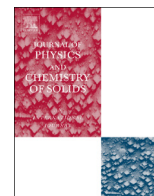




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journal homepage: [www.elsevier.com/locate/jpcs](http://www.elsevier.com/locate/jpcs)Ternary  $\text{LiBH}_4\text{-MgH}_2\text{-NaAlH}_4$  hydride confined into nanoporous carbon host for reversible hydrogen storage

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## ABSTRACT

Ternary hydride of  $\text{LiBH}_4\text{-MgH}_2\text{-NaAlH}_4$  confined into carbon aerogel scaffold (CAS) via melt infiltration for reversible hydrogen storage is proposed. Nanoconfinement of hydrides into CAS is obtained together with surface occupation of some phases, such as Al and/or LiH. Regarding nanoconfinement, not only multiple-step decomposition of  $\text{LiBH}_4\text{-MgH}_2\text{-NaAlH}_4$  hydride reduces to about single step, but also reduction of dehydrogenation temperature is significantly observed, for example,  $\Delta T$  up to 70 °C regarding last dehydrogenation step. Moreover, decomposition of  $\text{NaBH}_4$  in nanoconfined sample can be done at 360 °C (dehydrogenation temperature in this study), which is 115 and 180 °C lower than that of  $\text{NaBH}_4$  in milled  $\text{LiBH}_4\text{-MgH}_2\text{-NaAlH}_4$  and bulk  $\text{NaBH}_4$ , respectively. The reaction of  $\text{LiBH}_4 + \text{NaAlH}_4 \rightarrow \text{LiAlH}_4 + \text{NaBH}_4$  takes place during nanoconfinement and the decomposition of  $\text{LiAlH}_4$  is observed, resulting deficient hydrogen content liberated. However, hydrogen content released (1st cycle) and reproduced (2nd–4th cycles) from this ternary hydride enhances up to 11% and 22% of full hydrogen storage capacity due to nanoconfinement. After rehydrogenation ( $T=360$  °C and  $P(\text{H}_2)=50$  bar  $\text{H}_2$  for 12 h),  $\text{NaBH}_4$ ,  $\text{MgH}_2$ , and  $\text{Li}_3\text{AlH}_6$  are reversible, whereas  $\text{Li}_3\text{AlH}_6$  and  $\text{NaBH}_4$  in milled sample cannot be recovered due to deficient hydrogen pressure ( $T=360$  °C and  $P(\text{H}_2)=80$  bar) and probably evaporation of molten sodium during dehydrogenation, respectively. The latter results in inferior hydrogen content reproduced from milled sample to nanoconfined sample.

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## 1. Introduction

Lithium borohydride ( $\text{LiBH}_4$ ) is significantly of interest as hydrogen storage material due to its high storage capacity up to 18.5 wt%  $\text{H}_2$ , however, several drawbacks of unfavorable thermodynamics, sluggish kinetics, release of toxic diborane ( $\text{B}_2\text{H}_6$ ) gas during dehydrogenation, and severe temperature and pressure condition for reversibility ( $T=600$  °C,  $P(\text{H}_2)=150$  bar) obstruct its practical uses as onboard hydrogen storages [1–4]. One of the most promising strategies to solve the latter problems is compositing  $\text{LiBH}_4$  with other metal hydrides, such as  $\text{MgH}_2$ , called reactive hydride composite (RHC). RHC of  $2\text{LiBH}_4\text{-MgH}_2$  provided not only reduction of enthalpy by 25 kJ/mol  $\text{H}_2$  due to the formation of  $\text{MgB}_2$  upon dehydrogenation, but also milder condition for reversibility ( $T=350$  °C,  $P(\text{H}_2)=50$  bar) [5–7]. To further improve the performance of this RHC, several catalysts and additives, e.g.,  $\text{SiO}_2$ ,  $\text{VCl}_3$ , titanium isopropoxide (Ti-iso),  $\text{Sc}_2\text{O}_3$ ,  $\text{MgB}_2$ ,  $\text{MoCl}_3$ ,  $\text{NbF}_5$  [7–11], were doped by ball milling technique. For instance,  $2\text{LiBH}_4\text{-MgH}_2$  doped with Ti-iso performed about ten times faster

dehydrogenation kinetics ( $T=400$  °C and  $P(\text{H}_2)=5$  bar) as compared with the sample without Ti-iso and it could preserved 8–8.5 wt%  $\text{H}_2$  after three hydrogen release and uptake cycles [7,12]. It was found that comparable crystal structures of  $\text{MgB}_2$  and  $\text{TiB}_2$  formed upon dehydrogenation enhanced coherent interfaces for heterogeneous nucleation of  $\text{MgB}_2$  phase, resulting in kinetic improvement. Besides, by doping with  $\text{MoCl}_3$  onset temperature and activation energy for dehydrogenation of  $2\text{LiBH}_4\text{-MgH}_2$  composite reduced by 50 °C and 10.2 kJ/mol, respectively [9].

