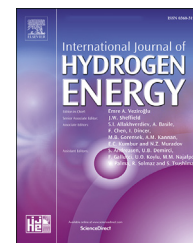


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# Synthesis and hydrogen storage property tuning of $Zr(BH_4)_4 \cdot 8NH_3$ via physical vapour deposition and composite formation

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## ARTICLE INFO

### Article history:

Received 22 June 2018

Received in revised form

16 August 2018

Accepted 27 August 2018

Available online 19 September 2018

### Keywords:

 $Zr(BH_4)_4 \cdot 8NH_3$ 

Synthetic method

Dehydrogenation mechanism

 $NaBH_4$ 

## ABSTRACT

$Zr(BH_4)_4 \cdot 8NH_3$  is considered to be a promising solid state hydrogen-storage material, due to its high hydrogen capacity and low dehydrogenation temperature. However, the possible applications of  $Zr(BH_4)_4 \cdot 8NH_3$  have been greatly hampered by the complicated and less applicable synthesis process, which must be operated at relatively low temperature (<20 °C). Herein, we reported a simple and facile “heating-(ball milling) BM vial” method via physical vapour deposition to tackle this issue. By this technique,  $Zr(BH_4)_4 \cdot 8NH_3$  was successfully synthesized. Furthermore, composite formation by adding 10 wt%  $NaBH_4$  to the as-prepared  $Zr(BH_4)_4 \cdot 8NH_3$  was found to be able to lower down the dehydrogenation peak of  $Zr(BH_4)_4 \cdot 8NH_3$  from 130 to 75 °C and more excitingly, the possible emission of  $B_2H_6$  and  $NH_3$  from dehydrogenation of only  $Zr(BH_4)_4 \cdot 8NH_3$  was completely suppressed after addition of  $NaBH_4$ . This research presents a new hydrogen-storage system based on  $Zr(BH_4)_4 \cdot 8NH_3 + NaBH_4$  composite and it also implies a new development methodology of future hydrogen storage materials.

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## Introduction

Hydrogen has been considered as a green and renewable energy carrier owing to the high energy density, and environmentally benign products of oxidation, which makes it a

potential candidate to replace fossil fuels [1–3]. The hydrogen-energy process chain consists of three major steps: hydrogen production [4,5], storage [6,7], and utilization [8]. To realize the widespread utilization of hydrogen energy, one critical challenge is to develop safe, inexpensive, lightweight and high hydrogen density storage materials that may operate at

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<https://doi.org/10.1016/j.ijhydene.2018.08.189>

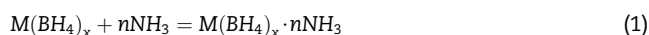
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moderate temperatures. In the past decade, tremendous efforts have been devoted to the study of hydrogen storage materials. Metal based hydrides, complex hydrides, carbon based materials, etc. have been widely investigated to meet these requirements, but unfortunately none of them could show satisfactory performances for commercial mobile application [9,10].

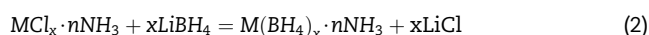
Due to their high hydrogen densities and mild dehydrogenation conditions, boron–nitrogen-based hydrides [11–14] and metal borohydrides [15,16] have been widely investigated as promising hydrogen storage materials. Nevertheless, borohydrides are still suffering from the drawbacks of relatively high desorption temperature and the potential release of toxic boranes. To overcome these drawbacks, the introduction of  $\text{NH}_3$  to form ammoniates is a useful way. Studies have demonstrated that some metal borohydrides can be turned into their metal borohydride ammoniates (MBAs) [17–23] by the reaction with ammonia. The local combination of  $\text{NH}^{\delta+} \dots \text{BH}^{\delta-}$  dihydrogen bonds in their structures may lead to a decrease in the temperature of hydrogen release and may also restrict the formation of diborane on heating [24,25].

Recently, we successfully synthesized zirconium borohydride octaammoniate,  $\text{Zr}(\text{BH}_4)_4 \cdot 8\text{NH}_3$ , with the highest coordination number of  $\text{NH}_3$  groups among all the reported MBAs [26].  $\text{Zr}(\text{BH}_4)_4 \cdot 8\text{NH}_3$  has high hydrogen capacity of 14.8 wt% and low main dehydrogenation temperature of around 130 °C. A couple of further studies were carried out focusing on improving the dehydrogenation and hydrolysis properties of  $\text{Zr}(\text{BH}_4)_4 \cdot 8\text{NH}_3$  [27–29]. However, the drawback of its synthesis process with the necessity of temperatures below 20 °C greatly hinder its research and practical applications.

In general, there were kind of synthetic methods to preparation MBAs. The first synthetic method was ammoniation of metal borohydride. This method was appropriate for the stable metal borohydride at room temperature (RT), such as  $\text{LiBH}_4$  and  $\text{Mg}(\text{BH}_4)_4$  [30,31].



Another synthesis method was replacement reaction between metal halide ammoniates and lithium borohydride. The second method was suitable to volatile metal borohydride at RT, such as  $\text{Zn}(\text{BH}_4)_2$  and  $\text{Y}(\text{BH}_4)_3$  [18,22]. The drawback of this method was generation of the byproduct of  $\text{LiCl}$ , which was hard to remove from MBAs.



