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Improved dehydrogenation performance of LiBH$_4$ by confining into porous TiO$_2$ micro-tubes

Huiqiao Liu, Lifang Jiao*, Yanping Zhao, Kangzhe Cao, Yongchang Liu, Yijing Wang, Huatang Yuan

Porous TiO$_2$ micro-tubes were fabricated by solvothermal method and the effect of TiO$_2$ micro-tubes on hydrogen desorption properties of LiBH$_4$ was systematically investigated. It was confirmed that LiBH$_4$ nanoparticles were successfully incorporated into these TiO$_2$ scaffolds via a chemical impregnation method. It was revealed by results of TPD, PCT and DSC that both lowering the desorption temperature and improving kinetics of desorption rate were owing to the synergistic effects of nanoconfinement and destabilization of TiO$_2$. The LiBH$_4$@2TiO$_2$ mixture (the preparation mass ratio is 1:2) started to release hydrogen at 180 °C, and the apparent activation energy (Ea) had been reduced from 146 kJ/mol (pure LiBH$_4$) to 121.9 kJ/mol. And it is interesting that the onset desorption temperature of LiBH$_4$@3TiO$_2$ composite was below 100 °C, reduced by about 300 °C compared to that of pure LiBH$_4$, which was lower than most of the current studies about LiBH$_4$.

1 Introduction

Hydrogen, due to its clean combustion and potentially renewable nature, has been regarded as a promising energy source. However, hydrogen storage is one of the most challenging barriers to realize the widespread commercialization of hydrogen-fueled vehicles.$^1$ Recently, complex hydrides, such as alanates (AlH$_3$)$_2$, amides (NH$_2$)$_2$, and borohydrides (BH$_3$)$_2$ have been investigated intensively because of their high hydrogen content and their associated use for hydrogen storage. Among these complex hydrides, lithium borohydride has a gravimetric capacity of 18.5 wt% and may be a promising candidate for onboard applications. However, it is too thermodynamically stable to decompose at ambient condition and reversibility requires pressures too high for practical applications.$^{11}$ According to the literature,$^{24}$ the transition temperature of LiBH$_4$ from the orthorhombic to the hexagonal is around 110 °C and the melting transition is about 270 °C. When heated to 600 °C, the following reaction occurs:

$$\text{LiBH}_4 \rightarrow \text{LiH} + \text{B} + \frac{3}{2}\text{H}_2$$

Several methods have been adopted to improve the dehydrogenation properties of LiBH$_4$. Doping additives, such as metal oxides, halides, hydrides and amides, has been focused to lower the dehydrogenation temperature of LiBH$_4$.$^{12-16}$ Yu and co-workers added SiO$_2$ to LiBH$_4$, showing that the addition of SiO$_2$ to LiBH$_4$ lowered the hydrogen desorption temperatures significantly.$^{17}$ It is reported by Kyle Crosby. that the onset dehydrogenation temperature of LiBH$_4$ was reduced to below 300 °C after ball milling with MgH$_2$,$^{18}$ and according to Chen’s work,$^{19}$ direct hydrogen liberation from the interaction of LiBH$_4$ and NH$_3$ was to be 17.8 wt% in the temperature range from 135 °C to 250 °C with the assistance of Co catalyst.

There were also some researchers attempting to reduce the size of materials to nanoscales to alter the kinetics and thermodynamics of hydrogen storage materials.$^{20, 21}$ However, the practical application of this approach can be limited by growth and agglomeration of particles during cycling. Recent literature reports showed that confining the hydrogen storage material in a scaffold host was beneficial. In this way, grain growth and particle agglomeration can be limited effectively.
during cycling. What’s more, fast kinetics may occur due to shorter diffusion paths. According to Cahen et al., LiBH₄/carbon composites were obtained by impregnation of the carbon matrix with LiBH₄ solubilized within ethers, and LiBH₄/carbon composites showed excellent desorption kinetics with a hydrogen release of 3.4wt.% in 90 min at 300 °C. Peter Ngene et al. also investigated that the confined LiBH₄ had enhanced hydrogen desorption properties, which desorption starting at 150 °C.

