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Effect of microwave irradiation on the hydrogen desorption properties of $MgH_2/LiBH_4$ composite

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ABSTRACT

The effect of microwave irradiation on the hydrogen desorption properties of $MgH_2 + xLiBH_4$ ($x = 0–30$ wt%) composite was systematically investigated. The results show that the composite can be heated rapidly with the addition of $LiBH_4$ by microwave heating which brings about the fast dehydrogenation of MgH_2. The heating rate of the samples depends on the content of $LiBH_4$ and the microwave power, because $LiBH_4$ acts as a microwave absorber above 107 °C. Isothermal kinetic results showed that the amount of hydrogen released from MgH_2 + 10 wt% $LiBH_4$ under microwave is 5 times more than that of under conventional heating at 300 °C in 30 min. After five cycles of hydrogen sorption at 350 °C, the sample can be heated even more rapidly by microwave heating. These results demonstrate that the microwave heating is an effective technology to improve the hydrogen desorption kinetics of the $MgH_2/LiBH_4$ composite with high energy efficiency. Causes for the improved microwave heating were discussed and a potential mechanism was proposed.

1. Introduction

Considering the imperious requirements of energy sustainability and environmental protection, human are devoting themselves to exploit the high efficiency usage of hydrogen energy. Hydrogen storage is an important link of the hydrogen energy utilization. As magnesium (Mg) is an abundant element in the earth's crust, magnesium based solid hydrogen storage materials which have the properties of light weight, low price, and large hydrogen storage capacity are considered to be the most promising solid hydrogen storage media [1,2]. However, high dehydrogenation temperature and relatively slow absorption and desorption dynamics make it unsuitable for practical application. In order to overcome these shortcomings, for a long time, numerous modification research have been carried out. One main method is the mechanical alloying method, which had been shown to be an effective way of activating or improving the hydrogen sorption properties of Mg [3–5]. Another effective method is to mix different metal additives with Mg, such as transition metals [6], transition metal oxides and halide [7,8] and various forms of carbon [9,10]. Special significantly, by addition of only 0.2–0.5 mol% Nb_2O_5 [11], full desorption of MgH_2 could be obtained within 90 s at 300 °C. Thus Nb or its oxide was often applied as catalysts to promote the hydrogen sorption in MgH_2 [12]. Recently, one promising hydrogen storage system has been proposed according to the interaction between MgH_2 and light complex hydrides $LiBH_4$ [13–33]. Vajo et al. [13] have demonstrated that $LiBH_4$ can be destabilized by MgH_2 via the formation of MgB_2 in the dehydrogenation process under appropriate hydrogen back pressure. Although the mixture of $LiBH_4$ and MgH_2 in a 2 : 1 mole ratio constitutes a promising system for hydrogen storage, its kinetics is too slow and its thermodynamics also requires further destabilization. Many strategies have been developed to improve the properties of the system of $2LiBH_4–MgH_2$ by reacting with other metal hydrides, like Mg_2NiH_4 [20], LaH_2 [21,22], CaH_2 [23], and $Ca(BH_4)_2$ [24], by catalyst doping such as TiF_3 [25], NbF_5 [26–28], $NiCl_2$ [29], and Mo_2S [30], and by nano-confinement using scaffolds such as resorcinol–furfural carbon aerogel scaffold [31], resorcinole–formaldehyde aerogel scaffolds [32], and active carbon [33]. On the other hand, it had been shown that the addition of small amount of $LiBH_4$ can significantly improve the hydrogen sorption performance of MgH_2 or Mg-based materials [15–19]. Johnson et al. [15] found that 10 mol.% $LiBH_4$ doped MgH_2 showed a superior hydrogen sorption kinetics to pure MgH_2. Similarly, Puszkiel and Gennari [17,18] reported that the composite of $Mg_{50}Ni$–10 mol.% $LiBH_4$ showed a hydrogen uptake of 7 wt.% H at 300 °C in just 300 s. However, Zeng et al. [34] found that the hydrogen desorption from catalyst doped MgH_2 is suppressed by the presence of $LiBH_4$ in the $MgH_2–2LiBH_4$ system, which would

