Hydrogen Storage Properties and Reactive Mechanism of LiBH₄/Mg₁₀YNi-H Composite

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The Mg₁₀YNi alloy was hydrogenated and then coupled with LiBH₄ to form LiBH₄/Mg₁₀YNi-H reactive hydride composite. The results indicate that thermal dehydrogenation stability of LiBH₄ can be remarkably reduced by combining with Mg₁₀YNi hydride. The starting and ending temperatures for hydrogen desorption from the LiBH₄/Mg₁₀YNi-H composite are approximately 275 and 430 °C, respectively. Dehydrogenation of the LiBH₄/Mg₁₀YNi-H composite proceeds mainly in two steps with a total reaction of 12LiBH₄ + 2.5Mg₁₀YNiH₁₀ → 24Mg + MgNi₆B₁₂ + 2.5YB₂ + 12LiH + 43H₂. After rehydrogenation at 450 °C under 9 MPa hydrogen pressure, the LiBH₄/Mg₁₀YNi-H composite starts to release hydrogen around 260 °C, and as much as approximately 5.2 wt.% of hydrogen can be desorbed during the second dehydrogenation process.

Keywords: Lithium borohydride, Reactive hydride composite, Hydrogen storage property, Reactive mechanism.

1. Introduction

The increasing consumption of fossil fuels makes it urgent to develop new energy carriers, in which hydrogen shows great promise as an ideal alternative due to its high calorific value, clean burning products and abundant resources. For safely storing hydrogen with high efficiency, solid-state hydrogen storage materials have been intensively studied during the last several decades. Among them, LiBH₄ has a theoretical hydrogen capacity as high as 13.8 wt.% through decomposition into LiH and B. However, the practical application of LiBH₄ is strongly limited by its high dehydrogenation temperature, sluggish dehydrogenation process and rigorous rehydrogenation conditions. To overcome these deficiencies, various approaches such as catalyst addition, cation/anion substitution and nanoc confinement have been developed and utilized.

Another effective way that has also been used to improve the hydrogen storage properties of LiBH₄ is the construction of reactive hydride composites. The primary strategy of this method is to combine LiBH₄ with a reactive hydride destabilizer, thus reducing the overall dehydrogenation enthalpy and enhancing the rehydrogenation ability via the change in de-/hydrogenation pathway. The LiBH₄/MgH₂ (2:1) composite, as a typical example, was reported to release hydrogen with an enthalpy lowered by 25 kJ/mol H₂ with respect to the pristine LiBH₄ according to the altered reaction of 2LiBH₄ + MgH₂ → MgB₁₂ + 2LiH + 4H₂. In addition, the formation of MgB₁₂ upon dehydrogenation can make rehydrogenation easier to proceed by overcoming the chemical inertness of pure B. Following this work, other binary metal hydrides (e.g., CaH₂, SrH₂, AlH₃, YH₃, CeH₃, and NdHₓ (x = 24), single metal (e.g., Al₂₅ and Ni₂₆), and complex hydrides (e.g., LiAlH₄, NaAlH₄, Li₂AlH₆, Mg(AlH₄)₂, LiNH₂, and NaNH₂) were also used to combine with LiBH₄ to form reactive hydride composites.

Considering that better de-/hydrogenation properties of LiBH₄ might be obtained by simultaneously introducing two kinds of destabilizing components, the LiBH₄/Mg-X (X = Al, Fe, Ni or La) alloy hydride composites were developed and investigated. For example, Zhou et al. introduced the hydrogenated La,Mgₓ, alloy into LiBH₄ by means of mechanochemical reaction under 40 bar hydrogen pressure and provided a synergetic thermodynamic and kinetic destabilization on the de/hydrogenation of LiBH₄ via the in situ formed MgH₂ and LaH₃. In our previous work, we prepared a reactive hydride composite of LiBH₄/MgₓCeNi hydride and improve the dehydrogenation property of LiBH₄ based on the combined destabilizing effect of Mg, MgNi and CeH₃. In order to enrich such an effect and further promote the development of LiBH₄-based hydrogen storage materials, the LiBH₄/Mg₁₀YNi-H composite was prepared to investigate its reversible hydrogen storage property and reactive mechanism in this paper.

