



Hydrogen storage properties of LiBH₄–Li₃AlH₆ composites

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ARTICLE INFO

Article history:

Received 5 September 2011

Received in revised form

12 December 2011

Accepted 13 December 2011

Available online 22 December 2011

Keywords:

Hydrogen storage materials

Complex hydrides

Hydrogen storage properties

Hydrogen

ABSTRACT

To improve the dehydrogenation properties of LiBH₄, a novel hydrogen storage system, LiBH₄–Li₃AlH₆, was synthesized by mechanical ball milling. The dehydrogenation/rehydrogenation properties of LiBH₄–Li₃AlH₆ (molar ratio: 1:1) composites were studied via thermogravimetry (TG), differential scanning calorimetry (DSC), mass spectral analysis (MS), powder X-ray diffraction (XRD), and Fourier transform infrared spectroscopy (FTIR). The experimental results show that the hydrogen desorption capacity reaches 8.5 wt% and that the whole dehydrogenation is a three-step process: (1) a decomposition reaction Li₃AlH₆ → 3LiH + Al + 3/2H₂, occurring at 160 °C; (2) formation of an intermediate product from 300 °C to 350 °C, and then subsequent transformation into Al, AlB₂, and H₂. (2LiBH₄ + Al → [Li₂B₂AlH₄] → x(AlB₂ + 2LiH + 3H₂) + (1 – x) [Li₂B₂AlH₄], (0 < x < 1)); and (3) final dehydrogenation of LiH + Al → LiAl + 1/2H₂, occurring at 415 °C, with sequential decomposition of the remaining intermediate ((1 – x)[Li₂B₂AlH₄] → (1 – x)(AlB₂ + 2LiH + 3H₂), (0 < x < 1)). Furthermore, the dehydrogenated products can be rehydrogenated to LiBH₄ at 8 MPa H₂ and 400 °C.

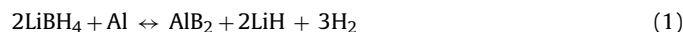
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1. Introduction

Hydrogen as an energy vector is taking more and more important action in the world energy systems because of its non-polluting characteristics. One of the key steps for the application of hydrogen energy is the development of appropriate hydrogen storage materials that have extremely high gravimetric and volumetric hydrogen storage densities, and perfect reversibility. In 2009, the U.S. Department of Energy (DOE) set final targets of 7.5 wt% (gravimetric hydrogen density) and 70 g H₂ L^{–1} (volumetric hydrogen density) for the vehicular application of hydrogen storage materials [1]. Traditional metal hydrides (e.g., LaNi₅, TiFe, TiMn₂) have relatively low hydrogen storage capacity, thus cannot meet the requirements of vehicular application of hydrogen storage systems. The research and development of new hydrogen storage materials with high hydrogen storage capacity and good reversibility is of great importance for the improvement of vehicular hydrogen storage systems.

Over the past few years, many studies have been focused on solid-state hydrogen storage materials using complex hydrides, including alanates, borohydrides, amide hydrides, and combinations thereof [2–21]. Among these hydrides, lithium borohydride

(LiBH₄) is a potential hydrogen storage material due to its large theoretical hydrogen capacity (18.5 wt%). Unfortunately, LiBH₄ is thermodynamically stable, the main evolution of hydrogen starts above 380 °C, and only half of the hydrogen can be released below 600 °C [18–20]. Furthermore, the conditions for forming LiBH₄ from its dehydrogenated products are rigorous (15.5 MPa H₂, 600 °C) [22]. Therefore, novel strategies and methods must be found to improve the hydrogen storage properties of LiBH₄. Some groups [23–25] proposed the destabilization of LiBH₄ by Al, and the results indicate that the decomposition of LiBH₄ starts at a lower temperature (320 °C) than pure LiBH₄ and that rehydrogenation can be achieved under conditions of 15 MPa H₂ and 350 °C (reaction (1)).



However, Al powders in the reaction easily form oxide layers which prevent Al from reacting with LiBH₄. For this reason, a LiBH₄–LiAlH₄ system was reported [26,27]. Furthermore, Li₃AlH₆ is a good candidate hydrogen storage material [28–30]. Unfortunately, to the best of our knowledge, few papers related to LiBH₄–Li₃AlH₆ system have been reported.

In the present work, the hydrogen storage performance of the LiBH₄–Li₃AlH₆ composite (molar ratio: 1:1) without any additives is investigated. The pathways of dehydrogenation/rehydrogenation and reversibility of LiBH₄–Li₃AlH₆ composite are discussed. The above studies would be helpful in improving the properties of Li–Al–B–H systems.

