



Experimental study on hydrogen storage properties of Li–Mg–N–H based tank



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ABSTRACT

Cylindrical lab-scale tank based on 98.0 g of the $\text{Mg}(\text{NH}_2)_2\text{-}2\text{LiH-}0.07\text{KOH}$ compacts was designed. Hydrogen storage properties of the tank, including bed temperature, hydrogen pressure and flow rate in the hydrogen absorption and desorption process were investigated under a variety of conditions. In the hydrogen absorption process of which the applied hydrogen pressure is 6.0 MPa, the central temperature of the hydride bed increases obviously from 453 K to 524 K. Furthermore, the increase of the applied hydrogen pressure can lead to greater changes in the bed temperature. The hydrogen desorption process exhibits 3 stages under the constant flow rate mode, and the hydrogen desorption of $\text{Mg}(\text{NH}_2)_2\text{-}2\text{LiH-}0.07\text{KOH}$ mainly carries out at stage II accompanied with a significant temperature drop. As the flow rate increases, the endothermic dehydrogenation of the hydride degrades the bed temperature to a lower value, and the amount of hydrogen released also decreases at this stage. The results indicate that an efficient improvement of the heat transfer property for the Li–Mg–N–H based tank is needed to improve its sorption behavior.

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1. Introduction

Hydrogen is considered as a promising alternative energy carrier for the future stationary and mobile applications due to its high calorific value and environmental friendliness. However, safe and efficient hydrogen storage is still the most critical technical barrier for practical applications of hydrogen energy, especially for automotive applications.

In the past decade, light complex hydrides have attracted great research interest due to the successful development of some hydrides which have high theoretical hydrogen storage capacity of more than 5 wt%, such as NaAlH_4 , MgH_2 and Li–Mg–N–H system [1–6]. NaAlH_4 has a theoretical gravimetric hydrogen storage capacity of 5.5 wt%, but it is only with a proven reversible capacity of about 3.5 wt% under moderate conditions [7]. MgH_2 presents a high storage capacity of 7.6 wt%, however, the high operating temperature severely limits its practical application [8]. Compared to these two hydrides, Li–Mg–N–H is believed to be one of the most promising hydrogen storage materials for the onboard applications because of its moderate operating temperatures and a relatively high reversible hydrogen storage capacity of 5.6 wt% [9]. Enormous efforts have been made to improve its hydrogen sorption kinetics

by adjusting the composition, decreasing the particle size and doping additives [10–15]. Recent investigations show that the hydrogen sorption kinetics of the Li–Mg–N–H system can be enhanced obviously by introducing potassium-based additives. Liu et al. have found that the KF dopant greatly improves the dehydrogenation kinetics of $\text{Mg}(\text{NH}_2)_2\text{-}2\text{LiH}$ system [13]. Liang et al. have reported that KOH doped $\text{Mg}(\text{NH}_2)_2\text{-}2\text{LiH}$ system can reversibly desorb 4.92 wt% of hydrogen with an onset temperature of 348 K [14]. Recently, the KH doped $\text{Mg}(\text{NH}_2)_2\text{-}2\text{LiH}$ system has been found to reversibly store 5.2 wt% of hydrogen with an onset temperature of 343 K [15]. It is very close to the operating temperature of the proton exchange membrane fuel cells.

For practical application, the hydride must be integrated to an efficient hydrogen storage tank. The design, fabrication and optimization of the tank require a comprehensive understanding of the sorption process, which is quite complicated and involves coupled heat and mass transfer with chemical reaction. Several experimental and numerical studies have been conducted to improve the hydrogen storage properties of the Mg- and NaAlH_4 -based hydrogen storage tanks [16–20]. On the one hand, in order to improve the volumetric hydrogen storage capacity of the tank, the hydride powder is generally compressed to compacts to fill into the tank. On the other hand, the heat transfer properties of MgH_2 or NaAlH_4 tanks have been improved by incorporating heat exchanger into the tanks or enhancing the effective thermal conductivity of the

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hydride beds. However, investigations on the Li–Mg–N–H based tank are limited. In this paper, a lab-scale hydrogen storage tank based on $\text{Mg}(\text{NH}_2)_2\text{-2LiH-0.07KOH}$ system was fabricated to study its hydrogen storage properties.