However, it is a challenge to achieve the requirements of practical applications if the above methods were adopted separately. Here, we present a method that take advantage of the synergic action of nanoconfinement and destabilization to enhance the desorption performance of LiBH₄. During nanoconfinement process, the confined carrier itself can also act as the destabilization agent. And it can not only inhibit the growth and agglomeration of particles, but also give full play to destabilization effects of TiO₂. So this method has a great potential to improve the dehydrogenation of hydrides. In this report, we synthesized porous TiO₂ microtubes and successfully confined LiBH₄ nanoparticles within these scaffolds, hoping to take advantage of synergistic effect of nanoconfinement and destabilization effects of TiO₂ to improve the dehydrogenate properties of LiBH₄. In addition, the dehydrogenation performances and mechanism were investigated.

2. Experimental Method

LiBH₄ (95%) was purchased from Acros, TiOSO₄ (99.7%), glycerol (99%), ethyl ether (99%) and tetrahydrofuran (THF, 99.8%) were purchased from Guangfu technology company of Tianjin. All the other reagents were used as received besides THF need to be distilled.

Preparation of TiO₂ micro-tubes

Porous TiO₂ micro-tubes were synthesized via a solvothermal method according to the previous procedures. In a typical synthesis, 0.3120 g TiOSO₄ was added into a solvent containing 30 ml of ethanol, 15 ml of glycerol and 15 ml of ethyl ether. After stirring for 1 h, the solution was transferred into a 100 ml Teflon-lined stainless steel autoclave and maintained at 110 °C for 48 h for a hydrothermal reaction. The resulted white precipitate was centrifuged, washed thoroughly with distilled water and anhydrous alcohol, and then dried in a vacuum oven at 80 °C overnight, followed by a further thermal treatment at 550 °C in an air atmosphere for 6 h.

Preparation of LiBH₄@xTiO₂ composites

To prepare LiBH₄@TiO₂ (the preparation mass ratio is 1:1), 0.200 g of LiBH₄ was dissolved in anhydrous THF with the ratio of 2 ml THF/0.1 g LiBH₄. After full dissolution, the solution was injected into a three nected-flash with TiO₂ put in advance and the TiO₂ was vacuum treatment ahead of time. The whole reaction unit was attached to a Schlenk line. After stirring for 6 h, the mixture was treated by heating to remove the THF residue. All handling of the samples were carried out in the glove box (Mikrouna Co., China) under purified argon atmosphere (H₂<1ppm; O₂<1ppm). The other LiBH₄@xTiO₂ (x=2, 3) composites were prepared in the same way. As a control sample, pure TiO₂ was also disposed by the same method.

Characterization

The phase structure and morphology of the materials were characterized by X-ray diffraction (XRD, Rigaku D/Max-2500, Cu Kα radiation), scanning electron microscopy (SEM, Hitachi X-650) and transmission electron microscopy (TEM Tecnai 20). X-ray diffraction (XRD) patterns were recorded at a scanning rate of 4° min⁻¹ in a 20 range of 10° to 80° under identical conditions. For XRD studies, all the nanocomposite samples were smeared on a glass slide in an argon glove box and then covered with parafilm tape for the avoidance of moisture and oxygen contact during the measurement. N₂ adsorption-desorption isotherms were measured with Quantachrome Instruments (NoVA 2200e) and the N₂ desorption temperature was 50°C. The pore size distributions were obtained from the adsorption branches of the isotherms using the Barrette-Joyner-Halenda (BJH) method and the surface areas were calculated by the Brunauer-Emmett-Teller (BET) method. FT-IR spectra were collected at room temperature via a FT-IR-650 spectrometer (Tianjin Gangdong) at a resolution of 4 cm⁻¹. X-ray photoelectron spectrometer (XPS, PHI 5000 Versaprobe, ULVAC PHI) was also used to characterize the dehydrogenated materials. The actual loadings of LiBH₄ in the resulted LiBH₄@xTiO₂ samples were deduced from the measurements of Li contents through inductively coupled plasma atomic emission spectroscopy (ICP-AES) using a USA Thermo Jarrel-Ash Corp instrument. The dehydrogenation behaviors of the samples were measured under flowing argon (about 35.0 ml min⁻¹) in a home-made temperature programmed desorption (TPD) system at a ramping rate of 2 °C min⁻¹ in the temperature range from 30 °C to 600 °C. Kinetics performances were examined by Sieverts-type isothermal measurement at different temperatures using a volumetric method. DSC analysis was conducted on TA instruments to obtain the activation energy of the samples.

