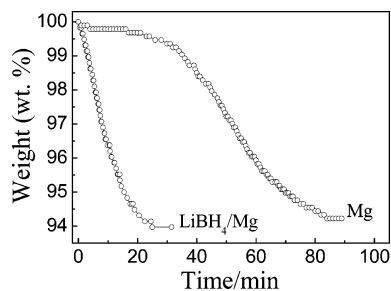


Figure 4. Dehydrogenation kinetic curves of Mg and LiBH₄/Mg (1:4) at 350 °C.

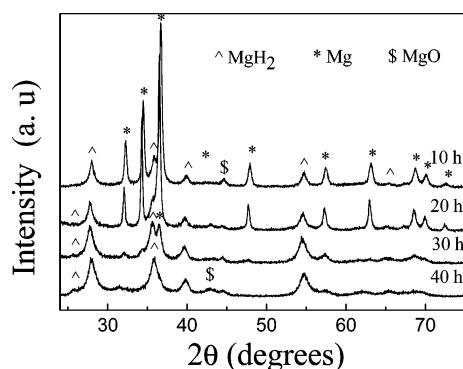


Figure 5. X-ray diffraction patterns of LiBH₄/Mg (1:10) after ball milling under 3 MPa hydrogen pressure for 10, 20, 30, and 40 h.

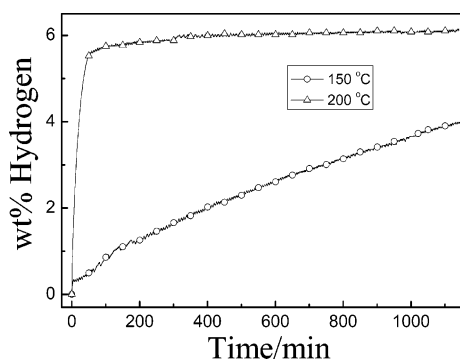


Figure 6. Hydrogen absorption at 150 and 200 °C under 3 MPa H₂ for LiBH₄/Mg (1:10) samples, milled under 3 MPa hydrogen pressure for 40 h and dehydrogenated at 350 °C for 2 h.

synthesized by ball milling the LiBH₄/Mg mixture under 3 MPa H₂ with no external heating. Figure 5 shows the X-ray diffraction patterns of the milled LiBH₄/Mg mixture after milling times of 10, 20, 30, and 40 h. It can be seen that MgH₂ began to form after 10 h of milling and became the major phase after 30 h of milling. After 40 h of ball milling, there was very little Mg phase remaining. The appearance of MgO is likely due to contamination during ball milling. No LiBH₄ pattern was detected for the mixture, which is likely due to the low concentration as well as the formation of a nanocrystalline/disordered structure during the ball milling.

Hydrogen absorption curves of the 40 h milled LiBH₄/Mg sample after dehydrogenation at 350 °C for 2 h is shown in Figure 6. The hydrogen absorption properties of the dehydrogenated sample were improved significantly, absorbing 5.78 wt % hydrogen at 200 °C in 100 min. Furthermore, this sample absorbed 1.30 wt % hydrogen at 150 °C within 200 min. This suggests that the synthesized LiBH₄/MgH₂ shows superior hydrogen absorption properties than Mg on its own. The different hydrogenation kinetics of samples milled under Ar and

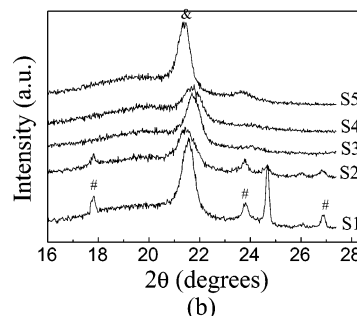
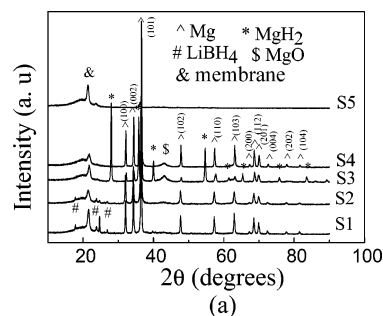


Figure 7. X-ray diffraction patterns for LiBH₄/Mg (1:4) at (a) 10–90° and (b) 16–27.4°. S1: before ball milling; S2: after ball milling for 1 h under Ar; S3: S2 sample after hydrogenation at 300 °C for 80 min; S4: S3 sample after dehydrogenation under vacuum at 350 °C and 2 h; and S5: membrane. New phase observed at 24.7 and 26.1° 2θ may be oxidation of LiBH₄.

H₂ atmospheres can be attributed to the difference in mechanical properties.²¹ Ball milling in Ar applied to a ductile material tends to smear the product but does not decrease the particle size. Ball milling in H₂ leads to the formation of a brittle material, lending it to be broken by brittle failure leading to a substantial decrease in the particle size. The formation of a hydride layer on the sample surface was not sensitive to oxygen as compared to the pure Mg particle and limited the formation of any passivation layers. Indeed, the formation of MgH₂ during ball milling in H₂ modified the ball milling conditions, including a reduction in grain size, the destruction of the surface layer of MgO, and a uniform distribution of the catalyst.

