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Investigation on reversible hydrogen storage properties of $Li_3AlH_6/2LiNH_2$ composite

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ABSTRACT

To obtain promising materials for hydrogen storage, a composite of Li_3AlH_6 and $LiNH_2$ with molar ratio of 1:2 was prepared by ball-milling, and its hydrogen storage properties were investigated. The microstructures of the composite after hydrogen desorption/absorption were characterized by XRD and FTIR analysis. The results show that 0.65 wt% H_2 was released during ball-milling process and 5.97 wt% H_2 was desorbed when the post-milled composite was heated from room temperature to 450 °C. The total hydrogen desorption capacity reached 6.62 wt%. And no NH_3 is detected by the mass spectrum (MS) analysis over dehydrogenation process. The hydrogen desorption process of $Li_3AlH_6/2LiNH_2$ composite occurs according to the following reaction: $Li_3AlH_6 + 2LiNH_2 \rightarrow Li_3AlN_2 + 2LiH + 4H_2$. Furthermore, 3.57 wt% H_2 can be reabsorbed at 400 °C and under hydrogen pressure of 110 bar.

1. Introduction

Hydrogen is a promising alternative energy carrier for hydrogen fuel cell electric vehicles. The key challenge for the practical application of hydrogen energy is hydrogen storage technology. Therefore, wide concerns have been concentrated on safe and efficient hydrogen storage systems [1–5]. Since Bogdanović [6] and Chen et al. [7] reported that metal alanates and metal nitrides were interesting hydrogen storage materials because of higher gravimetric hydrogen storage density, lots of studies on complex hydrides were pursued [8–10]. Because of light atomic weight, lithium related complex hydrides became one of the hot topics [11–18]. For example, $LiAlH_4$ was known to proceed in steps as follows during the thermal decomposition.

$$3LiAlH_4 \rightarrow Li_3AlH_6 + 2Al + 3H_2 \quad (1)$$

$$Li_3AlH_6 \rightarrow 3LiH + Al + 3/2H_2 \quad (2)$$

However, $LiAlH_4$ is not a reversible hydrogen storage material because of the nature of heat liberation in the hydrogen desorption process, even though it has higher hydrogen storage capacity than other alanates. Therefore, interest in mechanochemical interactions between complex hydrides has made great progress in the recent years. New complex compounds were formed by ball-milling the mixture of complex [13,14]. One of the best known mechanochemical compounds is Li_3AlH_6, which is synthesized from ball-milling the mixture of $LiAlH_4$/LiH (molar ratio = 1:2) [15]. The transformation reaction is as follows:

$$LiAlH_4 + 2LiH \rightarrow Li_3AlH_6 \quad (3)$$

In addition, among other complex hydrides, especially interesting one is $LiNH_2$/LiH system, which occurs in two steps as shown in Eq. (4):

$$LiNH_2 + 2LiH \rightarrow Li_2NH + LiH + H_2 \rightarrow Li_3N + 2H_2 \quad (4)$$

Recently, Lu et al. [16] and Kojima et al. [17] reported that $Li_3AlH_6/LiNH_2$ system could reversibly absorb/desorb hydrogen. Obviously, complex hydrides of amide–hydride systems could be brilliant as a hydrogen storage medium.

In this paper, we focus on the $Li_3AlH_6/LiNH_2$ system with the molar ratio of $Li_3AlH_6:LiNH_2 = 1:2$. The $Li_3AlH_6/2LiNH_2$ composite was prepared by ball-milling, and the hydrogen desorption and reversible absorption properties were investigated. In addition, the microstructures were analyzed by using X-ray diffraction (XRD), synchronous thermal analyses (TG/DSC) and Fourier infrared spectrometer (FTIR), and the hydrogen absorption/desorption mechanism was discussed.