2. Experimental

$\text{Mg}(\text{NH}_2)_2$ was supplied by Zhejiang University. LiH (purity > 95%) was purchased from Sigma–Aldrich and used without pretreatment. KOH (purity > 82%, Beijing Chemical Industry Company) was ground into fine powder using an agate mortar and pestle and then dried in vacuum at 333 K for 12 h. A mixture was prepared by mixing the $\text{Mg}(\text{NH}_2)_2$, LiH and KOH together in the molar ratio of 1:2:0.07. The mixture was mechanically ball-milled in a stainless steel vial with the ball-to-powder weight ratio of 10:1 by using a QM-1SP4 ball mill at the speed of 500 rpm under 5.0 MPa hydrogen pressure for 36 h. The hydrogen sorption properties of the $\text{Mg}(\text{NH}_2)_2\text{-2LiH-0.07KOH}$ mixture was studied by means of volumetric method on a homemade Sieverts-type apparatus.

$\text{Mg}(\text{NH}_2)_2\text{-2LiH-0.07KOH}$ compacts were used instead of the powder to improve the volumetric hydrogen storage capacity of the tank [21,22]. The as-milled $\text{Mg}(\text{NH}_2)_2\text{-2LiH-0.07KOH}$ powder was compressed into the compact with a diameter of 30 mm and a height of 10 mm under 33.0 MPa. 20 pieces of the $\text{Mg}(\text{NH}_2)_2\text{-2LiH-0.07KOH}$ compacts with a total weight of 98.0 g were filled into the tank. Fig. 1 illustrates the structure of the cylindrical hydrogen storage tank, which has a height of 205 mm, a diameter of 32 mm, and a loading density of 0.616 g/cm³. A porous sintered metal tube with a diameter of 6.0 mm acted as the hydrogen supply path. Three thermocouples imbedded respectively at the central, middle and surface regions of the hydride bed were used to measure the temperature variation during the hydrogen absorption/desorption process. To prevent contamination from air and moisture, all handling procedures in this work were performed in a glove-box filled with purified argon to keep the H₂O and O₂ levels below 1 ppm.

The hydrogen absorption of the tank was carried out in the oil bath heated at 453 K. The quasi-constant hydrogen pressure of 6.0 MPa, 8.0 MPa and 10.0 MPa was brought into the tank to study its absorption behavior, respectively. After hydrogen absorption, the tank was quickly heated from 453 K to 493 K by the oil bath, and the isothermal hydrogen desorption measurement was carried out at the given flow rate of 0.4 L/min, 0.6 L/min and 0.8 L/min, respectively.

3. Results and discussion

3.1. Hydrogen sorption of the $\text{Mg}(\text{NH}_2)_2\text{-2LiH-0.07KOH}$ mixture

Fig. 2 shows the sorption profiles for the as-milled $\text{Mg}(\text{NH}_2)_2\text{-2LiH-0.07KOH}$ mixture. The $\text{Mg}(\text{NH}_2)_2\text{-2LiH-0.07KOH}$ mixture can release 4.5 wt% of hydrogen in the temperature range from 373 K to 510 K under 0.1 MPa hydrogen pressure, and absorb 4.6 wt% of hydrogen from 373 K to 420 K under quasi-constant hydrogen pressure of 8.0 MPa. The reversible hydrogen storage capacity of the mixture is consistent with the data reported in Ref. [14].

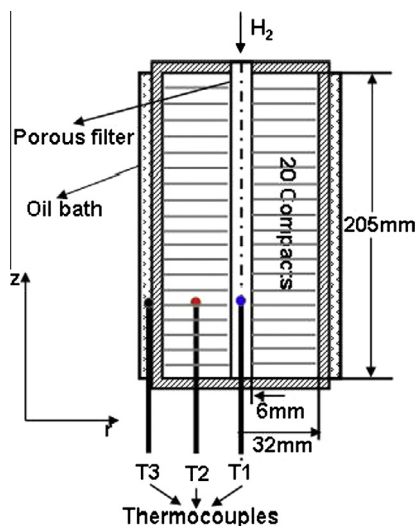


Fig. 1. Schematic diagram of the $\text{Mg}(\text{NH}_2)_2\text{-2LiH-0.07KOH}$ based tank.