3. Results and discussion

Structural and morphology characterization

The morphologies of the as-prepared TiO₂ and LiBH₄@TiO₂ composites were demonstrated in Fig. 1. Fig. 1a gives an overall view of TiO₂ microtubes, of which the walls are made of interconnected particles. And large numbers of mesopores also present (see Fig. 1b). It is this unique porous structure that provides the possibility of confining LiBH₄ nanoparticles. From Fig. 1c, the outer and inner diameters of the tubular materials are measured to be around 1 μm and 0.8 μm, respectively. While, as it can be seen from the TEM of LiBH₄@TiO₂ composite displayed in Fig. 1e, the micro-tube structure still exists and the pipe thickness increases to 0.5 μm, which can be
attributed to the appearance of LiBH₄ nanoparticles inside and outside the porous tube walls. The fact that TiO₂ frameworks are not destroyed during the nanoconfinement process indicating that it is feasible to choose this scaffold as confined carrier. From the HR-TEM image (Fig. 1d) taken from the selected area, the spacing of the lattice fringes is calculated to be 0.35 nm, corresponding well to the d-spacing for the (101) plane of TiO₂ anatase phase. While, except the above lattice fringes, a weak lattice fringe of 0.164 nm is also measured among LiBH₄@TiO₂ composite as Fig. 1f presents. Interestingly, these lattice fringes are completely consistent with the (300) planes of tetragonal LiBH₄. What’s more, those lattice fringes distribute among TiO₂ nanoparticles. It is well verified that the LiBH₄ granules are confined into porous TiO₂ tube walls.

To further demonstrate the confinement of TiO₂ carriers, the pore size distributions, pore volumes and BET surface area of LiBH₄@xTiO₂ composites and pure TiO₂ are conducted and display in Fig. S1 of supporting information, and the relative values are listed in table 1. From the figures we can see that when incorporated by LiBH₄ nanoparticles, the pore diameter, pore volume and BET surface area of TiO₂ all appear declining trends. With increasing amount of LiBH₄ in the mixture, the pore sizes of composites gradually decreasing. So it can be concluded that a part of LiBH₄ particles have been incorporated into TiO₂ micro-tubes.

Table 1 Values of pore diameter, pore volume and BET surface area of TiO₂ and LiBH₄@xTiO₂ samples

<table>
<thead>
<tr>
<th>Samples</th>
<th>Pore Diameter (nm)</th>
<th>Pore Volume (cm³/g)</th>
<th>BET surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiBH₄@TiO₂</td>
<td>3.80</td>
<td>0.030</td>
<td>5.4</td>
</tr>
<tr>
<td>LiBH₄@2TiO₂</td>
<td>3.82</td>
<td>0.062</td>
<td>11.0</td>
</tr>
<tr>
<td>LiBH₄@3TiO₂</td>
<td>7.66</td>
<td>0.218</td>
<td>76.8</td>
</tr>
<tr>
<td>TiO₂</td>
<td>7.79</td>
<td>0.258</td>
<td>95.1</td>
</tr>
</tbody>
</table>

Fig. 2 X-ray diffraction patterns of (a) as-prepared TiO₂, (b) LiBH₄@TiO₂, (c) LiBH₄@2TiO₂, and (d) LiBH₄@3TiO₂ composites.

LiBH₄@xTiO₂ composites and pure TiO₂ are conducted and display in Fig. S1 of supporting information, and the relative values are listed in table 1. From the figures we can see that when incorporated by LiBH₄ nanoparticles, the pore diameter, pore volume and BET surface area of TiO₂ all appear declining trends. With increasing amount of LiBH₄ in the mixture, the pore sizes of composites gradually decreasing. So it can be concluded that a part of LiBH₄ particles have been incorporated into TiO₂ micro-tubes.