2. Experimental Details

2.1 Sample preparation

Commercial LiBH₄ powder (95%, Alfa Aesar), Mg ribbon (90+%, Alfa Aesar), Ni foil (99.994%, Alfa Aesar) and Y ingot (99.9%, Alfa Aesar) were used as-received. The Mg₁₀YNi (x = 4, 10 and 12) alloys were prepared by induction melting of appropriate amounts of Mg, Y and Ni metals under argon atmosphere. In order to compensate the
losses of Mg and Y during melting. Extra 18 wt.% of Mg and 3 wt.% of Y were added on the basis of stoichiometric amounts of starting materials, and the alloys were remelted two times to ensure homogeneity. After melting, the as-cast alloys were mechanically crushed into powders of 300 mesh and then subjected for hydrogen absorption/desorption. The LiBH₄ ·Mg₁₀ YNi-H composite was prepared by ball-milling the mixture of LiBH₄ and Mg₁₀ YNi hydride with a 24:5 molar ratio under 0.5 MPa hydrogen pressure at a rotation speed of 400 rpm for 2 h using a QM-3SP2 planetary mill. Stainless steel vials (250 mL in volume) and balls (10 mm in diameter) were used. The ball to sample weight ratio was 30:1. To avoid air-exposure, all sample handling was carried out in an Ar-filled glove box equipped with a purification system, in which the typical O₂/H₂O levels are below 1 ppm.

2.2 Sample characterization

Hydrogen absorption/desorption properties of the samples were examined using a carefully calibrated Sieverts-type apparatus (Suzuki Shokan Co., Ltd., Japan). For the Mg-Y-Ni alloys, the powder samples were activated by two hydrogen absorption/desorption cycles. During each cycle, the samples were hydrogenated at 300 °C under 4 MPa hydrogen pressure for 2 h and subsequently evacuated for 1 h. After activation, isothermal hydrogenation was performed at 300 °C under the initial hydrogen pressure of 4 MPa. For the LiBH₄ ·Mg₁₀ YNi-H composite, the temperature dependence of dehydrogenation was determined by heating the sample from ambient temperature to 500 °C at the heating rate of 2 °C/min under ~0.1 MPa hydrogen backpressure. Rehydrogenation of the samples was carried out at 450 °C for 10 h under an initial hydrogen pressure of 6 or 9 MPa.

X-ray diffraction (XRD) measurements were performed using a Rigaku D/Max 2500VL/PC diffractometer with Cu Kα radiation at 50 kV and 150 mA. The XRD samples were loaded and sealed in a special holder that can keep the sample under argon atmosphere. In addition, the XRD pattern of the dehydrogenated product was analyzed with the Rietveld refinement program RIETAN-2000. Fourier transform infrared (FTIR) spectra were collected at ambient conditions using a Nicolet 6700 FTIR spectrometer. The FTIR samples were prepared by cold pressing the mixture of testing powder and KBr with a 1:300 weight ratio.

3. Results and Discussion

3.1 Hydrogenation characteristics of Mg-Y-Ni alloys

Fig. 1 gives the isothermal hydrogenation curves of the Mg-YNi (x = 4, 10 and 12) alloys after two hydrogen absorption/desorption cycles (the samples were hydrogenated at 300 °C under 4 MPa hydrogen pressure for 2 h and subsequently evacuated for 1 h).

The saturated hydrogenation amount for the Mgₓ YNi alloy is only approximately 3.4 wt.% because of a relative low Mg content. For the Mg₁₀ YNi alloy, though a higher hydrogenation amount can be obtained, the hydrogenation process cannot be finished within 160 min due to the inadequate catalytic effect of YH₂/YH₃ and MgNi (or Mg₂NiH₄) nanoparticles embedded in MgH₂ matrix. In contrast, the Mg₁₀ YNi alloy can absorb as much as approximately 4.8 wt.% of hydrogen and accomplish the hydrogenation process within 100 min, exhibiting the best comprehensive property in terms of the hydrogenation amount and relative hydrogenation rate.

To clarify the hydrogenation mechanism, the XRD patterns of the Mgₓ YNi alloy as-cast and hydrogenated are shown in Fig. 2, indicating that the as-cast Mg₁₀ YNi alloy contains Mg, MgNi and Mg₂Ni, while the hydrogenated sample is composed of MgH₂, Mg₂NiH₄, YH₃ and little amount of YH₂. It can be superficially concluded that the Mgₓ YNi alloy reacted with H₂ to form MgH₂, Mg₂NiH₄, YH₃ and YH₂.
Hydrogen Storage Properties and Reactive Mechanism of LiBH₄/Mg₁₀YNi-H Composite

which is similar to other Mg-rich and Mg-RE-Ni alloys. According to the hydrogenation amount of approximately 4.8 wt.% experimentally obtained, the hydrogen gas absorbed can be calculated to be 20 equivalents per Mg₁₀YNi.