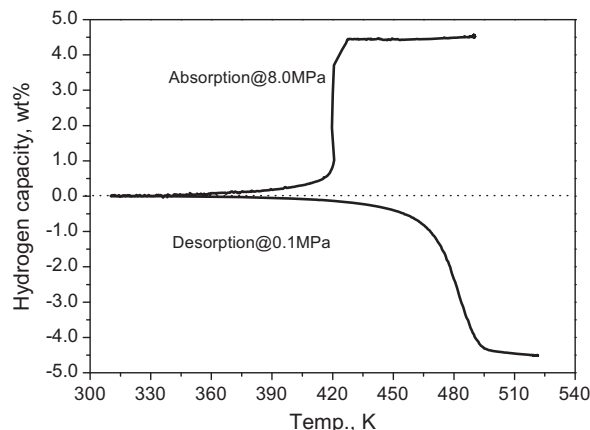


Fig. 2. Hydrogen sorption profiles for the as-milled $\text{Mg}(\text{NH}_2)_2\text{-2LiH-0.07KOH}$ mixture.

3.2. Hydrogen absorption measurement of the tank

Fig. 3 shows the temperature and hydrogen absorption capacity profiles for the $\text{Mg}(\text{NH}_2)_2\text{-2LiH-0.07KOH}$ based tank measured at 453 K and quasi-constant hydrogen pressure of 8.0 MPa. During the first 2 min, the tank stores 29.0 L of hydrogen, and the bed temperature increases obviously. Besides, the values of the temperature rise are different for the different region of the hydride bed. It can be seen from Fig. 3a that the temperature of the central hydride rises to 528 K, while the surface temperature only rises to 495 K. After 2 min, the absorption rate of the tank decreases and the bed temperature progressively returns back to 453 K.

It is well known that the driving force for the hydrogenation is closely related to the difference between the absorption equilibrium pressure P_{abs} of the hydride and the applied hydrogen pressure P . The hydrogenation of the hydride starts only when the P_{abs} is lower than the P . Due to the higher driving force and the excellent intrinsic absorption kinetic of the hydride, the tank quickly stores the hydrogen in the first 2 min of the absorption process. The exothermic reaction also produces lots of heat to elevate the bed temperature. However, with the limited heat transfer ability of the hydride bed, the heat at the central region can not be effectively transferred out and the hydride bed exhibits an obvious temperature gradient between the central and the surface parts.

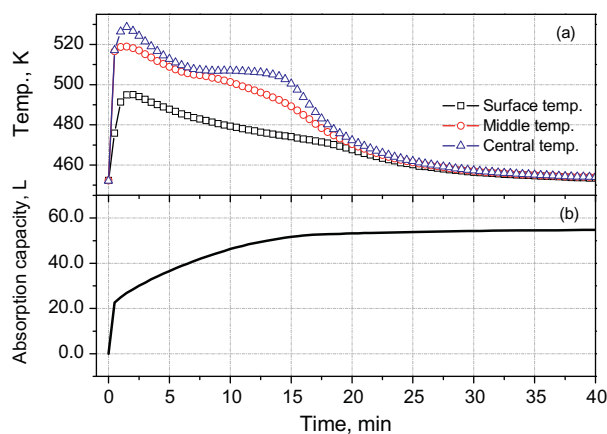


Fig. 3. Hydrogen absorption profiles for the $\text{Mg}(\text{NH}_2)_2\text{-2LiH-0.07KOH}$ based tank measured at 453 K and quasi-constant hydrogen pressure of 8.0 MPa: (a) temperatures of the hydride bed, and (b) hydrogen absorption capacity.

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