Fig. 2 represents the powder X-ray diffraction patterns of the as-prepared TiO₂ and LiBH₄@xTiO₂. The phase of the as-prepared TiO₂ can be indexed to anatase (JCPDS 1(562), indicating that a pure phase of TiO₂ has been obtained from the original material of TiOSO₄ by a solvothermal method. The diffraction peaks of all LiBH₄@xTiO₂ composites bear similar to those of pure TiO₂. According to Peter Ngene, no specific reflections of LiBH₄ indicates that the clusters are amorphous and present in TiO₂ micro-tubes.

Hydrogen desorption properties

Fig. 3 TPD dehydrogenation curves of (a) pure TiO₂, (b) LiBH₄@3TiO₂, (c) LiBH₄@2TiO₂, (d) LiBH₄@TiO₂ and (e) bulk LiBH₄.
Fig. 3 shows TPD curves of the LiBH₄@xTiO₂ composites, pure TiO₂ and bulk LiBH₄. From TPD curves of bulk LiBH₄ (see Fig. 3a), we can get that it shows multiple desorption peaks. The onset dehydrogenation temperature of bulk LiBH₄ is around 275 °C, close to its melting point, and the majority of the hydrogen is only released above 400 °C. While, compared with the multiple desorption peaks of pure LiBH₄, the composites of LiBH₄@xTiO₂ tend to be a unimodal pattern during dehydrogenation, especially for LiBH₄@2TiO₂. And the dehydrogenation temperatures of LiBH₄ decrease obviously. For LiBH₄@TiO₂ and LiBH₄@2TiO₂, the starting hydrogen release temperatures are around 193 °C and 180 °C, respectively, and the main dehydrogenation temperatures are around 290 °C. While only a broad peak at 50–150 °C appears in the TPD curves of LiBH₄@3TiO₂. When the amount of LiBH₄ is above 23 wt%, the pores of TiO₂ are fully filled, and naturally some bulk LiBH₄ is outside the pores. Certainly, an inferior peak around 440 °C is observed from the TPD dehydrogenation curve of LiBH₄@TiO₂, which is similar to that of bulk LiBH₄. In addition, there is a weak peak occurring at around 70 °C in Fig. 4. As reported by Guo et al., this peak may attribute to the volatilization of little THF residue in the sample. However, in our work, without dissolving in THF, the dehydrogenation curves of bulk LiBH₄ also appears the weak peak at about 70 °C. And we can’t observe any peaks from TPD curve of TiO₂ in Fig. 3a. Therefore, the weak peak of LiBH₄@xTiO₂ composites related neither to THF nor to TiO₂. It is corresponded to the phase transformation of LiBH₄.

The quantification of the total amount of hydrogen release evaluated is given in Fig. 4. As is shown in the insert chart of Fig. 4, due to the presence of TiO₂ in samples, the total amount of hydrogen desorbed from LiBH₄@xTiO₂ composites is far lower than pure LiBH₄. While, through the curves that hydrogen released from pure LiBH₄, we can see that the dehydrogenation rates of samples (LiBH₄@xTiO₂) gradually increase with the amount of TiO₂ from 0 to 3 below 150 °C. After heating to 150 °C, the dehydrogenation rate of LiBH₄@3TiO₂ slows down and the final hydrogen production is less than others. However, it is inspiring that most of materials start to release hydrogen around 200 °C. The hydrogen release characteristics of all the above samples are summarized in Table 2.

In order to investigate the kinetic properties of LiBH₄ in LiBH₄@xTiO₂ composites, the isothermal hydrogen desorption measurements are conducted. As it displays in Fig. 5, the hydrogen desorption rates are significantly higher for LiBH₄@xTiO₂ composites compared with pure LiBH₄, especially during the first 60 min of measurements. What’s more, with the increasing amount of TiO₂ in the composites, the dehydrogenation kinetic performances are gradually improved. It is noteworthy that LiBH₄ in LiBH₄@3TiO₂ composite reached the maximum dehydrogenation platform in 15 min at 310 °C, and LiBH₄ in LiBH₄@2TiO₂ composite finishes hydrogen desorption during the initial one hour. While, there are no obviously platforms for LiBH₄@TiO₂ composite and bulk LiBH₄ during the whole measurement time. Meanwhile, the dehydrogenation capacities of pure LiBH₄, LiBH₄@TiO₂, LiBH₄@2TiO₂ and LiBH₄@3TiO₂ in 60 min at 310 °C are 0.43 wt%, 1.00 wt%, 2.47 wt% and 0.71 wt%, respectively. The inferior desorption weights are related to the low content of LiBH₄ in the composites. But it is encouraging to see that