3.2 Thermal dehydrogenation properties of LiBH₄/Mg₁₀YNi-H composite

The above hydrogenated Mg₁₀YNi alloy was applied to couple with LiBH₄, and Fig. 3 gives the temperature-programmed dehydrogenation curve for the LiBH₄/Mg₁₀YNi-H composite. For comparison, the hydrogen desorption curve of pristine LiBH₄ is also included in Fig. 3. It can be seen that thermal dehydrogenation of the LiBH₄/Mg₁₀YNi-H composite starts around 275 °C and proceeds mainly in two steps. The first step occurs in the temperature range from 275 to 350 °C, and releases approximately 4.1 wt.% of hydrogen. The second step starts following the first one and finishes at approximately 430 °C, with approximately 2.3 wt.% of hydrogen desorbed. In contrast, the pristine LiBH₄ starts to release detectable hydrogen at temperatures as high as 350 °C, and only approximately 1.6 wt.% of hydrogen was desorbed when heating to 450 °C. These results indicate that dehydrogenation stability of LiBH₄ can be remarkably reduced by combining with Mg₁₀YNi hydride.

As reported in our previous work, thermal dehydrogenation of the LiBH₄/MgH₂ (2:1) composite initiates at approximately 340 °C and cannot be accomplished even though the temperature rose to 550 °C. For the LiBH₄/YH₃ (4:1) composite as low as approximately 0.7 wt.% of hydrogen was desorbed at 350 °C for 10 h under 0.1 MPa hydrogen backpressure. For the LiBH₄/Mg₂NiH₄ (4:5) composite, thermal dehydrogenation ends at approximately 450 °C, with approximately 5.7 wt.% of hydrogen released. There can be no doubt that the present LiBH₄/Mg₁₀YNi-H composite exhibits lower dehydrogenation temperature and/or higher dehydrogenation amount than the individually MgH₂-, YH₃- or Mg₂NiH₄-coupled LiBH₄.

3.3 Dehydrogenation reactions of LiBH₄/Mg₁₀YNi-H composite

To elucidate the dehydrogenation reactive mechanism of the LiBH₄/Mg₁₀YNi-H composite, Figs. 4 and 5 present the XRD patterns and FTIR spectra of the samples after ball-milling and dehydrogenation at 350 and 450 °C, respectively. As seen from Fig. 4a, the phases MgH₂, Mg₂NiH₄, YH₃, and YH₂ are present in the as-milled sample. Though LiBH₄ is not found in XRD data due to its relatively low content and/or amorphization by ball milling, the obvious signature bands for the B-H bond vibrations located at 2362, 2293, 2225 and 1126 cm⁻¹ in Fig. 5a confirm its existence. The results suggest that no obvious reactions occurred between the starting materials during ball milling. When heating the LiBH₄/Mg₁₀YNi-H composite to 350 °C, as shown in

Figure 3. Temperature-programmed dehydrogenation curves of the LiBH₄/Mg₁₀YNi-H composite and pristine LiBH₄.

Figure 4. XRD patterns of the LiBH₄/Mg₁₀YNi-H composite as-milled (a) and dehydrogenated at 350 (b) and 450 ºC (c), respectively.

Figure 5. FTIR spectra of the LiBH₄/Mg₁₀YNi-H composite as-milled (a) and dehydrogenated at 350 (b) and 450 ºC (c), respectively.
Figs. 4b and 5b, MgH$_2$ and Mg$_2$NiH$_4$ almost disappeared with the emergence of Mg and Mg$_2$Ni. In addition, the phase content of YH$_2$ is enhanced. Evidently, the first-step dehydrogenation for the LiBH$_4$/Mg$_{10}$YNi-H composite should be assigned to the decomposion of MgH$_2$ and Mg$_2$NiH$_4$ to form Mg and Mg$_2$Ni, respectively. Meanwhile, partial YH$_3$ decomposed into YH$_2$. Upon further increasing the dehydrogenation temperature to 450 ºC, the diffraction peaks arising form Mg$_2$Ni, YH$_1$ and YH$_2$ disappeared, and the solid residues are composed of Mg, MgNi$_{2.5}$B$_2$, YB$_4$ and LiH (see Fig. 4c). Moreover, almost no FTIR bands for the B-H bond vibrations can be observed in Fig. 5c, strongly implying that LiBH$_4$ was completely decomposed. To further confirm these existing phase components, the XRD pattern in Fig. 4c was refined by the Rietveld method. It can be seen from Fig. 6 that the diffraction pattern calculated from the structure models of the phases Mg, MgNi$_{2.5}$B$_2$, YB$_4$ and LiH is in good agreement with the measured pattern.