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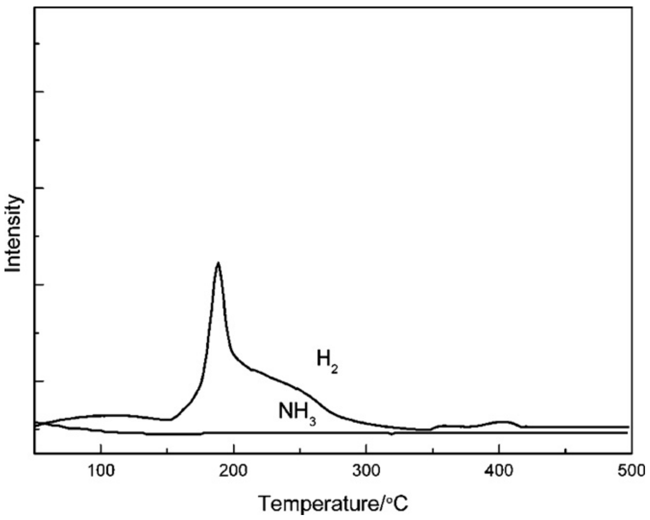

Fig. 1. MS measurement of Li_3AlH_6/2$LiNH_2$ composite during dehydriding process.

2. Experimental

2.1. Materials

$LiAlH_4$ (95% purity) and $LiNH_2$ (95% purity) were the product of Acros. LiH (99% purity) was purchased from Alfa. Li_3AlH_6 was synthesized at room temperature by ball-milling $LiAlH_4$ and LiH with a molar ratio of 1:2 for 24 h under 1 bar argon atmosphere. The structure of Li_3AlH_6 was confirmed by X-ray diffraction.

2.2. Ball-milling treatment

Ball-milling was conducted in a planetary mill (QM-3SP4, Nanjing) at 410 rpm with ball to sample weight ratio of 60:1. The prepared Li_3AlH_6 was ball-milled with $LiNH_2$ at a molar ratio of 1:2 for 48 min. The milling jar was equipped with a valve for measurement of the change of inside pressure when the milling was completed. At the same time, the released gas was flown through ammonia sensitive reagent ($Co(NO_3)_3$) to identify whether NH_3 was released or not.

2.3. Methods

The handling of the reactants and products was carried out in a glove box (MBRAUN) filled with a circulating pure argon to prevent air and moisture contamination. The hydrogen desorption properties of post-milled composite was characterized with a synchronous thermal analyses (thermogravimetry/differential scanning calorimetry/mass spectroscopy (TG/DSC/MS). The temperature was raised gradually from room temperature to 450 °C at a rate of 5 °C/min. A home-made apparatus was used to investigate the dehydriding/hydriding reversibility of the composite. About 500 mg sample was loaded into a sample holder which was connected with a thermocouple to control the temperature of sample. Hydrogen absorption properties were carried out under conditions of 110 bar hydrogen pressure and 400 °C.

The microstructures of the samples were determined by a Rikagu D/Max-RA X-ray diffractometer with Cu Kα. The X-ray intensity was measured over a diffraction angle from 10° to 90° with a velocity of 0.02° per step. To avoid oxidation, a specially designed sample holder, which could be filled with Ar, was used for XRD measurements. A Bruker Vector 22 Fourier infrared spectrometer (FTIR, Germany, using sample pellets made with KBr) was used for the characterization of N–H vibrations, and transmission mode was adopted.

3. Results and discussion

3.1. Thermal decomposition of Li_3AlH_6/2$LiNH_2$ composite

NH_3 release is a serious matter in case of using amides as hydrogen storage medium, because NH_3 not only would lower the hydrogen storage capacity of the system, but also would lead to the possible changes in stoichiometry, which would be disadvantage to the system reversibility. In the present work, the thermal decomposition of the ball-milled Li_3AlH_6/2$LiNH_2$ composite was characterized by TG/DSC/MS, in which mass spectra was used to identify the release of NH_3. Fig. 1 is the curves obtained from MS during the hydrogen desorption process. It is clear that no NH_3 was detected.

