Improved Dehydrogenation Performance of Li-B-N-H by Doped NiO

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Abstract: In order to improve the dehydrogenation properties of the Li-B-N-H system, a flower-like NiO was successfully synthesized using the hydrothermal method. The effect of the NiO on the dehydrogenation properties of the LiBH₄-2LiNH₂ system was studied. The results showed that the dehydrogenation properties of the LiBH₄-2LiMH₂ system were significantly enhanced by doping with NiO. The composite doped with 5 wt. % NiO exhibited optimal hydrogen storage properties. It released about 10.5 wt. % hydrogen below 300 °C, and the onset dehydrogenation temperature was only 90 °C, 110 °C lower than that of LiBH₄-2LiNH₂. The isothermal dehydrogenation experiment indicated that the LiBH₄-2LiNH₂-5 wt. % NiO composite released 8.8 wt. % hydrogen within 15 min at 150 °C. Structural analysis revealed that the as-prepared NiO was reduced to metallic Ni, which worked as an active catalytic species in the remainder of the dehydrogenation process. The Mass Spectrometer (MS) analyses showed that the doped NiO inhibited the content of NH₃ released in the process of the dehydrogenation of LiBH₄-2LiNH₂-NiO.

Keywords: lithium borohydride; lithium amide; flower-like NiO; hydrogen storage

1. Introduction

In recent years, solid-state complex hydrides bearing lightweight elements or compounds, such as sodium aluminum hydrides, lithium aluminum hydrides, lithium borohydrides, and lithium amides—have been proven to be potential candidates for hydrogen storage [1–3]. Amongst these hydrides, LiBH₄ holds the maximum hydrogen capacity of 18.4 wt. %. However, high thermodynamic stability and poor reversibility limit its practical application as an onboard hydrogen storage medium [4,5].

To overcome these problems, several attempts have been explored, including destabilization [6,7], catalyst additives [8–10], and partial anion–cation substitution [11,12]. For example, Li et al. [13] found that nano-sized Ni could effectively improve the thermodynamic properties of the dehydrogenation of LiBH₄. With the addition of 25 wt. % Ni, the dehydrogenation peak temperature of LiBH₄ was reduced from 470 to 423 °C, and the dehydrogenation content of LiBH₄ was raised from 4.3 to 10.8 wt. %. Zhang et al. [6] found that nano-sized nickel ferrite (NiFe₂O₄) could effectively destabilize LiBH₄, liberating 10.75 wt. % of hydrogen at 89 °C. As mentioned above, the addition of Ni or nickel-based oxides into LiBH₄ was an efficient way to enhance its dehydrogenation kinetics [14].

In addition, a series of LiBH₄-metal hydride composites were studied, including LiBH₄-MgH₂ [15,16], LiBH₄-CaH₂ [17,18], LiBH₄-Li₃AlH₆ [19] and LiBH₄-Mg₂NiH₄ [20]. These studies showed that the
The dehydrogenation temperature of LiBH$_4$ could be reduced, and the dehydrogenation kinetics could be improved. Furthermore, the research revealed that the strong affinity between protic H$^+$ and hydridic H$^-$ can provide the driving force for hydrogen release [21]. Taking advantage of the interaction between the [B-H] bond and [N-H] bond, the combination of LiBH$_4$ and amides was an effective way in which to decrease the dehydrogenation temperature of LiBH$_4$. Pinkerton et al. [22] were the first to dope LiNH$_2$ into LiBH$_4$. They found that the LiBH$_4$-2LiNH$_2$ system released more than 10% hydrogen when heated to 350 °C. The dehydrogenation property was significantly improved compared with the individual LiBH$_4$ and LiNH$_2$. However, the dehydrogenation temperature was still high, and the dehydrogenation kinetics were also slow. One of the most effective approaches to improving the dehydrogenation property of LiBH$_4$-2LiNH$_2$ was to dope transition metals. Pinkerton et al. [23] reported the influence of doped transition metals (Fe, Ni, and Zn) on LiBH$_4$-2LiNH$_2$. Recently, Zhang et al. [24] synthesized metallic Ni nanoparticles supported on carbon (Ni@C), and doped 10 wt. % Ni@C into LiBH$_4$-2LiNH$_2$. The onset dehydrogenation temperature of the sample was 135 °C, and approximately 10 wt. % hydrogen was released within 25 min at 220 °C.

