

## Catalytic effect of graphene on the hydrogen storage properties of Mg-Li alloy



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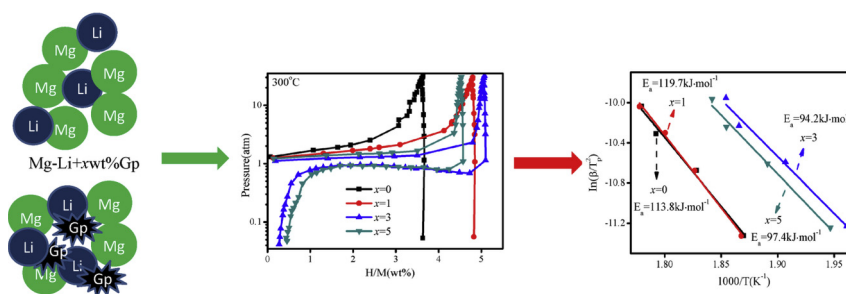
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### HIGHLIGHTS

- The onset dehydrogenation temperature for the Mg-Li-Gp composite is significantly lower than at of the Mg-Li alloy.
- Graphene can enhance the reversible hydrogen storage property of the Mg-Li alloy.
- The hydrogen storage thermodynamic property of the Mg-Li-Gp composite is better than that of the Mg-Li alloy.

### GRAPHICAL ABSTRACT



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### ABSTRACT

The Mg-Li-xgraphene(Gp) ( $x = 0, 1, 3, 5$ ) composites were synthesized by sintering and ball-milling, and the catalytic effect of the graphene on the hydrogen storage properties of the Mg-Li-xGp ( $x = 0, 1, 3, 5$ ) composites was investigated. Experimental results indicated that the addition of the graphene enhanced the reversible hydrogenation reaction of the Mg-Li alloy and reduced significantly the onset hydrogenation/dehydrogenation temperature of the Mg-Li alloy. For example, the reversible hydrogenation reaction occurred in the case of the Mg-Li-xGp ( $x = 3, 5$ ) composites at 300 °C, while it did not occur in the case of the Mg-Li alloy at the same temperature. The onset temperature of dehydrogenation for Mg-Li alloy was about 338 °C, by comparison, and the onset temperature of dehydrogenation for Mg-Li-xGp ( $x = 3, 5$ ) composites decreased to 276 °C. In addition, the Mg-Li-xGp ( $x = 1, 3, 5$ ) composites could release more than 90% of the hydrogen absorbed when heated at a rate of 2 °C/min from room temperature to 353 °C, while only 39% of the hydrogen absorbed in the Mg-Li alloy was released in the same condition, which is resulted from the decrease of the apparent activation energy ( $E_a$ ) of dehydrogenation for the Mg-Li alloy with the graphene addition. Graphene acts as a catalyst, thereby lowering the reaction barrier for dehydrogenation of the Mg-Li alloy, which in turn promotes the reversible hydrogenation/dehydrogenation reaction of the alloy.

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## 1. Introduction

Owing to its high hydrogen storage capacity (7.6 wt.%) and low cost,  $\text{MgH}_2$  is considered one of the most promising hydrogen storage materials. However, the relatively high dehydrogenation temperature ( $>350^\circ\text{C}$ ) and poor kinetic properties hinder its use in practical applications [1,2]. Therefore, to overcome these drawbacks, several methods have therefore been used to improve the poor thermodynamic properties of  $\text{MgH}_2$ . These methods included reducing the grain size [3–5], alloying with the metal or intermetallic compounds [6–8], doping with catalyst [9–13] and combining with complex hydride composites [14]. For example, the Mg nanocrystals of controllable size prepared by chemical reduction method could provide a simple route to significantly improved hydrogen sorption kinetics [5]. The hydrogen desorption temperature of a  $\text{LaCl}_3\text{-MgH}_2$  composite prepared via ball milling was significantly reduced and the hydrogen storage properties improved [7]. A Mg–5wt.% $\text{LaNi}_5$  nanocomposite exhibited excellent sorption kinetics, as evidenced by absorption, at  $200^\circ\text{C}$ , of 3.5 wt.% of  $\text{H}_2$  in  $<5$  min [8]. Santos et al. [9] prepared the  $\text{MgH}_2\text{+FeNb}$  nanocomposites by high-energy ball-milling and found that the FeNb with coarse granulates had an positive effective on the reversible hydrogen storage of the  $\text{MgH}_2$ . Furthermore, the addition of  $\text{NbH}_x$  nanoparticles could also significantly enhance the de/hydrogenation kinetics of  $\text{MgH}_2$  [11]. Shahi et al reported that  $\text{TiF}_3$  as a catalyst had a positive effect in improving the hydrogen storage property of  $\text{MgH}_2$ , the hydrogen desorption temperature for  $\text{MgH}_2\text{-TiF}_3$  was  $120^\circ\text{C}$  lower than that of the pristine ball-milled  $\text{MgH}_2$  [12]. Previous studies have reported that nanostructured Mg-based alloys exhibit excellent hydrogen storage properties, owing to their extremely high specific surface area and short diffusion paths [15,16]. Ball milling, as a high-energy operation process, constitutes an effective means of preparing Mg-based nanostructures. Ball milling with carbon material such as graphite [17–19], carbon nanotubes (CNT) [20–22] or graphene nanoplatelets (GNP) [13,23] had been considered an effective way to enhance the comprehensive properties for Mg or Mg-based alloys. Graphene, as a peculiar carbon material, has a unique atom-thick 2D structure, superior electrical conductivity, high specific surface and excellent mechanical properties [24,25]. With these particular inherent advantages, graphene can have a positive impact on performance of the Mg-based hydrogen storage alloy. In addition, Li is a promising hydrogen carrier, owing to its high hydrogen storage capacity (11.5 wt.%) and high chemical activity. This suggests that Mg-Li alloys may exhibit high hydrogen storage capacity. Therefore, in this study, a method to prepare Mg-Li alloys, via sintering and ball-milling, is developed and the catalytic effect of graphene on the hydrogen storage properties of Mg-Li alloys is investigated.

