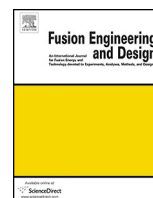




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# Improvement of the dehydrogenating kinetics of the $\text{Mg}(\text{NH}_2)_2/\text{LiH}$ materials by inducing $\text{LiBH}_4$

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### HIGHLIGHTS

- This work indicates that inducing 10 wt.%  $\text{LiBH}_4$  into the  $\text{Mg}(\text{NH}_2)_2/\text{LiH}$  mixture significantly improves the dehydrogenating kinetics. It has a near 40 times as large as the effect of the  $\text{Ti}_3\text{Cr}_3\text{V}_4$  nanoparticles catalyst under the 200 °C and 0.1 MPa dehydrogenating environment.
- Based on diffusion model, the dehydrogenating kinetic curve was fitted for illuminating the mechanism of dehydrogenation improvement.
- The mechanism is proposed that the eutectic reaction takes a big role in the catalysis process as the arising of nanorods inside of the matrix after several re-/dehydrogenation cycles.

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### ABSTRACT

The lightweight high-capacity Li-Mg-N-H system is a promising candidate for the hydrogen energy storage materials. Nevertheless, the slow dehydrogenating process limits its application. This work is focusing on the effect of  $\text{LiBH}_4$  on the dehydrogenating kinetics of the  $\text{Mg}(\text{NH}_2)_2/\text{LiH}$  mixture. It indicates that inducing 10 wt.%  $\text{LiBH}_4$  into the  $\text{Mg}(\text{NH}_2)_2/\text{LiH}$  mixture significantly improves the dehydrogenating kinetics. As a result, it has a near 40 times as large as the effect of the Ti alloy nanoparticles catalyst, under the 200 °C and 0.1 MPa dehydrogenating environment. Based on our previous dehydrogenating kinetics model, the mechanism of this improving effect of  $\text{LiBH}_4$  is discussed as well, which shows that the eutectic reaction takes a big role in the catalysis process as the arising of nanorods inside of the matrix after several re-/dehydrogenation cycles.

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## 1. Introduction

Complex hydrides become a promising candidate of hydrogen storage materials, due to its high capacity, accessible thermodynamics [1–10]. The emerging isotope effect may also cause interests in fusion energy field [11]. However, the dehydrogenation process requires more external energy. Usually, the dehydrogenating temperature is beyond 200 °C for the acceptable hydrogen release rate. The metal nitrides and alloy nanoparticles (NPs) were reported to affect the dehydrogenation process of Li-Mg-N-H system by activating the N–H bond and improving the hydrogen atom diffusion within the matrix [1,6,8,9]. However, the surface region is mainly focusing on the contact area, which is minority of materials [1]. Looking into the limiting point, much work was done to research the dehydrogenating mechanism, and found that the main limiting

steps were the active hydrogen ions ( $\text{H}^{\delta+}$ ) generating and diffusing processes during the dehydrogenating reaction in the complex hydrides, eg. Metal-N-H and Metal-Al-H systems [3,11,12], which was verified by the isotope effect in the hydrogen atom diffusion kinetics due to the mass difference. The reported TiCrV alloy NPs have a promising effect on the mass transport, but little effect on the  $\text{H}^{\delta+}$  generation for the Li-Mg-N-H system. The objective of this work is to find an effective catalyst, which will weaken the N–H bond and improving  $\text{H}^{\delta+}$  diffusion as well. It was expected to enhance significantly the dehydrogenating kinetics of Li-Mg-N-H system.

Gregory et al. obtained a quasi-equilibrium phase diagram between the  $\text{LiNH}_2$  and  $\text{LiBH}_4$ . [2]. There was an eutectic point at 20 wt.%  $\text{LiNH}_2$  and 150 °C condition, which means a liquid region between the  $\text{LiNH}_2/\text{LiBH}_4$  interface when temperature is beyond 150 °C. Adding  $\text{LiBH}_4$  into  $\text{LiNH}_2$  materials, it will be expected to have a more promising mass diffusion and thermal exchange [4,5]. Here, this work induced  $\text{LiBH}_4$  into  $\text{LiNH}_2/\text{MgH}_2$  mixing to a some extent for improving the dehydrogenating kinetics. Furthermore, by applying our previously established mechanism mathematical

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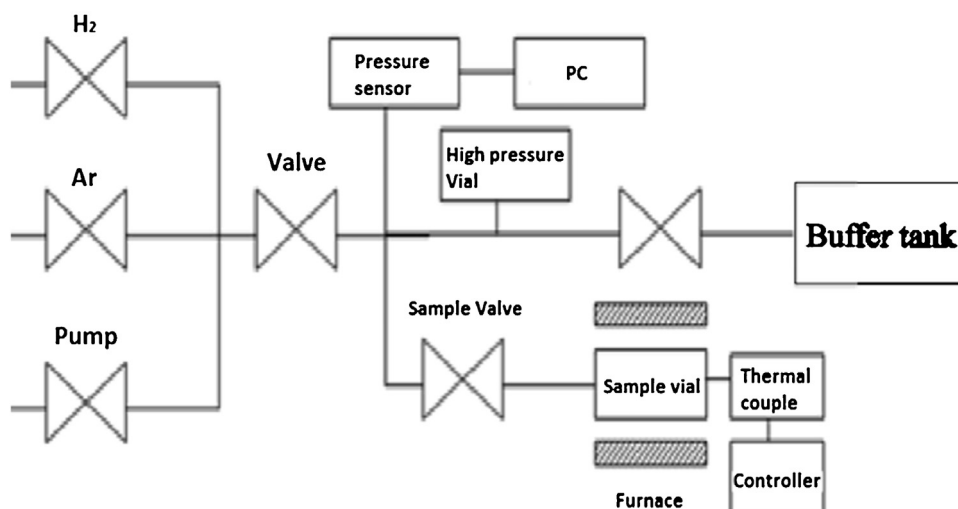


Fig. 1. Illustration for hydrogen storage property test system.

model to fit these dehydrogenation curves [10], the results will give the dehydrogenating kinetic formula and related mechanism.