As previously reported, 3D hierarchical flower-like MoS$_2$ presented a better catalytic effect on the dehydrogenation of LiBH$_4$ compared to that of the powder MoS$_2$ [25]. This was attributed to the enlarged interlayer distance of the MoS$_2$ nanosheets, 3D architectures, and hierarchical structures. Zhang reported that the as-prepared Co$_3$O$_4$ exhibited much better catalytic activity for the Li-B-N-H system than the powder sample, the end temperature of dehydrogenation for the majority of the sample with 0.05/3 mol as-prepared Co$_3$O$_4$ was decreased by 64 °C, compared to the powder sample Co$_3$O$_4$ [26]. The catalysts with specific structure and size exhibited much better catalytic activity than the powder samples. NiO powders were easy to agglomerate during catalytic reaction, while NiO with a flower-like structure could avoid the agglomeration, and had the advantages of a nanometer effect, as well as a large specific surface area [27]. In this work, we successfully synthesized flower-like NiO via the hydrothermal method, and doped the NiO into the Li-B-N-H system. LiBH$_4$-2LiNH$_2$-NiO composite was prepared by ball milling. The influence of NiO on the dehydrogenation performance of the Li-B-N-H system was studied. The results of the experiment showed that doped NiO could enhance the dehydrogenation property and inhibit the release of NH$_3$ in the dehydrogenation of the Li-B-N-H system.

2. Materials and Methods

2.1. Sample Preparation

Commercial chemicals LiBH$_4$ 95% (Sigma Aldrich, Shanghai, China), LiNH$_2$ 95% (Alfa Aesar, Shanghai, China), commercial NiO powder (Sinopharm Chemical Reagent Co., Ltd, Shanghai, China) and Ni (J&K, Shanghai, China) were used without further purification. The NiO was prepared using the following hydrothermal method: 5 mmol NiCl$_2$-6H$_2$O and 30 mmol NaOH were dissolved (in that order) into 20 mL distilled water to obtain NiCl$_2$ solution and NaOH solution. Ethanediamine (2 mL) was added to the NiCl$_2$ solution while stirring, and a purple solution was obtained. After being stirred for a further 30 min, the above-mentioned NaOH solution was added to the purple solution. Following that, the mixed solution was poured into a 40 mL Teflon-lined autoclave with a stainless steel coat, heated at 140 °C for 4 h, and then left to cool naturally to room temperature. The precipitate was filtered and washed twice with ethanol and distilled water, and was then dried at 80 °C for 4 h under a vacuum. Finally, the dried product was placed in a muffle furnace and heated at 450 °C for 2 h, and the final product was NiO.

The LiBH$_4$-2LiNH$_2$-x wt. % NiO composites (x = 0, 1, 3, 5, 10 or 15) were prepared by ball milling (Retsch PM 400, Arzberg, Germany) at 200 rpm under Ar for 2 h. The ball-to-sample weight ratio was 200:1. All samples were handled in a glove box (MABRAUN, Munich, Germany) filled with argon (H$_2$O < 0.01 ppm; O$_2$ < 0.01 ppm) in order to avoid H$_2$O and O$_2$ contamination.
2.2. Sample Characterization

The dehydrogenation properties of the samples were measured using a pressure composition temperature system (PCT) (pro-2000, Setaram, Lyon, France). The samples were heated from room temperature to 300 °C at a rate of 2 °C/min under N₂ flow. For the isothermal dehydrogenation, the sample was quickly heated to the desired temperature. The gas quantities produced were analyzed using a temperature programmed desorption (TPD, Quantachrome, FL, USA) system equipped with a mass spectrometer (MS, GAM-200, InProcess Instruments, Bremen, Germany). The samples were heated from room temperature to 400 °C at a rate of 5 °C/min by using pure He as the carrier gas.

The phase structures of the samples were characterized using a powder X-ray diffractometer (XRD, Bruker, Karlsruhe, Germany) (Cu Kα, 40 KV, 40 mA) over the 2θ range of 10–90° in an increment of 0.01°. During the process of XRD measurements, a special sample holder with an airtight mantle was used to protect samples from H₂O and O₂ contamination. The morphology of the samples was observed using a scanning electron microscope (SEM, S-4800, Hitachi, Tokyo, Japan).