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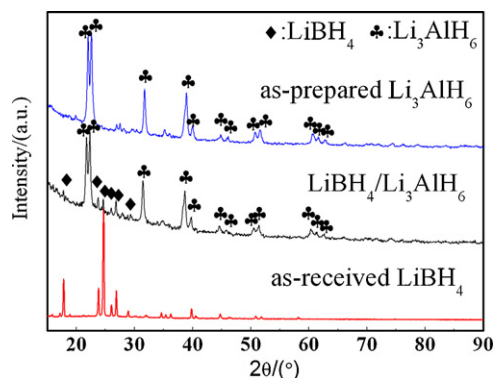


Fig. 1. XRD patterns of as-prepared Li_3AlH_6 , as-received LiBH_4 and $\text{LiBH}_4/\text{Li}_3\text{AlH}_6$.

2. Experimental

2.1. Sample preparation

Lithium borohydride (LiBH_4 , 95% powder, Acros Organics), lithium alanate (LiAlH_4 , 97% powder, Alfa Aesar), and lithium hydride (LiH , 98% powder, Alfa Aesar) were used as received without further purification. All sample storage and handling were performed in a Mikrouna glove box filled with high-purity argon (Ar , 99.999%) and controlled H_2O (<0.5 ppm) and O_2 (<0.1 ppm) concentrations. QM-3SP4 planetary ball mill is used to prepare Li_3AlH_6 and $\text{LiBH}_4/\text{Li}_3\text{AlH}_6$ composites.

Li_3AlH_6 was synthesized through the mechanochemical reaction between LiH and LiAlH_4 . LiH and LiAlH_4 , with a molar ratio of 2:1, were loaded into a 100-ml stainless milling pot (1Cr18Ni9Ti) with 25 steel balls (10 mm in diameter); the ball-to-powder weight ratio is about 45:1. Ball milling was performed for 6 h under a 0.1 MPa argon atmosphere, and the rotation speed is 500 rpm. $\text{LiBH}_4/\text{Li}_3\text{AlH}_6$ composites without any additives were prepared by ball milling a mixture of LiBH_4 and Li_3AlH_6 (molar ratio: 1:1) for 0.5 h under a 0.1 MPa argon atmosphere.

2.2. Sample characterization

Non-isothermal dehydrogenation was investigated using a Netzsch STA449F3 synchronous thermal analysis (thermogravimetry/differential scanning calorimetry (TG/DSC)) system equipped with a Netzsch QMS403C mass spectrometer (MS) at a heating rate of 5°C min^{-1} in a flow of high purity Ar (50 ml min^{-1}).

Investigations of dehydrogenating/hydrogenating reversibility were carried out on a Sieverts-type apparatus [31–33]. About 0.2 g of the sample was loaded into a stainless holder connected to a thermocouple to control the sample temperature. Hydrogenation measurements were performed under 8 MPa H_2 by heating from room temperature to 400°C at a rate of 5°C min^{-1} , and then holding at 400°C for 300 min.

Powder X-ray diffraction (XRD) analysis was carried out using a PANalytical X-ray diffractometer (X'Pert PRO, $\text{Cu-K}\alpha$, 3 kW). Samples were mounted onto a 1-mm-deep glass board in an Ar -filled glove box and sealed with an amorphous membrane to avoid oxidation during the XRD measurements.

Infrared measurements were performed on a Beaker-Vector22 Fourier transform infrared spectroscopy (FTIR) in transmission mode. The samples were pressed with potassium bromide (KBr) powder at a weight ratio of 1:99 to form a pellet. To avoid oxidation, a specially designed sample holder, which could fill with Ar , was used for FTIR measurements. The sample preparation and transformation are carried out in an Ar -filled glove box.

All the samples for XRD and FTIR measurements were cooled to room temperature after isothermal dehydrogenation under 0.01 MPa hydrogen at different temperatures ($T = 160, 220, 250, 300, 350, 415, 450, \text{ and } 500^\circ\text{C}$)

3. Results and discussion

3.1. Dehydrogenation performance

The XRD patterns of as-prepared Li_3AlH_6 , as-received LiBH_4 , and as-milled $\text{LiBH}_4/\text{Li}_3\text{AlH}_6$ are shown in Fig. 1, from which it can be seen that after LiBH_4 and Li_3AlH_6 (molar ratio: 1:1) are mixed and ball milled for 0.5 h, the characteristic diffraction peaks of LiBH_4 and Li_3AlH_6 remain, and no other diffraction peaks are detected. However, the intensity of the peaks of both LiBH_4 and Li_3AlH_6 decrease. This suggests that LiBH_4 and Li_3AlH_6 do not interact with each other during ball milling.