The other group of additive doped in  $2\text{LiBH}_4\text{-MgH}_2$  composite is metallic aluminum (Al) and complex hydrides of light metal cations and aluminum hydride (e.g.,  $\text{LiAlH}_4$  and  $\text{NaAlH}_4$ ). For example, at 400 °C under 1 mbar  $\text{H}_2$ ,  $4\text{LiBH}_4\text{-MgH}_2\text{-Al}$  released up to 9 wt%  $\text{H}_2$  within 42 min, while that of  $2\text{LiBH}_4\text{-MgH}_2$  was ~6 wt%  $\text{H}_2$ . The formation of  $\text{MgAlB}_4$  observed during dehydrogenation instead of amorphous boron led to improvement of de/rehydrogenation performance of  $\text{LiBH}_4$ . However, complete rehydrogenation ( $T=400$  °C and  $P(\text{H}_2)=40$  bar) could not be obtained, especially Mg to  $\text{MgH}_2$  because some Mg alloyed with Al to form  $\text{Mg}_2\text{Al}_3$ , extremely stable at 400 °C [13]. Regarding  $\text{LiAlH}_4$  and  $\text{NaAlH}_4$ , they acted not only as Al source for  $2\text{LiBH}_4\text{-MgH}_2$  composite, but also as hydrogen storage materials due to their high storage capacities of 10.5 and 7.5 wt%, respectively [14,15]. Ternary

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hydride of  $\text{LiAlH}_4\text{-MgH}_2\text{-LiBH}_4$  liberated hydrogen up to 9 wt% in three steps at 120–450 °C, corresponding to the decomposition of  $\text{LiAlH}_4$ ,  $\text{MgH}_2$ , and  $\text{LiBH}_4$ , respectively [14]. By doping with  $\text{TiF}_3$  ( $\text{LiAlH}_4\text{-MgH}_2\text{-LiBH}_4\text{-0.05TiF}_3$ ), onset and end temperatures for dehydrogenation decreased to about 50 and 400 °C, respectively, together with reduction of dehydrogenation enthalpy by  $\sim 20$  kJ/mol  $\text{H}_2$  as compared with bulk  $\text{LiBH}_4$  [14]. For  $\text{NaAlH}_4\text{-MgH}_2\text{-LiBH}_4$  composite, the reaction of  $\text{NaAlH}_4 + \text{LiBH}_4 \rightarrow \text{LiAlH}_4 + \text{NaBH}_4$  proceeded during ball milling and three-step dehydrogenation of  $\text{LiAlH}_4$ ,  $\text{MgH}_2$ , and  $\text{NaBH}_4$  was observed at 150–500 °C with 9.5 wt%  $\text{H}_2$  [15]. During dehydrogenation of both  $\text{LiAlH}_4\text{-MgH}_2\text{-LiBH}_4$  and  $\text{NaAlH}_4\text{-MgH}_2\text{-LiBH}_4$  composites, formation of Li–Mg, Mg–Al, and Mg–Al–B alloys favored thermodynamics by altering de/rehydrogenation pathway. However, less than 50% of  $\text{H}_2$  content was reproduced from both ternary hydrides, for example, only 4–4.5 wt%  $\text{H}_2$  was recovered in the 2nd and 3rd cycles at 350–400 °C under 40–50 bar  $\text{H}_2$  [14,15]. This could be due to the fact that stable  $\text{Mg}_2\text{Al}_3$  alloy formed upon dehydrogenation required high hydrogen pressure of  $> 100$  bar (at 350 °C) to proceed the reaction  $\text{Mg}_2\text{Al}_3 + 2\text{H}_2 \rightarrow 2\text{MgH}_2 + 3\text{Al}$  [15–17].