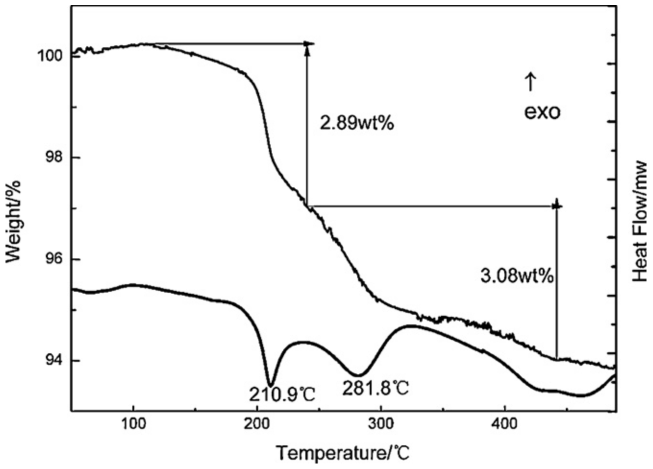

Fig. 2. TG and DSC curves of post-milled Li_3AlH_6/2$LiNH_2$ composite.

Fig. 2 shows the TG and DSC curves of the post-milled Li_3AlH_6/2$LiNH_2$ composite. It can be seen from Fig. 2 that a total weight loss of 5.97 wt% occurs when the composite was heated from room temperature to 450 °C. This weight loss is related to the endothermic peaks in DSC curve. The hydrogen desorption process of Li_3AlH_6/2$LiNH_2$ composite proceeded in two stages: (a) a low temperature stage, from 110 to 240 °C, accompanied by the release of 2.89 wt% H_2, and (b) a high temperature stage, from 240 to 450 °C, during which 3.08 wt% of H_2 is released. In the ball-milling process, 0.65 wt% hydrogen was desorbed and no NH_3 was detected by $Co(NO_3)_3$ reagent. In total, 6.62 wt% H_2 are evolved from the Li_3AlH_6/2$LiNH_2$ composite.

Fig. 3 shows the XRD patterns of Li_3AlH_6/2$LiNH_2$ composite in different hydrogen desorption stages. It can be seen that the post-milled composite mainly consists of the starting chemicals, Li_3AlH_6 and $LiNH_2$. When the post-milled composite was heated to 300 °C, Li_3AlH_6 and $LiNH_2$ phases disappeared, while LiH and an uncertainly phase appeared. When the composite was heated to 450 °C, the final phase after dehydring were Li_3AlN_2 and LiH.

From the TG/DSC analysis, it can be seen that hydrogen liberation occurred in two stages, and nearly equal amount of H_2 were released in the first and second stages. Xiong et al. [18] reported that [$Li_3AlN_2H_4$] was formed as an intermediate prod-

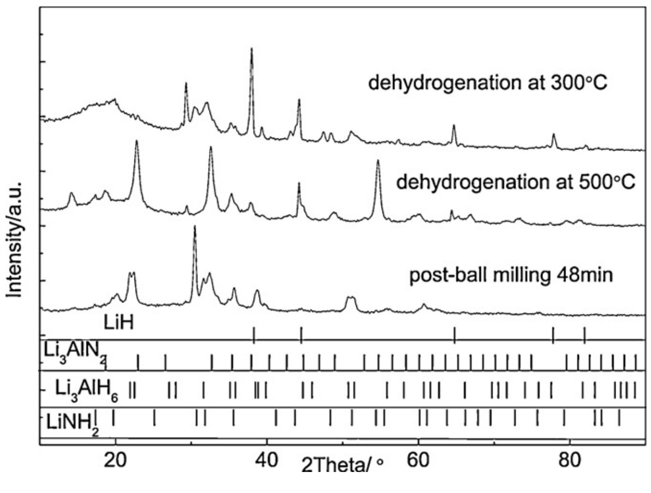

Fig. 3. XRD patterns of Li_3AlH_6/2$LiNH_2$ composite at different hydrogen desorption stages.