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature at the major H₂ release(°C)</th>
<th>Actual weight loadings of LiBH₄/wt%</th>
<th>Calculated H₂ released from LiBH₄ at 600 °C/wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiBH₄ bulk</td>
<td>294/445</td>
<td>100</td>
<td>13.7</td>
</tr>
<tr>
<td>LiBH₄@TiO₂</td>
<td>194/292</td>
<td>25.856</td>
<td>14.658</td>
</tr>
<tr>
<td>LiBH₄@2TiO₂</td>
<td>183/291</td>
<td>22.969</td>
<td>14.715</td>
</tr>
<tr>
<td>LiBH₄@3TiO₂</td>
<td>252/301</td>
<td>13.578</td>
<td>8.5</td>
</tr>
</tbody>
</table>

Fig. 4 Hydrogen weight loss of (a) TiO₂, (b) LiBH₄@3TiO₂, (c) LiBH₄@2TiO₂, (d) LiBH₄@TiO₂ and (e) pure LiBH₄ calculated H₂ released from LiBH₄ and from LiBH₄@xTiO₂ composites (inside chart) at 600 °C.

Fig. 5 Hydrogen release from (a) pure LiBH₄, (b) LiBH₄@TiO₂, (c) LiBH₄@2TiO₂, (d) LiBH₄@3TiO₂ at 310 °C.
LiBH₄ in LiBH₄@2TiO₂ composite shows a superior performance compared to other two composites. Considering both lower desorption temperature and higher hydrogen capacity, we choose LiBH₄@2TiO₂ for further investigations.

To investigate the effect of as-prepared TiO₂ on desorption rate of LiBH₄, experiments of LiBH₄@2TiO₂ sample dehydrogenated at 205 °C, 265 °C, 310 °C and 365 °C are operated respectively. From Fig. 6, we can project that as the temperature increase from 205 °C to 365 °C, the decomposition kinetics augment gradually, leading to the improvement in reactivity. 2.8 wt% of hydrogen is released from LiBH₄@2TiO₂ within 1 h at 365 °C, which corresponds to 10.8 wt% when calculated by pure LiBH₄.

To further shed light on the kinetics of LiBH₄@2TiO₂ sample, the apparent activation energy (Ea) related to the dehydrogenation is calculated according to the following equation (Kissinger method):

\[
\frac{d\ln(\beta/T_m^2)}{d(1/T_m)} = \frac{E_a}{R}
\]

Where, \( \beta \) is the heating rate, \( T_m \) is the absolute temperature for the maximum desorption rate and \( R \) is the gas constant. In addition, \( T_m \) is obtained using DSC measurements with the heating rates of 2, 5, 8, 10 °C min⁻¹, which display in Fig. S2 (supporting information). Fig. 7 shows the Kissinger plots of the dehydrogenation of LiBH₄@2TiO₂ composite. The activation energy (Ea) for the mixture is calculated to be 121.9 kJ/mol of first step and 122.9 kJ/mol of second step. These values are much lower than that of pure LiBH₄ (146 kJ/mol) in the literature,²⁵ which indicates that the synergistic effect between nanoconfinement and destabilization of TiO₂ has enhanced desorption kinetics of LiBH₄ greatly.

**Deduction of the dehydrogenation mechanism**

Fig. 8 displays the XRD patterns of LiBH₄@xTiO₂ composites after dehydrogenation at 600 °C. The materials with different mass ratios between TiO₂ and LiBH₄ have different diffraction peaks after dehydrogenation. For LiBH₄@TiO₂, the main peaks are attached to LiTiO₂. While, apart from the LiTiO₂ phase, there appears LiTi₂O₄ phase in the dehydrogenated products of LiBH₄@2TiO₂ composite. From above results, it can be inferred that during the hydrogen desorption process, following reactions may occur:

\[
\begin{align*}
\text{TiO}_2 + \text{LiBH}_4 & \rightarrow \text{LiTiO}_2 + \text{B} + 2\text{H}_2 \uparrow \quad (1) \\
2\text{TiO}_2 + \text{LiBH}_4 & \rightarrow 2\text{LiTi}_2\text{O}_4 + \text{B} + 2\text{H}_2 \uparrow \quad (2)
\end{align*}
\]

With the increasing amount of TiO₂, the final products are gradually altered from LiTiO₂ to LiTi₂O₄. When adding more amount of TiO₂ to the composite, taking LiBH₄@3TiO₂ for example, the ultimate products are the mixture of TiO₂ and LiTi₂O₄. Therefore, the main dehydrogenation product of LiBH₄@xTiO₂ composites is LiTi₂O₄.

