



ELSEVIER

Available online at [www.sciencedirect.com](http://www.sciencedirect.com)

ScienceDirect

journal homepage: [www.elsevier.com/locate/he](http://www.elsevier.com/locate/he)

# Synthesis and thermal decomposition properties of a novel dual-cation/anion complex hydride $\text{Li}_2\text{Mg}(\text{BH}_4)_2(\text{NH}_2)_2$

Yongfeng Liu <sup>a,b</sup>, Ni Jian <sup>a</sup>, Zhuanghe Ren <sup>a</sup>, Jianjiang Hu <sup>c</sup>, Fang Du <sup>c</sup>,  
Mingxia Gao <sup>a</sup>, Hongge Pan <sup>a,\*</sup>

<sup>a</sup> State Key Laboratory of Silicon Materials, Key Laboratory of Advanced Materials and Applications for Batteries of Zhejiang Province and School of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, China

<sup>b</sup> Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education), Nankai University, Tianjin 300071, China

<sup>c</sup> Laboratory for Energetics and Safety of Solid Propellants, Hubei Institute of Aerospace Chemotechnology, Xiangyang 441003, China

## ARTICLE INFO

### Article history:

Received 31 October 2017

Received in revised form

16 November 2017

Accepted 16 November 2017

Available online xxx

### Keywords:

Hydrogen storage

Complex hydrides

Borohydrides

Amides

Thermal decomposition

## ABSTRACT

A novel dual-cation/anion complex hydride ( $\text{Li}_2\text{Mg}(\text{BH}_4)_2(\text{NH}_2)_2$ ), which contains a theoretical hydrogen capacity of 12.1 wt%, is successfully synthesized for the first time by ball milling a mixture consisting of  $\text{MgBH}_4\text{NH}_2$  and  $\text{Li}_2\text{BH}_4\text{NH}_2$ . The prepared  $\text{Li}_2\text{Mg}(\text{BH}_4)_2(\text{NH}_2)_2$  crystallizes in a triclinic structure, and the  $[\text{NH}_2]$  and  $[\text{BH}_4]$  groups remain intact within the structure. Upon heating, the prepared  $\text{Li}_2\text{Mg}(\text{BH}_4)_2(\text{NH}_2)_2$  decomposes to release approximately 8.7 wt% hydrogen in a three-step reaction at 100–450 °C. In addition, a small amount of ammonia is evolved during the first and second thermal decomposition steps as a side product. This ammonia is responsible for the lower experimental dehydrogenation amount compared to the theoretical hydrogen capacity. The XRD and FTIR results reveal that  $\text{Li}_2\text{Mg}(\text{BH}_4)_2(\text{NH}_2)_2$  first decomposes to  $\text{LiMgBN}_2$ ,  $\text{LiBH}_4$ ,  $\text{BN}$ ,  $\text{LiH}$  and  $\text{MgBNH}_8$  at 100–250 °C, and then, the newly formed  $\text{MgBNH}_8$  reacts with  $\text{LiH}$  to form  $\text{Mg}$ ,  $\text{LiBH}_4$  and  $\text{BN}$  at 250–340 °C. Finally, the decomposition of  $\text{LiBH}_4$  releases hydrogen and generates  $\text{LiH}$  and  $\text{B}$  at 340–450 °C.

© 2017 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

## Introduction

As a promising alternative energy carrier, hydrogen, which is considered to be an environmentally friendly fuel, has been the focus of extensive research on the development of fuel cell technology [1–4]. However, one of the major obstacles to the widespread use of hydrogen as an energy carrier is the lack of

a safe and efficient method of storage [5–10]. Therefore, metal complex hydrides that possess high gravimetric and volumetric hydrogen storage capacities have been studied as a potential candidate for use as hydrogen storage materials [11–14]. As representative complex hydrides, metal borohydrides  $\text{M}(\text{BH}_4)_n$  have attracted considerable interest due to their extremely high gravimetric and volumetric hydrogen

\* Corresponding author.

E-mail address: [hspan@zju.edu.cn](mailto:hspan@zju.edu.cn) (H. Pan).

<https://doi.org/10.1016/j.ijhydene.2017.11.104>

0360-3199/© 2017 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

densities that potentially meet the capacity requirements of practical applications [15–18]. Typically,  $\text{LiBH}_4$  delivers a gravimetric hydrogen density as high as 18.5 wt% and a volumetric hydrogen density of  $121 \text{ kg/m}^3$  [15]. However, a high operating temperature, sluggish kinetics and poor reversibility for hydrogen storage in  $\text{LiBH}_4$  due to the strong and highly directional covalent and ionic bonds between  $\text{Li}^+$  and  $[\text{BH}_4]^-$  prevent its practical application.