In previous study,  $\text{Zr}(\text{BH}_4)_4 \cdot 8\text{NH}_3$  was synthesized by a ball-milling method: 1) a mixture of  $\text{LiBH}_4$  and  $\text{ZrCl}_4$  was mechanically milled, and then the solid-state  $\text{Zr}(\text{BH}_4)_4$  crystals were obtained on the lid of the vial; 2) the solid-state  $\text{Zr}(\text{BH}_4)_4$  crystals were scrapped and collected in the reactor tube in the glove box; and finally 3) the collected  $\text{Zr}(\text{BH}_4)_4$  was taken the ammonification to obtain  $\text{Zr}(\text{BH}_4)_4 \cdot 8\text{NH}_3$ . Due to the volatility of  $\text{Zr}(\text{BH}_4)_4$ , the sublimated  $\text{Zr}(\text{BH}_4)_4$  would separate with the solid  $\text{LiCl}$  byproduct and deposit on the lid of the ball mill vial, and finally the  $\text{LiCl}$ -free  $\text{Zr}(\text{BH}_4)_4 \cdot 8\text{NH}_3$  can be obtained. However, owing to the high volatility of  $\text{Zr}(\text{BH}_4)_4$ , this method was only feasible in low temperature (<20 °C) and therefore the applicability was very poor. Additionally, since the

$\text{Zr}(\text{BH}_4)_4$  was synthesized in the glove box and needed to be transferred to a reactor tube, the inner atmosphere of the glove box usually was contaminated due to the partial sublimation of  $\text{Zr}(\text{BH}_4)_4$ . Thus, a more applicable and convenient synthesis method for  $\text{Zr}(\text{BH}_4)_4 \cdot 8\text{NH}_3$  is greatly desirable.

In 2009, Gennari et al. reported that  $\text{Zr}(\text{BH}_4)_4$  can be synthesized by a mechanochemical reaction between  $\text{NaBH}_4$  and  $\text{ZrCl}_4$  [32]. And then, based on the different physical properties of the reaction products,  $\text{Zr}(\text{BH}_4)_4$  was separated and collected from milling vial. Inspired by this research, a “heating-(ball milling) BM vial” method was developed, and  $\text{Zr}(\text{BH}_4)_4 \cdot 8\text{NH}_3$  was successfully synthesized by this method. Besides the study of “heating-BM vial” method,  $\text{NaBH}_4$  was used to replace  $\text{LiBH}_4$  in the starting materials to make this process safer and more economical. Meanwhile, the special effect of  $\text{NaBH}_4$  in the dehydrogenation of  $\text{Zr}(\text{BH}_4)_4 \cdot 8\text{NH}_3$  was investigated.

## Experimental

### Preparation

The starting materials,  $\text{LiBH}_4$  (>98%)/ $\text{NaBH}_4$  (>95%) and anhydrous  $\text{ZrCl}_4$  (>99.5%) were purchased from Sigma-Aldrich and Alfa Aesar, respectively. Ammonia (>99.9%) was obtained from Guangdong Huate Gas Co. All the materials were used as-received without further purification except  $\text{NH}_3$ , which was purified by soda lime prior to use.

For the study of the “heating-BM vial” method from  $\text{NaBH}_4$  and  $\text{ZrCl}_4$ , the synthesized product was named #Na (h-BM) hereafter. Firstly,  $\text{Zr}(\text{BH}_4)_4$  was synthesized by ball milling  $\text{NaBH}_4$  and  $\text{ZrCl}_4$ . And then by heating the ball-milling vial to 70 °C,  $\text{Zr}(\text{BH}_4)_4$  was forced to sublimate. Afterward, the  $\text{Zr}(\text{BH}_4)_4$  gas was introduced into a reaction tube under ice-water bath and crystallized there. Finally,  $\text{Zr}(\text{BH}_4)_4$  crystals were exposed to ammonia gas to synthesize #Na (h-BM).

For the study of replacement of  $\text{NaBH}_4$  to  $\text{LiBH}_4$ , the products called #Li or #Na, originated from ball milling a mixture of  $\text{LiBH}_4$  with  $\text{ZrCl}_4$  or a mixture of  $\text{NaBH}_4$  and  $\text{ZrCl}_4$  by the traditional synthesis method as shown in this reference [26], respectively. According to our previous study, the #Li is  $\text{Zr}(\text{BH}_4)_4 \cdot 8\text{NH}_3$  sample and it was used as the standard sample to compare with other ones. To further confirm the existence of  $\text{Zr}(\text{BH}_4)_4$ , the solid crystals on the lid of the vial were collected and determined by X-ray diffraction (XRD).

In short, the references of  $\text{Zr}(\text{BH}_4)_4 \cdot 8\text{NH}_3$  synthesized by various methods was showed as Table 1.

### Characterization

The composition phases of the synthesized  $\text{Zr}(\text{BH}_4)_4 \cdot 8\text{NH}_3$  were determined by X-ray diffraction (XRD, PANalytical) with

**Table 1 – References of  $\text{Zr}(\text{BH}_4)_4 \cdot 8\text{NH}_3$  synthesized by various methods.**

Method	+ $\text{LiBH}_4$	+ $\text{NaBH}_4$
Traditional ball milling	#Li	#Na
“Heating-(ball milling) BM vial”		#Na (h-BM)

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