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be caused by the H–H exchange phenomenon between MgH_2 and $LiBH_4$. Our previous work further confirmed that $LiBH_4$ played both positive and negative effects on the hydrogen sorption of MgH_2, which were mainly attributed to the more uniform powder mixture with smaller particle size playing the positive role and the H–H exchange between $LiBH_4$ and MgH_2 playing the negative role [35]. The negative effect of $LiBH_4$ on MgH_2 was also observed in $LiBH_4$–Mg_3La system [36] and $50MgH_2 + Ni + LiBH_4$ system [37]. Therefore, a new strategy is needed for the improvement of the hydrogen storage properties of Mg.

In recent years, the using of microwave radiation to improve hydrogen sorption performances of hydrogen storage materials becomes one of research focuses [38–41]. Microwave heating has a series of particular properties such as selective heating, quick heating rate, high heating efficiency, and so on. The effects of microwave heating can be divided into two kinds: thermal effects and non-thermal effects [42–44]. Nakamori et al. [40] studied the effect of single mode microwave radiation on the properties of metal hydride and complex borohydride. The study found that $LiBH_4$ could be rapidly heated by microwave irradiation above 107 °C which is the approximate temperature where the crystal transformation of $LiBH_4$ occurs [45]. Considering the rapid heating character of $LiBH_4$ under microwave and the favorable cycle performance of MgH_2, we added $LiBH_4$ into MgH_2 and studied the effect of microwave radiation on the $MgH_2/LiBH_4$ composite, so as to further improve the hydrogen storage performance of the system and make it more close to the practical application requirements.

2. Experimental

The starting materials, MgH_2 (98%) and $LiBH_4$ (99%) were purchased from Alfa-Aesar Co., Ltd. The composites of MgH_2 and $LiBH_4$ were ball milled for 2 h under 0.1 MPa Ar by a Fritsch planetary ball mill at a speed of 400 rpm. The milling vial was made of stainless steel with an interior volume of 80 cm^3 and the mass ratio of ball to powder was 20:1. In order to investigate the mechanism of microwave heating on the $MgH_2/LiBH_4$ composite, pure MgH_2, $LiBH_4$, B, MgB_2 and the composites of MgH_2 and B were also prepared by ball milling. The ball milling parameters were kept constant for all trails. The components of samples are listed in Table 1.

The dehydrogenation of the samples under microwave irradiation was carried out as follows: approximately 0.5 g of samples was placed in a crucible of BN which was placed in a hermetic Teflon container as shown in Fig. 1a. The container, which was equipped with a K-type thermocouple, air inlet and outlet, was inserted into the cavity of multi-mode microwave instrument (SYNO-THERM WG3/2.45). In order to investigate the effect of microwave irradiation on the hydrogen desorption properties of $MgH_2/LiBH_4$ composite, the isothermal desorption kinetics of the samples both under microwave heating and conventional electrical resistant heating were measured by using volumetric method as shown in Fig. 1b, where the desorbed hydrogen gas was collected and its volume was measured in the water trap, which consists of an inverted water-filled 500 mL graduated cylinder immersed in a water tray. The hydrogen sorption cycles of the samples were measured using automatic apparatus from SUZUKI HOKAN.CO., Ltd. The phase structures of the samples before and after microwave irradiation were examined using a D \ max-2550 X-ray diffractometer (XRD) with Cu Kα radiation. Samples were sealed with a polyvinylchloride membrane to avoid the oxidation during the XRD measurement. In order to detect the $LiBH_4$, the sample was examined using Fourier transform infrared spectrometer (FTIR) (Avatar 360 FT-IR, Nicolet, USA). The samples were diluted by KBr with a mass ratio of 1:100 (sample: KBr) and pressed into pellets for FT-IR analysis. To prevent powder oxidation, all handlings were performed in a glove box (MBraun Labstar) under high purity argon.

Table 1
Components of the samples.