To improve the hydrogen storage properties of  $\text{LiBH}_4$ , various strategies have been explored and developed including catalyst doping, reactant destabilization, anion/cation substitution and nanoporous scaffold incorporation [18–26]. In particular, by reacting  $\text{LiBH}_4$  with elemental metals, metal hydrides or metal amides, the operating temperatures for hydrogen desorption from  $\text{LiBH}_4$  have been significantly reduced, and the reversibility of hydrogen storage has been improved. For example, when combined with  $\text{MgH}_2$  at a molar ratio of 2:1, the onset dehydrogenation temperature of  $\text{LiBH}_4$  was decreased to approximately  $270^\circ\text{C}$ , and the hydrogen storage is completely reversible below  $450^\circ\text{C}$  [27]. Similar phenomena were also observed in the  $2\text{LiBH}_4\text{--Al}$  and  $6\text{LiBH}_4\text{--CaH}_2$  systems [28,29]. More interestingly, combining  $\text{LiBH}_4$  and  $\text{LiNH}_2$  resulted in the generation of a new family of mixed borohydride-amide compounds, such as  $\text{Li}_2\text{BH}_4\text{NH}_2$ ,  $\text{Li}_3\text{BH}_4(\text{NH}_2)_2$  and  $\text{Li}_4\text{BH}_4(\text{NH}_2)_3$  [30–32]. Among these compounds,  $\text{Li}_3\text{BH}_4(\text{NH}_2)_2$  released more than 10 wt% of hydrogen in a temperature range of  $250\text{--}350^\circ\text{C}$ , which is superior to the hydrogen desorption performance of the independent components (i.e.,  $\text{LiBH}_4$  and  $\text{LiNH}_2$ ) [30,31]. The coexistence of  $\text{H}^{\delta+}$  in the  $\text{NH}_2$  groups and  $\text{H}^{\delta-}$  in the  $\text{BH}_4$  groups provided a strong driving force for hydrogen desorption from the combination of borohydrides and amides [33–39].

In addition, a close relationship exists between the thermodynamic stability and the Pauling electronegativity of metal cations for borohydrides [40]. When  $M$  is more electronegative,  $M(\text{BH}_4)_n$  becomes more unstable. Therefore, a series of mixed-cation borohydrides with decreased decomposition temperatures were synthesized by combining a less electronegative metal with a more electronegative metal (i.e.,  $\text{LiK}(\text{BH}_4)_2$ ,  $\text{LiZn}_2(\text{BH}_4)_5$ ,  $\text{NaZn}(\text{BH}_4)_3$ ,  $\text{NaZn}_2(\text{BH}_4)_5$ ,  $\text{LiSc}(\text{BH}_4)_4$ ,  $\text{NaSc}(\text{BH}_4)_4$ ,  $\text{KSc}(\text{BH}_4)_4$ ,  $\text{Li}_4\text{Al}_3(\text{BH}_4)_{13}$ ,  $\text{LiZr}(\text{BH}_4)_5$  and  $\text{Li}_2\text{Zr}(\text{BH}_4)_6$ ) [41–44]. More importantly, Noritake et al. recently reported a new mixed borohydride-amide compound with a  $\text{MgBH}_4\text{NH}_2$  composition that exhibits a  $50^\circ\text{C}$  reduction in the dehydrogenation temperature with respect to that of  $\text{Li}_2\text{BH}_4\text{NH}_2$  [45]. All of these results inspired us to synthesize mixed cation/anion complex hydrides with a high hydrogen content and potentially favourable thermodynamic properties for hydrogen storage applications.

Herein, we report an attempt to develop novel dual-cation/anion complex hydrides with a high hydrogen capacity and low decomposition temperature.  $\text{Li}_2\text{Mg}(\text{BH}_4)_2(\text{NH}_2)_2$  was successfully synthesized by ball milling a mixture consisting of  $\text{Li}_2\text{BH}_4\text{NH}_2$  and  $\text{MgBH}_4\text{NH}_2$  at a molar ratio of 1:1. Approximately 8.7 wt%  $\text{H}_2$ , which is equivalent to 4.3  $\text{H}_2$  molecules, were released from  $\text{Li}_2\text{Mg}(\text{BH}_4)_2(\text{NH}_2)_2$  with an on-set temperature of  $100^\circ\text{C}$ , which is significantly lower than those of the independent components (i.e.,  $\text{Li}_2\text{BH}_4\text{NH}_2$  and  $\text{MgBH}_4\text{NH}_2$ ).

