

## 2LiBH<sub>4</sub>–MgH<sub>2</sub> nanoconfined into carbon aerogel scaffold impregnated with ZrCl<sub>4</sub> for reversible hydrogen storage



Rapee Utke<sup>a,\*</sup>, Sophida Thiangviriya<sup>a</sup>, Payam Javadian<sup>c</sup>, Torben R. Jensen<sup>c</sup>, Chiara Milanese<sup>d</sup>, Thomas Klassen<sup>b</sup>, Martin Dornheim<sup>b</sup>

<sup>a</sup> School of Chemistry, Institute of Science, Suranaree University of Technology, Nakhon Ratchasima 30000, Thailand

<sup>b</sup> Institute of Materials Research, Helmholtz-Zentrum Geesthacht, Geesthacht 21502, Germany

<sup>c</sup> Center for Energy Materials, iNANO and Department of Chemistry, University of Aarhus, Aarhus C8000, Denmark

<sup>d</sup> Pavia Hydrogen Lab, C. S.G. I.–Department of Chemistry–Physical Chemistry Division, University of Pavia, Pavia 27100, Italy

### HIGHLIGHTS

- Nanoconfined 2LiBH<sub>4</sub>–MgH<sub>2</sub> in carbon aerogel scaffold (CAS) doped with ZrCl<sub>4</sub>.
- Studies of hydride: ZrCl<sub>4</sub>-doped CAS weight ratio affecting on H<sub>2</sub> desorption.
- Reduction of H<sub>2</sub> desorption temperature and faster kinetics after ZrCl<sub>4</sub> doping.
- Up to 97 and 93% of theoretical H<sub>2</sub> capacity released and reproduced, respectively.

### ARTICLE INFO

#### Article history:

Received 20 December 2014

Received in revised form

13 July 2015

Accepted 21 November 2015

Available online 11 December 2015

#### Keywords:

Nanostructures

Metals

Alloys

Fourier transform infrared spectroscopy

(FTIR)

Powder diffraction

### ABSTRACT

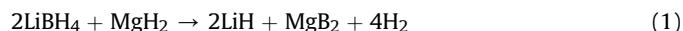
Nanoconfinement of 2LiBH<sub>4</sub>–MgH<sub>2</sub> composite into carbon aerogel scaffold (CAS) impregnated with zirconium (IV) chloride (ZrCl<sub>4</sub>) for reversible hydrogen storage is proposed. Nanoconfined samples prepared with hydride:ZrCl<sub>4</sub>-doped CAS weight ratios of 1:1, 1:2, and 1:3 are prepared by melt infiltration technique. Successful nanoconfinement of all samples is confirmed and it is found that the sample with high content of hydride with respect to ZrCl<sub>4</sub>-doped CAS (1:1 weight ratio) shows partial pore blocking. The most suitable hydride:ZrCl<sub>4</sub>-doped CAS weight ratio providing the best performance based on dehydrogenation temperature and kinetics as well as hydrogen storage capacity is 1:2. Reduction of dehydrogenation temperature and faster kinetics are obtained after doping with ZrCl<sub>4</sub>. Up to 97 and 93% of theoretical hydrogen storage capacity are released and reproduced after four cycles of nanoconfined sample with ZrCl<sub>4</sub> (1:2 weight ratio). Deficient hydrogen content with respect to theoretical capacity can be due to partial dehydrogenation during melt infiltration and formation of thermally stable [B<sub>12</sub>H<sub>12</sub>]<sup>2-</sup> phases during cycling.

© 2015 Elsevier B.V. All rights reserved.

### 1. Introduction

Due to high thermodynamic stability and kinetic restrictions of lithium borohydride (LiBH<sub>4</sub>), its ability to release and uptake hydrogen at moderate condition is hampered [1–3]. Compositing with magnesium hydride (MgH<sub>2</sub>) to form reactive hydride composite (RHC) is one of the most promising concepts to destabilize LiBH<sub>4</sub> [4,5]. The RHC of 2LiBH<sub>4</sub>–MgH<sub>2</sub> begins to liberate hydrogen at about 350 °C and complete below 500 °C as the following

reaction.