Sample	Component
MH + 5LBH	MgH_2 + 5 wt%$LiBH_4$
MH + 10LBH	MgH_2 + 10 wt%$LiBH_4$
MH + 20LBH	MgH_2 + 20 wt%$LiBH_4$
MH + 30LBH	MgH_2 + 30 wt%$LiBH_4$
MH + 10LBH + 1NO	MgH_2 + 10 wt%$LiBH_4$ + 1 mol%Nb_2O_5
MH	MgH_2
MH + 30B	MgH_2 + 30 wt%B

3. Results and discussion

3.1. Effects of rapid heating by microwave irradiation

According to the report of Nakamori et al. [40], $LiBH_4$ can be heated rapidly under microwave above 107 °C due to its lattice transformation, while MgH_2 cannot be heated under microwave. We expect that the composite of MgH_2 and $LiBH_4$ can be heated under microwave due to the addition of $LiBH_4$. In order to study the optimal content of $LiBH_4$, the composites with different amount of $LiBH_4$ from 5 wt% to 30 wt% were heated under microwave with a constant power (400 W) for 30 min. For comparison, MgH_2 without addition of $LiBH_4$ and the crucible without any sample were also heated under same condition. The temperature curves of the samples under microwave with heating time are showed in Fig. 2. It can be seen that the empty crucible could be slowly heated up to 175 °C after 30 min microwave irradiation. The temperature curve of MgH_2 under microwave is almost same as that of the empty crucible, therefore, the temperature rising of pure MgH_2 highly possibly profits from the heating of crucible. However, the maximum temperature is still far below the hydrogen desorption temperature of MgH_2. For the samples with $LiBH_4$ addition, the heating rates at initial stage are slow, but when the temperature is higher than the lattice transformation temperature (around 107 °C) of $LiBH_4$, the composites are rapidly heated since $LiBH_4$ acts as a microwave absorbing phase. When the temperature is over 300 °C, the heating rate starts to decrease. This might be due to the start of hydrogen desorption reaction from MgH_2 during the microwave heating process, which is an endothermic reaction. After reaching the maximum, the temperatures of the composites become constant with some slight fluctuations, which mean that the decompositions of $LiBH_4$ and MgH_2 have been finished. In order to study the effect of $LiBH_4$ amount, the temperature curves below 300 °C were compared because MgH_2 started to decompose over 300 °C which obviously affected the temperature curves. A dependence of the heating rate on the content of $LiBH_4$ can be observed below 300 °C. As shown in Fig. 3a, below 107 °C the average heating rates are slow and increase slowly with the content of $LiBH_4$ increasing. When the temperatures are above 107 °C, the average heating rates become fast and increase significantly with the content of $LiBH_4$ increasing. For example, the heating rate increased by 54% and 147% with the content of $LiBH_4$ increasing from 5 wt% to 10 wt% and from 10 wt% to 20 wt%, respectively. But when the content of $LiBH_4$ increased further up to 30 wt%, the heating rate increased only 16% compared with that of 20 wt% $LiBH_4$, which means the effect of $LiBH_4$ amount on heating rate may become saturated. Except the sample MgH_2 + 5 wt% $LiBH_4$ (MH + 5LBH), all samples with $LiBH_4$ addition can be heated over 500 °C within 600 s. Considering the composite of MgH_2 with 10 wt% $LiBH_4$ has the best kinetic properties reported by previous paper [35] since larger amount of $LiBH_4$ could deteriorate the hydrogen desorption kinetics of MgH_2 owing to the H–H exchange between MgH_2 and $LiBH_4$ [34,35], we focus on the composite with 10 wt% $LiBH_4$ addition. It is noticed that our samples can be heated to 107 °C within 300 s, which is much shorter than the result reported by Nakamori et al. [40] where 60 min are needed to heat $LiBH_4$ to 107 °C under microwave irradiation. It may be due to the crucible of BN used in our work which can be heated to 107 °C within 300 s as shown in Fig. 2.

Fig. 4 shows XRD results of sample MgH_2 + 10 wt% $LiBH_4$ (MH + 10LBH) after ball milling and microwave heating respectively. After ball milling (Fig. 4a), the phases are mainly MgH_2, and the peaks of $LiBH_4$ are hardly observed due to its amorphization during ball milling. Fig. 4b shows XRD profile of the sample after microwave heating up to the highest temperature and holding for 2 min. The products are mainly composed of Li_3Mg_{17}