The Fourier-transform infrared spectroscopy (FTIR) analysis was performed using a Nicolet 6700 Fourier-transform infrared spectrometer (Thermo Scientific, Waltham, MA, USA). The powder samples and potassium bromide (KBr) powder were mixed in a 1:100 weight ratio compressed to form a pellet as a test sample. FTIR spectra were recorded from 800 cm⁻¹ to 4000 cm⁻¹.

The nitrogen adsorption and desorption isotherms of the as-prepared NiO and commercial NiO powder were measured at 77 K using nitrogen in a conventional volumetric technique with a Quantachrome Autosorb-iQ2 sorptometer (Quantachrome, FL, USA). Before being measured, the samples were outgassed at 100 °C in a vacuum for 8 h. The specific surface areas of the composites were calculated from the adsorption branch according to the Brunauer–Emmett–Teller (BET) method.

3. Results and Discussion

3.1. The Phase Structure and Morphology of the Synthesized NiO

Figure 1 shows the XRD pattern and SEM image of the as-prepared NiO sample. From Figure 1a, the diffraction peaks at the 2θ = 37.2°, 43.2°, 62.8°, 75.2°, and 79.4° are observed in as-prepared NiO and commercial NiO powder, which can be indexed as (111), (200), (311), (222) lattice planes, in agreement with the standard spectrum (JCPDS, No. 47-1049). In addition, the full width at half maximum of the as-prepared NiO is wider than that of commercial NiO powder, which indicates the smaller crystallite size. Meanwhile, the as-prepared NiO sample is highly purified, as no additional peaks can be observed on the XRD curve. Further SEM observations reveal that the as-prepared NiO sample shows a flower-like structure assembled by numerous nanosheets (see Figure 1b,c).

![Figure 1. X-ray diffractometer (XRD) pattern (a) and the Scanning Electron Microscope (SEM) images (b) and (c) of the as-synthesized NiO.](image)
In order to further investigate the structure of the as-prepared NiO, the sample nitrogen sorption isotherms are characterized (Figure 2). A distinct hysteresis loop can be observed from 0.4 to 1.0 P/P₀ of the as-prepared NiO, indicating the presence of mesopores. However, the commercial NiO powder has almost no pores. The BET specific surface area of the as-prepared NiO is 59.9 m²·g⁻¹. The as-prepared NiO maintains a larger specific surface area and mesopores, giving it better catalytic performance than NiO powder for dehydrogenation reactions.

3.2. Structural Characteristics of As-Milled Samples

The as-synthesized NiO was introduced into the LiBH₄-2LiNH₂ system by ball milling. Figure 3 shows the XRD patterns and FTIR measurements of the LiBH₄-2LiNH₂-x wt. % NiO composites (x = 0, 1, 3, 5, 10, or 15). It can be seen from Figure 3a that the LiBH₄-2LiNH₂ sample consists of the Li₄BN₃H₁₀ primary phase (α phase) and minor Li₂BNH₆ phase (β phase) [28]. After doping NiO, the Li₄BN₃H₁₀ phase still dominates the XRD profile, but the diffraction pattern of Li₂BNH₆ phase is not observed, indicating that the addition of NiO facilitates the formation of the Li₄BN₃H₁₀ phase. However, by increasing the content of NiO, the Li₄BN₃H₁₀ phase is gradually weakened. As the content of NiO increases to 5 wt. %, the characteristic diffraction peaks of NiO are clearly visible and are gradually enhanced by increasing the NiO content. Further FTIR measurements (see Figure 3b) indicate the characteristic B-H stretching modes (2376 and 2225 cm⁻¹), BH₂ deformation bands (1125 and 1077 cm⁻¹), and N-H stretches (3375 and 3245 cm⁻¹) [29] in FTIR curves, all of which confirm the presence of the Li₄BN₃H₁₀ phase.

Therefore, we conclude that the Li₄BN₃H₁₀ phase is formed by the reaction between LiBH₄ and LiNH₂ during the ball milling process of the LiBH₄-2LiNH₂-x wt. % NiO mixture. The NiO remains nearly unchanged.