Nevertheless, under isothermal and isobaric condition ( $T = 400$  °C and  $p(\text{H}_2) = 5$  bar), sluggish kinetics was observed, for example, complete dehydrogenation required up to 25 h, [6]. Two approaches of catalytic doping [7–17] and particle size reduction [18–21] have been applied to develop hydrogen sorption properties of 2LiBH<sub>4</sub>–MgH<sub>2</sub> composite. Several metal oxides (titanium isopropoxide (Ti-iso) and SiO<sub>2</sub>) [6], fluorides (CeF<sub>3</sub>, NbF<sub>5</sub>, TiF<sub>3</sub>, LaF<sub>3</sub>, and FeF<sub>3</sub>) [11–15], and chlorides (VCl<sub>3</sub>, CeCl<sub>3</sub>, MoCl<sub>3</sub>, TiCl<sub>3</sub>, HfCl<sub>4</sub>, ZrCl<sub>4</sub>) [6,10,15–17] were doped to 2LiBH<sub>4</sub>–MgH<sub>2</sub> composite via ball

\* Corresponding author.

E-mail address: [rapee.g@sut.ac.th](mailto:rapee.g@sut.ac.th) (R. Utke).

milling technique. For instance, with 5 wt. % of Ti-iso, dehydrogenation rate of  $2\text{LiBH}_4\text{--MgH}_2$  at  $400\text{ }^\circ\text{C}$  under 5 bar  $\text{H}_2$  was up to ten times faster than milled sample without catalyst [6]. In the case of  $2\text{LiBH}_4\text{--MgH}_2$  composite doped with metal fluorides and chlorides, reduction of onset and main dehydrogenation temperatures was obtained. Especially,  $2\text{LiBH}_4\text{--MgH}_2$  doped with  $\text{NbF}_5$  revealed onset dehydrogenation at  $300\text{ }^\circ\text{C}$  and allowed complete dehydrogenation below  $450\text{ }^\circ\text{C}$ , which were approximately  $50\text{ }^\circ\text{C}$  lower than those of milled sample without catalyst [11,12].

Regarding particle size reduction, high-energy mechanical ball milling has been thoroughly conducted to prepare nanoparticles of  $2\text{LiBH}_4\text{--MgH}_2$  composite. However, particle agglomeration and grain growth were clearly detected upon hydrogen release and uptake cycles [15]. Therefore, nanoconfinement of hydride composite into nanopores of inert carbon aerogel scaffold (CAS) has been recently of interest due to several advantages of constraining particle growth upon cycling, increasing surface area and grain boundaries, and shortening the diffusion lengths of hydrogen [22,23]. It was reported that nanoconfined  $2\text{LiBH}_4\text{--MgH}_2$  into CAS was prepared by two techniques, i.e., (i) direct melt infiltration of milled  $2\text{LiBH}_4\text{--MgH}_2$  [19,20] and (ii) solution impregnation of  $\text{MgH}_2$  precursor (magnesium dibutyl,  $\text{MgBu}_2$ ) and melt infiltration of  $\text{LiBH}_4$  [18]. It should be remarked that not only dehydrogenation rate of nanoconfined  $2\text{LiBH}_4\text{--MgH}_2$  was ten times faster as compared with milled sample, but also significant reduction of activation energy (e.g.,  $\Delta E_A \sim 68 \pm 2\text{ kJ/mol}$  for  $\text{MgH}_2$ ) [19,24]. Moreover, dehydrogenation kinetics of nanoconfined  $2\text{LiBH}_4\text{--MgH}_2$  was further developed by  $\text{TiCl}_3$  doping [25]. Nanoconfined  $2\text{LiBH}_4\text{--MgH}_2\text{--TiCl}_3$  could complete dehydrogenation within 2 h, while those of nanoconfined sample without catalyst and bulk material required 4 and up to 25 h, respectively. However, onset dehydrogenation temperatures of both nanoconfined samples with and without  $\text{TiCl}_3$  were comparable at  $250\text{ }^\circ\text{C}$ .