In order to have a better understand of the effect of TiO₂ on the dehydrogenation process of LiBH₄, XRD patterns and FT-IR spectra of LiBH₄@2TiO₂ composite and its dehydrogenated
products at different temperatures are conducted and present in Fig. 9. In the FT-IR spectrum, typical B-H vibrations in LiBH$_4$ are observed at 2385, 2289, 2223, 1634 and 1124 cm$^{-1}$, confirming the emergence of LiBH$_4$ in the LiBH$_4$@2TiO$_2$ composite. Moreover, the absorbance intensities of B-H detected gradually become weak with the heating temperature rising and completely vanish when heating above 310 °C. Meanwhile, the XRD patterns of LiBH$_4$@2TiO$_2$ show different peaks after desorption at various temperatures. When heating at a lower temperature, taking 205 °C for example, Li$_{0.5}$TiO$_2$ is detected as the mean product. As temperature raises, the ultimate products are Li$_{0.3}$TiO$_2$ and LiTiO$_2$. In addition, a trace amount of Li$_2$O, TiB$_2$ and TiO can also be detected. The above results show that a redox reaction has taken place during the dehydrogenation process of LiBH$_4$@2TiO$_2$ composites. Chemical states of titanium are characterized by XPS for further investigation. As is shown in Fig. 10, the Ti2p$_{3/2}$ peak becomes asymmetric and shifts to lower banding energies with the increasing heating temperature. The Ti2p$_{3/2}$ peaks are range from 459.4 eV to 456.2 eV, which represent titanium species with oxidation states between +3 and +4, illustrating the local chemical environments of Ti have been significantly influenced by the emerged Li ions and the forming of Li$_4$TiO$_2$ phase due to the redox reaction.}

In summary, the dehydrogenation mechanism may be ascribed as following. First, the porous TiO$_2$ tube can act as carrier to confine LiBH$_4$, thus TiO$_2$ can not only contact directly to LiBH$_4$ granules, also inhibit the growth and agglomeration of particles. Then, when heating, LiBH$_4$ granules would react with the TiO$_2$ support that around them. The porous structure of TiO$_2$ can introduce a large amount of reaction nucleation sites and hydrogen diffusion channels for the dehydrogenation process. Simultaneously, the formation of Li-Ti oxide suggests that Ti$^{4+}$ has been reduced to lower valance state, and hydrogen released during this process. What’s more, the TiO$_2$ support can prevent the hydrogenation products from agglomeration during the whole dehydrogenation process, which may contribute to the improved desorption kinetics.

3 Conclusions

In this study, we successfully synthesized porous micro-tube structure TiO$_2$. Experiment results show that the frameworks are not destroyed when LiBH$_4$ incorporated into TiO$_2$ scaffold host via a chemical impregnation method, which indicate that choosing this scaffold as confined carrier is feasible. Simultaneously, the dehydrogenation properties of LiBH$_4$ are significantly enhanced after being confined into TiO$_2$ scaffold. The onset dehydrogenation temperature for LiBH$_4$@2TiO$_2$ is reduced to 180 °C, and the maximal desorption peak occurs at about 290 °C. Meanwhile, the dehydrogen temperature of LiBH$_4$@3TiO$_2$ is around 100 °C, which is much lower than that of the bulk LiBH$_4$. What’s more, the apparent activation (Ea) has reduced to 121.9 KJ/mol. And the desorption mechanism investigation of LiBH$_4$@2TiO$_2$ indicates that the products are ranged from Li$_{0.3}$TiO$_2$ to LiTiO$_2$ as heating temperature raises.

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Notes and References