Figure 3. XRD patterns (a) and FTIR spectra (b) of the LiBH₄-2LiNH₂-x wt. % NiO.
3.3. Dehydrogenation Behaviors of Doped NiO Samples

The dehydrogenation behaviors of doped NiO samples were evaluated by PCT. Figure 4 presents the curves of hydrogen-releasing LiBH$_4$-2LiNH$_2$-x wt. % NiO samples. From Figure 4, it is clear that doped NiO significantly improves the dehydrogenation properties of the LiBH$_4$-2LiNH$_2$ system. After adding 1 wt. % NiO, the onset dehydrogenation temperature was reduced to 140 °C. The onset dehydrogenation temperature was reduced by 60 °C in contrast with the pristine LiBH$_4$-2LiNH$_2$ sample. With the content of NiO increasing, the onset dehydrogenation temperature gradually decreases. However, as the content of NiO reaches 10 wt. %, the amount of hydrogen released decreases too. Therefore, the doped 5 wt. % NiO sample has the best dehydrogenation performance—the starting dehydrogenation temperature is only 90 °C, and decreases by about 110 °C compared with the pristine LiBH$_4$-2LiNH$_2$ sample, and approximately 10.5 wt. % of hydrogen is liberated when heated to 300 °C. Moreover, as doped NiO is greater than 5 wt. %, the dehydrogenation process is divided into two stages, occurring at 90–140 °C and 140–300 °C respectively, meaning that the doped NiO is able to change the dehydrogenation pathway, as has been previously reported [28]. Furthermore, the as-prepared NiO shows much better catalytic activity than that of the powder sample. Results demonstrate that the onset dehydrogenation temperature of the 5 wt. % as-prepared NiO sample is 55 °C lower than that of the 5 wt. % NiO powder-added LiBH$_4$-2LiNH$_2$ sample (Figure 5). This is possibly due to its high specific surface area and nanometer effect [30].

![Figure 4. PCT curves of the LiBH$_4$-2LiNH$_2$-x wt. % NiO samples.](image)

![Figure 5. PCT curves of 5 wt. % as-prepared NiO and 5 wt. %NiO powder-added LiBH$_4$-2LiNH$_2$ samples.](image)

For the LiBH$_4$-2LiNH$_2$-5 wt. % NiO sample, the isothermal dehydrogenation property has been studied at 90 °C and 150 °C respectively, as shown in Figure 6. From Figure 6, we can see that the
isothermal dehydrogenation property of the LiBH$_4$-2LiNH$_2$-NiO is significantly enhanced. Even at a temperature as low as 90 °C, the LiBH$_4$-2LiNH$_2$-5 wt. % NiO composites release 3.1 wt. % of hydrogen in 15 min. When heated to 150 °C, the LiBH$_4$-2LiNH$_2$-5 wt. % NiO sample releases 8.8 wt. % hydrogen in 15 min. For the pristine LiBH$_4$-2LiNH$_2$ sample, almost no hydrogen desorption is detected under the same conditions. These results show that LiBH$_4$-2LiNH$_2$-NiO have better dehydrogenation kinetics than the pristine LiBH$_4$-2LiNH$_2$.

![Figure 6](image)

**Figure 6.** Isothermal dehydrogenation curves of the LiBH$_4$-2LiNH$_2$-NiO.

### 3.4. MS Analysis

Figure 7 presents the TPD-MS curves of the LiBH$_4$-2LiNH$_2$-x wt. % NiO composites. As shown in Figure 7a, one strong dehydrogenation peak at 330 °C is observed in the TPD-MS curve of the pristine LiBH$_4$-2LiNH$_2$ system, which indicates a one-step reaction of dehydrogenation corresponding to the decomposition of the Li$_4$BN$_3$H$_{10}$. After doping NiO, two dehydrogenation peaks appear in their TPD-MS curves, and these peaks appear sooner than in the case of the LiBH$_4$-2LiNH$_2$ system. Because the first peak is very small, as doped NiO is 1 wt. %, its PCT curve only shows one stage (see Figure 4). This result is further evidence that the doped NiO can change the dehydrogenation pathway.

![Figure 7](image)

**Figure 7.** MS-H$_2$ signals (a) and NH$_3$ signals (b) of the as-milled LiBH$_4$-2LiNH$_2$-x wt. % NiO.

According to Figure 7b, the NH$_3$ by-product, which originates from the decomposition of the NH$_2$ group in the Li$_3$BN$_2$H$_8$ as previously reported [31], is still present during the dehydrogenation process, however its amounts are obviously reduced. It follows that doped NiO inhibits the release of NH$_3$ in the dehydrogenation process.