In this work, we further extend our studies on kinetic behavior and detailed reaction mechanisms of nanoconfined  $2\text{LiBH}_4\text{--MgH}_2$  doped with the other well-known catalyst of zirconium (IV) chloride ( $\text{ZrCl}_4$ ). Carbon aerogel scaffold prepared by carbonization of resorcinol-formaldehyde aerogel was embedded with  $\text{ZrCl}_4$  via solution impregnation. Afterward, milled  $2\text{LiBH}_4\text{--MgH}_2$  was nanoconfined into carbon aerogel scaffold impregnated with  $\text{ZrCl}_4$  by melt infiltration technique at  $310\text{ }^\circ\text{C}$  under 60 bar  $\text{H}_2$  back pressure to prevent dehydrogenation during melting. Successful nanoconfinement of  $2\text{LiBH}_4\text{--MgH}_2$  composite into carbon aerogel scaffold impregnated with  $\text{ZrCl}_4$  was investigated by  $\text{N}_2$  adsorption-desorption experiments. Dehydrogenation profiles and kinetics were studied by temperature programmed desorption (TPD) and titration measurements, respectively. For reaction mechanisms during melt infiltration, dehydrogenation and rehydrogenation, ex situ synchrotron radiation powder X-ray diffraction (SR-PXD) and Fourier transform infrared spectroscopy (FTIR) were carried out.

## 2. Experimental details

### 2.1. Sample preparation

Resorcinol-formaldehyde (RF) aerogel was synthesized according to the previous procedures [26]. The mixture of 41.4290 g resorcinol (99%, Aldrich), 56.66 mL deionized water, 56.92 mL formaldehyde solution (37 wt. % formaldehyde solution in water stabilized by 10–15 wt. % methanol, Sigma–Aldrich), and 0.0340 g  $\text{Na}_2\text{CO}_3$  (99.999%, Aldrich) was continuously stirred until homogeneity. The polymer solution sealed in polypropylene bottles was aged at room temperature for 24 h, at  $50\text{ }^\circ\text{C}$  for 24 h, at  $90\text{ }^\circ\text{C}$  for 72 h, and cooled to room temperature. The aerogel achieved was soaked in an acetone bath three times within 3–4 days and dried at

room temperature for several days in the fume hood. The dried aerogel was cut into small pieces (ca.  $0.4\text{ cm}^3$ ) and carbonized in a tubular oven at constant temperature of  $800\text{ }^\circ\text{C}$  ( $2.6\text{ }^\circ\text{C/min}$ ) for 6 h under  $\text{N}_2$  flow. The furnace was turned off and the sample was cooled down to room temperature. The gel obtained was further treated at  $500\text{ }^\circ\text{C}$  under vacuum for 16 h to obtain carbon aerogel scaffold, denoted as CAS.

Hydride composite of  $2\text{LiBH}_4\text{--MgH}_2$  under 2:1 ( $\text{LiBH}_4\text{:MgH}_2$ ) molar ratio was prepared by milling 5.3442 g of  $\text{LiBH}_4$  (90+ % hydrogen storage grade, Aldrich) with 3.1580 g of  $\text{MgH}_2$  (hydrogen storage grade, Aldrich) in a stainless steel vial (Evico Magnetic, Germany) to obtain the powder sample, denoted as milled 2Li–Mg. Milling was carried out at 400 rpm under an argon atmosphere in a glove box by using a Fritsch Pulverisette 6 classic line planetary. A milling time and a ball-to-powder weight ratio (BPR) of 5 h and 10:1, respectively, were used.