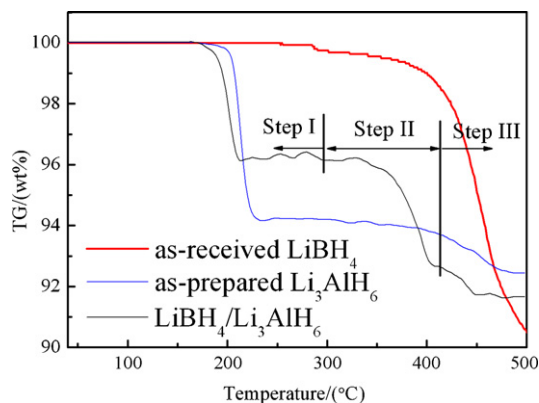


Fig. 2. The comparison of TG curves for as-received LiBH_4 , as-prepared Li_3AlH_6 and $\text{LiBH}_4/\text{Li}_3\text{AlH}_6$ composite at a heating rate of 5°C min^{-1} .

Fig. 2 shows the non-isothermal dehydrogenation performances of as-received LiBH_4 , as-prepared Li_3AlH_6 , and as-milled $\text{LiBH}_4/\text{Li}_3\text{AlH}_6$ heated from room temperature to 500°C at a heating rate of 5°C min^{-1} . The as-milled $\text{LiBH}_4/\text{Li}_3\text{AlH}_6$ clearly shows three-step hydrogen release. The first step begins at 160°C , which is 20°C lower than the initial decomposition temperature of Li_3AlH_6 . The particle size reduction may be one of the main reasons for the decrease. Approximately 3.9 wt% (Fig. 3) of hydrogen could be released before 215°C . In the second step, hydrogen is released over a larger temperature range from 300 to 420°C , and the hydrogen desorption capacity reaches 3.7 wt% (Fig. 3). A fluctuation is observed in the TG curve of $\text{LiBH}_4/\text{Li}_3\text{AlH}_6$ in the temperature range of $215\text{--}300^\circ\text{C}$, which is caused by the fusion of LiBH_4 . After this fluctuation, the TG curve of the $\text{LiBH}_4/\text{Li}_3\text{AlH}_6$ composite dipped, corresponding to the weight loss of the composite. This indicates that the second hydrogen-release step begin after the fluctuation at 300°C . After heating to 415°C , the third step of dehydrogenation occurs with 0.8 wt% hydrogen released.

Fig. 3 presents the TG/DSC/MS curves of the $\text{LiBH}_4/\text{Li}_3\text{AlH}_6$ composite at a heating rate of 5°C min^{-1} . In the DSC curve, five endothermic peaks during the dehydrogenation of the $\text{LiBH}_4/\text{Li}_3\text{AlH}_6$ composite are observed. The peak maxima are at 112, 205, 272, 395, and 445°C . Among them, peaks at 112 and 272°C correspond to the structural transition and melting reaction

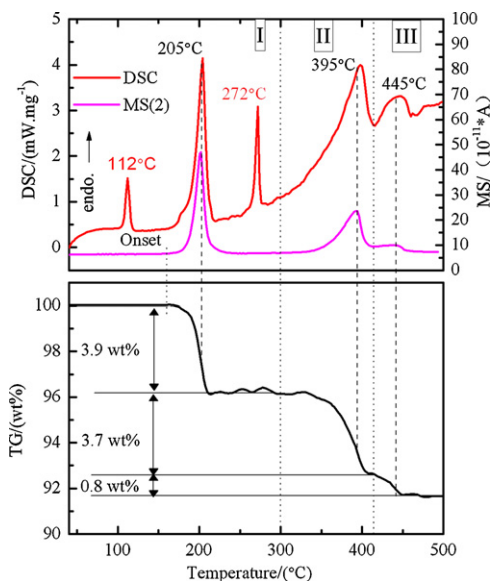


Fig. 3. TG/DSC/MS curves of $\text{LiBH}_4/\text{Li}_3\text{AlH}_6$ composite at a heating rate of 5°C min^{-1} .

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