## Experimental section

### Sample preparations

All of the sample handling was conducted in either a Schlenk apparatus or an argon-filled MBRAUN glove box equipped with a recirculation system to maintain water and oxygen concentrations of less than 1 ppm.

The commercial chemicals, such as sodium borohydride ( $\text{NaBH}_4$ , Alfa Aesar, 98%), lithium amide ( $\text{LiNH}_2$ , Alfa Aesar, 95%), lithium borohydride ( $\text{LiBH}_4$ , Sigma-Aldrich, 95%) and magnesium chloride ( $\text{MgCl}_2$ , Alfa Aesar, 99%), were purchased and used as received without further purification. Anhydrous diethyl ether was obtained from Sinopharm Chemical and dried with calcium hydride ( $\text{CaH}_2$ ). The anhydrous ammonia gas ( $\text{NH}_3$ , 99%) was used as received.  $\text{Mg}(\text{BH}_4)_2$ ,  $\text{Mg}(\text{BH}_4)_2 \cdot 2\text{NH}_3$  were prepared according to previously reported protocols [46–48].  $\text{Li}_2\text{BH}_4\text{NH}_2$  (viz.,  $\text{Li}_2\text{BNH}_6$ ) was obtained by ball milling the mixture of  $\text{LiBH}_4$  and  $\text{LiNH}_2$  at 500 rpm for 36 h.  $\text{MgBH}_4\text{NH}_2$  was synthesized by heating a mixture of  $\text{Mg}(\text{BH}_4)_2 \cdot 2\text{NH}_3$  and  $\text{MgH}_2$  at a molar ratio of 1:1 at  $110^\circ\text{C}$  for 24 h [47].  $\text{MgH}_2$  (Alfa Aesar, 98%) was ball milled under an 80 bar hydrogen atmosphere for 24 h to fully hydrogenate prior to use. The XRD measurement confirmed the formation of a single phase of  $\text{MgBH}_4\text{NH}_2$  and  $\text{Li}_2\text{BH}_4\text{NH}_2$ , respectively (Fig. S1) [34,45]. Three samples with  $\text{MgBH}_4\text{NH}_2\text{--}x\text{Li}_2\text{BNH}_6$  compositions ( $x = 0.5, 1$  and  $2$ ) were designed and prepared by ball milling the corresponding chemicals at 500 rpm for 24 h. Ball milling was performed on a plenary ball mill (QM-3SP4, Nanjing), and the ball-to-sample weight ratio was approximately 120:1. The mill was set to rotate for 12 min in one direction followed by a pause of 6 min and subsequent rotation in the reverse direction to minimize the temperature increase in the samples during ball milling.

### Property evaluations

Temperature-programmed desorption (TPD) measurements were performed using a homemade instrument equipped with an online mass spectrometer (MS), which simultaneously recorded the hydrogen ( $m/z: 2$ ) and ammonia ( $m/z: 15$ ). The temperature was gradually increased from room temperature to  $500^\circ\text{C}$  at a heating rate of  $2^\circ\text{C min}^{-1}$ . Approximately 30 mg of the sample was loaded into a custom designed tube reactor, and a constant flow of pure argon was maintained during heating. The quantitative dehydrogenation behaviour was characterized using a volumetric method on a homemade Sieverts-type apparatus. Approximately 60 mg of the sample was loaded into a stainless steel reactor inside a glove box. The reactor was first evacuated to  $10^{-3}$  bar prior to each experiment and then heated from room temperature to the desired temperature at a heating rate of  $2^\circ\text{C min}^{-1}$ . Based on the pressure and temperature data that was automatically recorded, the quantities of hydrogen desorbed from the sample were calculated using the equation of state. Thermal gravimetric analysis (TGA) was performed on a Netzsch STA 449 F3 thermal analyser to determine the weight loss of  $\text{Li}_2\text{Mg}(\text{BH}_4)_2(\text{NH}_2)_2$  upon heating. The desorption heat

Download English Version:

<https://daneshyari.com/en/article/7705382>

Download Persian Version:

<https://daneshyari.com/article/7705382>

[Daneshyari.com](https://daneshyari.com)