### 3.5. Dehydrogenation Mechanism of the LiBH$_4$-2LiNH$_2$-5 wt. % NiO

To clarify the chemical events occurring during the dehydrogenation process, XRD and FTIR examinations of LiBH$_4$-2LiNH$_2$-5 wt. % NiO composite at different dehydrogenation stages were
carried out, and their results are summarized in Figure 8. As shown in Figure 8a, the LiBH$_4$-2LiNH$_2$-5 wt. % NiO composite is mainly composed of two phases—that is, the Li$_4$BN$_3$H$_{10}$ [30] phase and the NiO phase. After dehydrogenation at 90 °C, it can be seen from the XRD pattern that the Li$_4$BN$_3$H$_{10}$ phase is still the primary phase; the characteristic peaks of NiO have disappeared, and a weaker peak of Ni appears at 44.5°, indicating that the NiO is reduced to the metallic Ni by the dehydrogenation process. According to its FTIR spectrum, the absorption peaks of the B-H stretching modes of the BH$_4$ group, the BH$_2$ deformation bands, and N-H stretches can still be observed, but clearly decreased. Meanwhile, a new absorption peak of the B-N vibration is observed from 1700 cm$^{-1}$ to 1750 cm$^{-1}$, which indicates the formation of Li$_3$BN$_2$ [32]. After dehydrogenation at 150 °C, the absorption peak of the B-N vibration becomes strong, indicating that the content of the compound containing a B-N bond is increasing. After full dehydrogenation at 300 °C, only the typical reflections of the Li$_3$BN$_2$ and Ni can be observed. Further FTIR analyses indicate that only the absorption peaks of the B-N bond are observed. Therefore, we speculate that the solid product is Li$_3$BN$_2$ after full dehydrogenation at 300 °C.

The obtained results demonstrate that the NiO is firstly reduced to Ni during the dehydrogenation process of LiBH$_4$-2LiNH$_2$-NiO. The newly formed metallic Ni works as an active catalytic species to reduce the dehydrogenation temperature of the LiBH$_4$-2LiNH$_2$-5 wt. % NiO composite. Similar results have also been observed for a directly Ni-doped Li-B-N-H system. The metallic Ni has high catalytic activity, and the B-N bonds can be easily created on the surface of metallic Ni [33]. As shown in Figure 9, the dehydrogenation properties of the Li-B-N-H system are improved by the doped NiO or metallic Ni. However, the onset dehydrogenation temperature of doped NiO is 85 °C lower than that of doped Ni, although their catalytic species are both Ni. This illustrates that while the effect of doped NiO is similar to that of doped Ni, the in situ produced Ni has better catalytic performance than that of the directly doped metallic Ni.

![Figure 8. XRD patterns (a) and FTIR spectra (b) of the dehydrogenated LiBH$_4$-2LiNH$_2$-5 wt. % NiO.](image)

![Figure 9. Non-isothermal dehydrogenation curves of the LiBH$_4$-2LiNH$_2$ with different additives.](image)
4. Conclusions

In this work, a flower-like NiO additive has been synthesized via a hydrothermal process, and doped into the LiBH4-2LiNH2 system in order to improve the hydrogen storage properties. The results indicated that by doping a small amount of NiO, the onset temperature of the LiBH4-2LiNH2 system can be reduced significantly, and the dehydrogenation kinetics can be enhanced. The LiBH4-2LiNH2-5 wt. % NiO composite exhibited optimal hydrogen storage properties, with the sample releasing approximately 10.5 wt. % hydrogen below 300 °C. The onset dehydrogenation temperature of the composite with an additive was only 90 °C, which was 110 °C lower than that of LiBH4-2LiNH2. The isothermal dehydrogenation indicated that the LiBH4-2LiNH2-5 wt. % NiO released 8.8 wt. % hydrogen within 15 min at 150 °C. Moreover, the LiBH4-2LiNH2-5 wt. % NiO exhibited a two-stage dehydrogenation process, indicating that the dehydrogenation pathway had changed. The NiO was reduced to Ni at the first stage of the dehydrogenation process, which worked as an active catalytic species for the remainder of the dehydrogenation process. The MS analyses showed that doping NiO can inhibit the release of NH3 in the process of dehydrogenation.

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