## 2. Experimental

### 2.1. The $\text{LiNH}_2/\text{MgH}_2/\text{LiBH}_4$ mixture preparation

All materials used in the work were purchased from Sigma-Aldrich at hydrogen storage material level ( $\text{LiNH}_2$ , assay grade 95%,  $\text{MgH}_2$ , 99% and  $\text{LiBH}_4$ , >90%). The mixture of  $\text{MgH}_2/\text{LiNH}_2$  with a molar ratio of 1.1:2 was prepared in the argon filled glovebox as the target material when the effect of  $\text{LiBH}_4$  on the dehydrogenation kinetics of the mixture was investigated. The oxygen and moisture level was controlled below 10 ppm. 10 wt.%  $\text{LiBH}_4$  was added into the reference sample to check out the catalyst effect, which was prepared by a high energy milling machine (SPEX8000, China). The  $\text{LiNH}_2/\text{MgH}_2$  mixture doped with 10 wt.%  $\text{Ti}_3\text{Cr}_3\text{V}_4$  body centre cubic (BCC) alloy hydride was prepared as the reference material with a ball-milling method and the alloy NPs were uniformly distributed in the Li-Mg-N-H substrate verified by SEM and XRD methods. The  $\text{Ti}_3\text{Cr}_3\text{V}_4$  alloy was prepared by Magnetic Suspended Furnace in our group and then forming hydride prior to using as catalyst [13]. The milling vial was pumped down and then filled with 1 MPa pressure hydrogen. All the samples used in the work

were milling 24 h and kept at 200 °C under 5 MPa hydrogen exposure overnight before taking de-/rehydrogenation measurements. All the data was taken at the steady state after 5 de-/absorption cycles.

### 2.2. Dehydrogenation curve measurement

The dehydrogenating kinetics measurement was taken by volumetric method, as shown in Fig. 1. All vials and valves are made of 316L stainless steel. The furnace temperature was controlled at the accuracy of 0.5 °C level. The  $\text{H}_2$  and Ar used in measurement are a high purity of 99.99% level. All the dehydrogenation measurements were taken into a 0.1 MPa environment, which was achieved by balancing the sample vial and buffer tank volume ratio. In this work, two kind of temperature conditions were taken to dehydrogenation, eg 180 °C and 200 °C.

### 2.3. Material characteristics

For SEM measurement, the HITACHI S4800 was used to analyze the morphology of powder samples. The accelerate voltage of 30 kV was taken to obtain a high amplified picture.

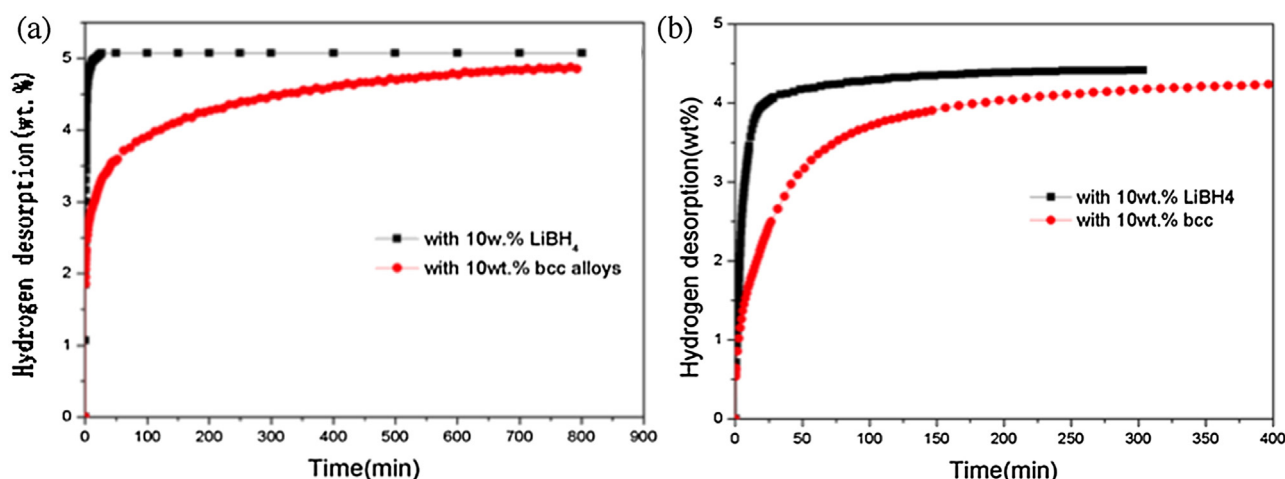


Fig. 2. (a) The contrast of the dehydrogenating kinetics of the samples with 10 wt.%  $\text{LiBH}_4$  and that of 10 wt.%  $\text{Ti}_3\text{Cr}_3\text{V}_4$  at 200 °C; (b) dehydrogenation at 180 °C.

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