## 2. Experimental

Powders of Mg (purity  $>99.5\%$ , 300 mesh) and LiH ( $>99.9$  wt.%, 200 mesh), purchased from Alfa Aesar, were used as raw materials. The Mg and LiH powders were mixed in a molar ratio of 77:23 and compressed, for 5 min under a pressure of 20 MPa, into tablets. The tablets were then sintered at  $550^\circ\text{C}$ , for 2 h, in a high-vacuum resistance furnace and subsequently cooled with furnace temperature. The as-sintered samples were crushed into a powder and ball milled (planetary miller, QM-WX04), at 300 rpm and a ball-to-powder mass ratio of 40:1, for 100 h in n-heptane liquid. Afterwards, the as-milled powders were dried under argon atmosphere, mixed with xwt.% ( $x = 0,1,3,5$ ) of graphene (Analytical reagent), purchased from JCNANO Technologic Co. Ltd., and milled for another 35 h; the resulting samples are referred to as Mg-Li-xGp( $x = 0,1,3,5$ ) composites. The phase structures of these

composites were characterized via X-ray diffraction (XRD; Rigaku-3015) using Cu  $K\alpha$  radiation and a voltage and current of 40 kV and 200 mA, respectively. The samples were subjected to hydrogenation and dehydrogenation testing. For fully activated, the samples have been gone through three times of hydrogen absorption/desorption activation cycle before hydrogen storage property testing. The pressure composition isotherms (PCI) of the samples were performed on an automatic Sieverts-type apparatus under a hydrogen pressure of 35 atm at different temperature. A home-made Sievert-type apparatus was used to measure the hydrogen absorption/desorption properties. For temperature-programmed hydrogenation process, the samples were heated to  $380^\circ\text{C}$  with a heating rate of  $2^\circ\text{C}/\text{min}$  under a hydrogen pressure of 65 atm. Similarly, for the dehydrogenation process, the sample was heated up to  $380^\circ\text{C}$  with a heating rate of  $2^\circ\text{C}/\text{min}$  after the reactor was evacuated to 0.06 atm. Moreover, differential scanning calorimetry (DSC) measurements were performed on the samples, using a simultaneous thermal analyzer (Setaram Labsys Evo). All samples were well activated before testing.

## 3. Results and discussion

### 3.1. Phase structure

The XRD patterns of the Mg-Li-xGp( $x = 0,1,3,5$ ) composites are shown in Fig. 1. The Mg-Li-xGp( $x = 0,1,3,5$ ) composites mainly consisted of Mg phase (Fig. 1(a)). The graphene phase was detected only in the Mg-Li-5Gp sample with the addition of 5 wt.% graphene. Besides, the MgO phase was also detected in the XRD pattern, which resulted from the oxidation of Mg in ball milling process. It had been reported that Mg easy to be oxidized during the preparation process [26,27]. Such as the  $\text{MgB}_2$  bulk and ultrafine which synthesized by solid state synthesis using the Mg powders and the amorphous boron, the MgO also could be detected in the product. Diffraction peaks corresponding to Li were absent from the patterns, indicating that Li atoms diffused into the Mg matrix, leading to the formation of a Mg-Li solid solution (i.e., Mg(Li)). The hydrogenation/dehydrogenation reaction process and the mechanism governing this process were investigated via XRD analyses of the hydrogenated (Fig. 1(b)) and dehydrogenated (Fig. 1(c)) Mg-Li-xGp( $x = 0,1,3,5$ ) composites. During hydrogenation, the Mg phase in the Mg-Li-xGp( $x = 3,5$ ) composites was completely transformed to  $\text{MgH}_2$  (Fig. 1(b)). However, a part of Mg phase still remained unchanged in the hydrogenated Mg-Li-xGp( $x = 0,1$ ) composites, suggesting that Mg-Li-xGp( $x = 0,1$ ) composites uneasy to be hydrogenated when adding nothing or a small amount of graphene. The addition of appropriate amount of the graphene can promote the hydrogenation reaction of the Mg-Li alloy. Compared with Fig. 1(a), it can be seen from Fig. 1(c) that the two XRD patterns are identical, indicating that the structure of the non-hydrogenated Mg-Li-xGp( $x = 0,1,3,5$ ) composite was restored after the hydrogenation/dehydrogenation cycle. The reversible hydrogenation reaction for the Mg-Li-xGp( $x = 0,1,3,5$ ) composite can be expressed as  $\text{Mg(Li)} + \text{H}_2 \leftrightarrow \text{Mg(Li)H}_2$ .

Fig. 2 shows the SEM images of Mg-Li-xGp( $x = 0,1,3,5$ ) composites. It can be seen that the Mg-Li alloy particle size decreased as the graphene added. Especially, the Mg-Li-xGp( $x = 3,5$ ) composites exhibited a more homogeneous and smaller particle size compared to the Mg-Li-xGp( $x = 0,1$ ) composites. The addition of the graphene can reduce the agglomeration of the Mg-Li alloy particles and make the particles disperse more uniform during milling process.

### 3.2. Hydrogen storage property

Fig. 3 shows the PCI curves of the composites measured at

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