Enhanced thermal diffusivity and dehydrogenation of $2LiNH_2–MgH_2$ by doping with super activated carbon

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ABSTRACT

Doping with the additives in metal-N–H system has been regarded as one of the most effective approaches to improve its hydrogen storage properties. Herein, we prepared super activated carbon (SuperC) through the activation of commercial activated carbon by KOH and evaluated its effect on dehydrogenation properties of $2LiNH_2–MgH_2$. Our studies show that doping with SuperC could effectively lower its dehydrogenation temperatures. For instance, $2LiNH_2–MgH_2$–10 wt% SuperC can release 4.86 wt% of hydrogen upon heating up to 300 °C with the onset and peak dehydrogenation temperatures of 71 °C and 168 °C, respectively. Moreover, the release of byproduct NH_3 was successfully suppressed. Measurement of thermal diffusivity suggests that the enhanced dehydrogenation properties may be ascribed to the improved heat transfer for solid-solid reaction resulting from doping with SuperC.

Introduction

Hydrogen is a satisfactory energy carrier to serve the current sustainable energy demand because it has a very high energy density. But the widespread applications of hydrogen encountered many difficulties, including hydrogen storage technology [1]. In hydrogen energy system, hydrogen storage acts as a bridge between hydrogen production and its application [2]. So we need safe, reliable, efficient, and economical storage technologies, which is a prerequisite for the implementation of large-scale applications of hydrogen energy [3]. A pioneering work on metal-N–H hydrogen storage system was

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discovered by Chen and coworkers [4]. They found that Li_3N could store reversibly more than 10 wt% of hydrogen by a two-step reaction:

$$Li_3N + H_2 \leftrightarrow Li_2NH + LiH + H_2 \leftrightarrow LiNH_2 + 2LiH \quad (1)$$
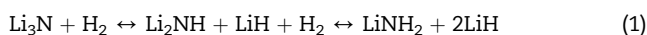
Due to the higher enthalpy of the first step, the extensive studies were mainly focused on the second one, which could store 6.5 wt% of hydrogen with a fairly good reversibility [5,6]. But the amide decomposition usually involves an emission of intermediate byproduct ammonia, which is extremely detrimental to proton-exchange membrane fuel cell (PEMFC) when used as hydrogen storage media [7–9]. Thus, a lot of research activities have been devoted to altering thermodynamics/kinetics and suppressing the release of ammonia [10–13].

In order to address these drawbacks, light-metal amides and the "hybrid" materials containing both NH_2^- and BH_4^- (or AlH_4^-) anionic units have attracted extensive interest as potential hydrogen storage materials [14–21]. Among the numerous metal-N–H systems, Luo et al. has reported the partial substitution of Li by Mg to form a $2LiNH_2$–MgH_2 system [22], which has an obvious destabilization effect on the lithium amide/hydride for storing hydrogen. The mixture of $2LiNH_2$–MgH_2 was converted to $2LiH$–$Mg(NH_2)_2$ after one complete absorption/desorption cycle according to the following reactions [14]:

$$2LiNH_2 + MgH_2 \rightarrow Li_2Mg(NH)_2 + 2H_2 \leftrightarrow Mg(NH_2)_2 + 2LiH \quad (2)$$
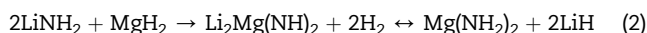
But Shaw et al. found that compared to $LiNH_2$–LiH, $2LiNH_2$–MgH_2 had a slower rate for approaching a certain percentage of its equilibrium pressure, high activation energy, and more ammonia emission [23]. To further improve hydrogen storage performance, many studies have indicated that reducing the size of sample particles, reactant composition alteration, and catalyst doping can effectively improve hydrogen storage properties to some extent [24–28]. But this kind of hydrogen storage materials still has some drawbacks, such as poor mass and heat transfer for solid-solid reaction, higher dehydrogenation temperature, and higher kinetic barrier.