It is believed that the second-step dehydrogenation for the LiBH$_4$/Mg$_{10}$YNi-H composite should come from the decomposition of LiBH$_4$ that was reactively destabilized by Mg, Mg$_2$Ni, YH$_3$ and YH$_2$ together. The total dehydrogenation reaction can be expressed as:

$$12LiBH_4 + 2.5Mg_{10}YNiH_{20} \rightarrow 24Mg + MgNi_{2.5}B_2 + 2.5YB_4 + 12LiH + 43H_2 \tag{1}$$

According to this reaction, the LiBH$_4$/Mg$_{10}$YNi-H composite should theoretically release 6.7 wt.% of hydrogen. This estimated value is in good agreement with the measured value of 6.4 wt.% as indicated in Fig. 3. For the present case, Mg formed during the first-step dehydrogenation process can act as the heterogeneous nucleation center for the second-step dehydrogenation$^{37,38}$.

### 3.4 Rehydrogenation characteristics of LiBH$_4$/Mg$_{10}$YNi-H composite

For the purpose to evaluate the rehydrogenation property of the LiBH$_4$/Mg$_{10}$YNi-H composite, the dehydrogenated sample was subjected to rehydrogenation at 450 ºC under different hydrogen pressures (6 and 9 MPa, respectively), and then the second temperature-programmed dehydrogenation curves were measured. It is indicated from Fig. 7 that the rehydrogenation pressure has an important effect on the rehydrogenation and subsequent second dehydrogenation properties. For the sample rehydrogenated under 6 MPa hydrogen pressure, only approximately 4.2 wt.% of hydrogen was desorbed during the second dehydrogenation process, with an onset dehydrogenation temperature of approximately 290 ºC. In contrast, the sample rehydrogenated under 9 MPa hydrogen pressure starts to release hydrogen around 260 ºC, with as much as approximately 5.2 wt.% of hydrogen desorbed.

Figs. 8 and 9 give the XRD patterns and FTIR spectra of the rehydrogenated samples, respectively. As shown in Fig. 8a, MgH$_2$ and YH$_3$ were regenerated after rehydrogenation under 6 MPa hydrogen pressure. Increasing the rehydrogenation pressure to 9 MPa, as indicated in Fig. 8b, LiBH$_4$ and Mg$_2$NiH$_4$ were reformed with an enhancement of the relative contents of MgH$_2$ and YH$_3$. It can be seen from Fig. 9 that the FTIR bands for the B-H bond vibrations are present, demonstrating the regeneration of LiBH$_4$. In addition, the relatively higher intensity of FTIR bands in Fig. 9b than in Fig. 9a suggests a higher hydrogenation degree of the sample under 9 MPa hydrogen pressure. These results clearly show that reaction (1) can proceed reversibly under the present rehydrogenation conditions. Moreover, a higher rehydrogenation pressure is helpful to increase the hydrogen storage reversibility, which is consistent with the results obtained from Fig. 7.
Hydrogen Storage Properties and Reactive Mechanism of LiBH₄/Mg₆₅YNi-H Composite

4. Conclusions

The hydrogen storage properties and reactive mechanism of the LiBH₄/Mg₆₅YNi-H composite were investigated. It was found that the Mg₁₀YNi hydride shows a strong destabilization effect on LiBH₄, and that the LiBH₄/Mg₁₀YNi-H composite exhibits lower dehydrogenation temperature and/or higher dehydrogenation amount than the individually MgH₂-, YH₃- or Mg₂NiH₄-coupled LiBH₄. Dehydrogenation of the LiBH₄/Mg₁₀YNi-H composite proceeds mainly in two steps: one comes from the decomposition of MgH₂, Mg₂NiH₄ and partial YH₃, and the other can be assigned to the decomposition of LiBH₄ destabilized by Mg, Mg_Ni, YH₁, and YH₂, together. After rehydrogenation at 450 °C under 9 MPa hydrogen pressure, LiBH₄, MgH₂, Mg₂NiH₄ and YH₃ were regenerated, and as much as approximately 5.2 wt.% of hydrogen can be released during the second dehydrogenation process with an onset temperature of approximately 260 °C.

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6. References