Catalytic doping of zirconium (IV) chloride ( $\text{ZrCl}_4$ ) in CAS was done by solution impregnation. The powder of CAS (0.5845 g) was immersed in  $\text{ZrCl}_4$  solution, prepared by dissolving 0.4659 g of  $\text{ZrCl}_4$  (99.9%, Aldrich) in 10.00 mL of distilled ethanol (99.99%, Aldrich) at room temperature in the glove box. As ethanol evaporated, 0.7547 g of  $\text{ZrCl}_4$ -impregnated CAS was achieved and denoted as  $\text{ZrCl}_4\text{--CAS}$ . The powder sample of milled 2Li–Mg was ground with  $\text{ZrCl}_4\text{--CAS}$  under three weight ratios of 1:1, 1:2, and 1:3 (milled 2Li–Mg: $\text{ZrCl}_4\text{--CAS}$ ). Nanoconfinement was carried out by using a Sievert-type apparatus (a PCTPro-2000, Hy-Energy LLC). All mixtures of different weight ratios of 1:1, 1:2, and 1:3 were heated to  $310\text{ }^\circ\text{C}$  ( $5\text{ }^\circ\text{C/min}$ ) under 60 bar  $\text{H}_2$ , dwelled at  $310\text{ }^\circ\text{C}$  for 30 min, and cooled to room temperature to obtain nanoconfined samples, denoted as nano 2Li–Mg–Zr (1:1), nano 2Li–Mg–Zr (1:2), and nano 2Li–Mg–Zr (1:3), respectively. For comparison, nanoconfined  $2\text{LiBH}_4\text{--MgH}_2$  without catalyst, named as nano 2Li–Mg (1:2) was also prepared under 1:2 weight ratio (milled 2Li–Mg:CAS) via similar procedures as nanoconfined samples with  $\text{ZrCl}_4$ .

### 2.2. Characterizations

Texture parameters of CAS, and nanoconfined samples were characterized by  $\text{N}_2$  adsorption-desorption measurements using a Nova 2000e surface area and pore size analyzer from Quantachrome and a BELSORP–mini II surface area and pore size analyzer, Bel–Japan. Prior to the measurements, a known amount of sample was degassed at room temperature under vacuum for several hours. All samples were studied with full adsorption and desorption isotherm in the pressure range of  $0\text{--}1\text{ } p/p_0$  at liquid nitrogen temperature with nitrogen gas as an adsorbent. The measurement was programmed to continuously change the pressure ratio to 1 for adsorption, and to 0 for desorption. Data were analyzed by t-plot method [27,28], the Brunner Emmet Teller (BET) method [29], and the Barret Joyner Halenda (BJH) method [30], and the highest point of the isotherm measurements (where  $p/p_0 \sim 1$ ) was used to calculate the total volume of the sample.

Dehydrogenation profiles of milled 2Li–Mg and nanoconfined samples with and without  $\text{ZrCl}_4$  were carried out by temperature programmed desorption (TPD) technique using a Chemisorption Analyzer, BelCatB, Bel–Japan [31]. The powder sample of  $\sim 50.0\text{ mg}$  was packed in the sample holder under Ar atmosphere in the glove box. The measurements were carried out by heating the powder sample from room temperature to  $500\text{ }^\circ\text{C}$  ( $5\text{ }^\circ\text{C/min}$ ) under Ar flow of 30 ml/min, dwelling at  $500\text{ }^\circ\text{C}$  for 20 min, and cooling to room temperature. The signal of hydrogen release was detected by thermal conductivity detector (TCD). For quantitative analyses, calibration was done by flowing 5%  $\text{H}_2/\text{Ar}$  (50 ml/min) to the TCD and using Ar (30 ml/min) as a carrier gas. The correlation between the hydrogen content and the peak area of TPD signal produced a

Download English Version:

<https://daneshyari.com/en/article/1521038>

Download Persian Version:

<https://daneshyari.com/article/1521038>

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