In order to overcome the aforementioned problems, we focus on doping additives to catalytically enhance the dehydrogenation properties and thermal conductivity of $2LiNH_2$–MgH_2. Here, we prepared super activated carbon [29] (referred as SuperC) through the activation of commercial activated carbon by KOH and examined its effect on dehydrogenation properties of $2LiNH_2$–MgH_2. The relationship between thermal conductivity and hydrogen storage properties was also discussed.

Experimental section

KOH (> 85% purity, XILONG SCIENTIFIC) and activated carbon (CP, XILONG SCIENTIFIC) in a weight ratio of 4:1 were added in distilled water under moderate stirring. Then the dispersed suspension was loaded into a Teflon-lined stainless steel autoclave and held at 120 °C for 12 h. The solution was naturally cooled down to room temperature and the solid sample was filtered and washed with ethanol. Finally, the product was obtained after drying in an electric oven under vacuum at 150 °C, and collected in glovebox.

$2LiNH_2$–MgH_2 samples were prepared by mechanically milling of $LiNH_2$ (95% purity, Sigma-Aldrich) and MgH_2 (98% purity, Sigma-Aldrich) with and without SuperC. The mechanical milling was performed using a Retsch PM400 planetary mill at 200 rpm under 0.1 MPa of an argon atmosphere. The ball-to-powder weight ratio was set to be about 60:1. To minimize the effect of temperature increment on the samples during ball milling process, there was a 30 s pause for each 2 min of milling. The total milling time was 20 h. All the sample handling was performed in an Ar-filled glovebox, in which the typical H_2O/O_2 levels were below 1 ppm.

Temperature-programmed desorption properties were measured by using automatic apparatus from ChemBet Pulsar TPD. The sample was heated up to 300 °C at a ramping rate of 5 °C/min in a flowing Ar gas. The temperature-dependence of hydrogen desorption accompanying with ammonia emission was performed on a thermogravimetric apparatus (TG, SETSYS Evolution)-mass spectrometer (MS, GAM 200) combined system. The sample was heated up to 400 °C at 5 °C/min in flowing Ar gas. The dehydrogenation capacity based on volumetric release was measured on a HyEnergy PCTPRO-2000 Sieverts-type apparatus. Approximately 150 mg of sample was loaded into the sample holder and heated at 2 °C/min from room temperature to 300 °C initially under dynamic vacuum.

Structural identification of the samples at different stages was carried on a Bruker D8 Advance diffractometer (Cu Kα radiation, 40 kV and 40 mA). Scanning electron microscopy (SEM Hitachi S-570) was used to detect the microscopic morphology of the samples. The thermal diffusivity of the samples was measured on a LINSEIS XFA 500 instrument under dynamic vacuum at different temperatures.

Results and discussion

Fig. 1 presents the typical SEM images of the as-prepared SuperC additive and the commercial activated carbon. The commercial activated carbon in Fig. 1 (b) consists of two-dimensional sheets, which are tightly stacked together. As for SuperC in Fig. 1 (a), the porous structure is formed after the activation of the commercial activated carbon by KOH, which potentially increases the surface area of the sample. As an additive in $2LiNH_2$–MgH_2, such a loose porous structure of SuperC is believed to be highly beneficial for improving the refinement of grain and uniformity of material, further resulting in an enhancement of dehydrogenation properties. XRD pattern (Fig. 1c) indicates that K_2CO_3 and $KHCO_3$ were formed during the synthesis of SuperC.

The hydrogen desorption performance of the as-prepared $2LiNH_2$–MgH_2 doped with the different amounts of SuperC was first evaluated and shown in Fig. 2 (a). Obviously, the operating temperatures for dehydrogenation are decreased after the addition of SuperC. Unfortunately, the amount of hydrogen released was found to be slightly decreased. A total of 5.15 wt% of hydrogen was liberated from $2LiNH_2$–MgH_2