As is commonly accepted, the hydrogenation process of magnesium consists of the following steps: dissociation of the hydrogen molecules, diffusion of hydrogen atoms, nucleation of the MgH₂ phase, and hydrogen diffusion into bulk magnesium through the formed MgH₂ layer. It also has been well-established that metallic catalysts may facilitate the dissociation of hydrogen molecules and that the increase of hydrogen concentration chemisorbed on the surface of Mg particles will result in enhanced kinetics of hydrogenation. In this regard, there are a number of possible factors that contribute to the observed enhancement in hydrogen absorption/desorption kinetics in the LiBH₄/Mg system. The XRD patterns for LiBH₄/Mg before and after ball milling in argon gas, and the milling products after absorption and desorption, are illustrated in Figure 7. Clearly, the milled reactant shows a physical mixture of Mg and LiBH₄. The weakness of the LiBH₄ peaks (S2) could be the result of a nanocrystalline/disordered phase formed during the ball milling process. After hydrogenation and dehydrogenation at 300 °C, the diffraction peaks of LiBH₄ disappeared, and no diffraction signal for any species containing Li or B was observed (S3 and S4). The disappearance of LiBH₄ can be ascribed to its melting reaction at 277 °C.²² The XRD pattern after dehydrogenation (S4) matches the diffraction pattern for Mg metal but not the

TABLE 1: Comparison of d -Spacings for S4 with Mg, $\text{Li}_3\text{Mg}_{17}$, and $\text{Li}_{0.92}\text{Mg}_{4.08}$

sample	d -spacings (Å)											
	(100)	(002)	(101)	(102)	(110)	(103)	(200)	(112)	(201)	(004)	(202)	(104)
Mg	2.779	2.605	2.452	1.901	1.604	1.473	1.390	1.366	1.343	1.303	1.226	1.179
S4	2.772	2.598	2.450	1.901	1.602	1.471	1.387	1.369	1.341	1.301	1.225	1.178
$\text{Li}_3\text{Mg}_{17}$	2.771	2.585	2.442	1.890	1.600	1.463	1.385	1.360	1.338	1.293	1.221	1.171
$\text{Li}_{0.92}\text{Mg}_{4.08}$	2.764	2.566	2.434	1.881	1.596	1.455	1.382	1.355	1.335	1.283	1.217	1.164

potential Li–Mg alloys (i.e., $\text{Li}_3\text{Mg}_{17}$ or $\text{Li}_{0.92}\text{Mg}_{4.08}$). (Table 1 presents the d -spacing data comparing the experimental results with the reference data for Mg, $\text{Li}_3\text{Mg}_{17}$, and $\text{Li}_{0.92}\text{Mg}_{4.08}$). It suggests that no Li–Mg phases were formed before and after dehydrogenation. As there was no observed change in the Mg d -spacing below 350 °C, this suggests that no B or Li doping occurred in the Mg phase; however, there will be Li^+ or H^- present either as LiH or LiBH_4 , and it would appear that it is these ions that interact with Mg and catalyze the reaction. To prove the catalysis effect of LiH on MgH_2 , hydrogen desorption properties of the LiH/ MgH_2 composite were investigated. Figure 8 shows the hydrogen desorption kinetic curves of MgH_2 and LiH/ MgH_2 (1:9) at 300 °C. It is apparent that the LiH/ MgH_2 composite has a faster hydrogen desorption rate than the pure MgH_2 . The LiH/ MgH_2 desorbed 5.1 wt % hydrogen after 110 min while just 3.5 wt % was released from MgH_2 over the same time period. These results suggest that LiH also plays an important role in improving the hydrogen desorption kinetic properties of MgH_2 . More detailed characteristic studies of the catalysis mechanism in the LiBH_4/Mg system are in progress.

Conclusion

The composite of LiBH_4/Mg , prepared by ball milling, possesses an improved hydrogen sorption performance as a result of a catalytic effect. A hydrogen capacity of 6.7 wt % can be reached in 60 min at 250 °C for 1 h milled LiBH_4/Mg , while only less than 1 wt % hydrogen was absorbed by pure magnesium over the same time period and temperature. The composite also exhibits superior hydrogen desorption kinetics

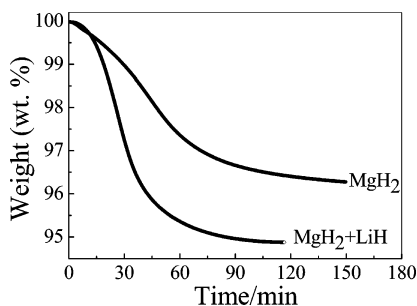


Figure 8. Dehydrogenation kinetic curves of MgH_2 and LiH/ MgH_2 (1:9) at 300 °C measured under argon at atmospheric pressure.

as compared to pure magnesium. In addition, highly activated magnesium hydride was directly generated by ball milling the LiBH_4/Mg mixture under 3.0 MPa hydrogen. The synthesized sample can absorb 5.78 wt % hydrogen at 200 °C within 100 min, showing promising prospects for applications.

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