In this work, we would like to propose another strategy to improve de/rehydrogenation performance of  $\text{LiBH}_4\text{-MgH}_2$  composite via synergetic effect of additive ( $\text{NaAlH}_4$ ) and nanoconfinement. Not only increase of surface area and grain boundaries, resulting in faster de/rehydrogenation rate can be obtained from nanoconfinement of hydrides into porous carbon hosts, but also particle growth and agglomeration during cycling was constrained [18,19]. Nanoconfined  $2\text{LiBH}_4\text{-MgH}_2$  in carbon aerogel scaffold (CAS) revealed ten times faster desorption kinetics than milled material as well as suppression of  $\text{B}_2\text{H}_6$  during dehydrogenation [19, 20]. For the present work, ternary hydride of  $\text{NaAlH}_4\text{-MgH}_2\text{-LiBH}_4$  under 1:1:1 molar ratio is melt infiltrated into CAS at melting point of  $\text{LiBH}_4$ . Nanoconfinement of hydride materials is studied by  $\text{N}_2$  adsorption-desorption and powder X-ray diffraction (PXRD). De/rehydrogenation performance is determined by temperature programmed desorption (TPD) and Sievert-type apparatus. To determine the mechanisms during hydrogen exchange reaction, PXRD, Fourier transform infrared spectroscopy (FTIR), and solid-state  $^7\text{Li}$ ,  $^{11}\text{B}$ , and  $^{23}\text{Na}$  magic angle spinning (MAS) nuclear magnetic resonance (NMR) are carried out.

## 2. Experiments

### 2.1. Sample preparation

Carbon aerogel scaffold (CAS) was synthesized according to the previous procedures [19,21]. The mixture of 41.4200 g of resorcinol (99%, Sigma-Aldrich), 56.60 mL of deionized water, 57.00 mL of formaldehyde in water (37 wt% stabilized by 10–15 wt% methanol, QRc), and 0.0780 g of anhydrous  $\text{Na}_2\text{CO}_3$  (99.999%, Aldrich) was continuously stirred till homogeneity. The mixture sealed in a polyethylene bottle was aged at room temperature for 24 h, at 50 °C for 24 h, and at 90 °C for 72 h, and cooled to room temperature to obtain a polymer aerogel. The aerogel was cut into small pieces, soaked in an acetone bath three times within 2 days, and dried at room temperature for several days in the fume hood. The dried aerogel was carbonized in a tubular furnace at constant temperature of 800 °C (2.6 °C/min) for 6 h under  $\text{N}_2$  flow. The furnace was turned off and the sample was cooled down naturally to room temperature. The gel obtained was further treated at 500 °C under vacuum for 6 h to obtain a carbon aerogel scaffold, denoted as CAS.

$\text{MgH}_2$  (95%, Acros) was packed in a sealed vial (8004 Tungsten carbide vial set, SPEX SamplePrep, USA) under an argon (Ar) atmosphere in a glove box and milled by using a SPEX SamplePrep

8000D DUAL Mixer/Mill<sup>®</sup>. Ball-to-powder weight ratio and milling time were 15:1 and 5 h, respectively. Milled  $\text{MgH}_2$  powder was physically mixed with  $\text{LiBH}_4$  ( $\geq 90\%$ , hydrogen storage grade, Across) and  $\text{NaAlH}_4$  ( $\geq 93\%$ , hydrogen storage grade, Sigma-Aldrich) under a molar ratio of 1:1:1 in the mortar. The mixture of  $\text{LiBH}_4\text{-MgH}_2\text{-NaAlH}_4$  was ground with CAS under a weight ratio of 1:1 (CAS:hydride composite) to obtain CAS- $\text{LiBH}_4\text{-MgH}_2\text{-NaAlH}_4$ . Nanoconfinement was carried out by heating the powder sample of CAS- $\text{LiBH}_4\text{-MgH}_2\text{-NaAlH}_4$  to 310 °C (5 °C/min) under 100 bar  $\text{H}_2$ , dwelling at 310 °C for 45 min, and cooling to room temperature to achieve nanoconfined sample of  $\text{LiBH}_4\text{-MgH}_2\text{-NaAlH}_4$  in CAS, denoted as nano Li–Mg–Na@CAS. The mixture of  $\text{LiBH}_4$ ,  $\text{MgH}_2$ , and  $\text{NaAlH}_4$  under the molar ratio of 1:1:1 was milled for 1 h by using ball-to-powder weight ratio of 30:1 to obtain ternary powder sample, denoted as milled Li–Mg–Na.

### 2.2. Characterizations

Texture parameters of CAS and nano Li–Mg–Na@CAS based on specific surface area, pore size, and pore volume were characterized by  $\text{N}_2$  adsorption-desorption measurements at 77 K using a BELsorp-mini II, Japan Prior to the measurements, a known amount of sample was degassed at 350 °C (CAS) and at room temperature (nano Li–Mg–Na@CAS) under vacuum for 24 h. All samples were studied with full adsorption and desorption isotherm in the pressure range of 0–1  $p/p_0$  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 was analyzed by the  $t$ -plot method [22,23], the Brunner Emmet Teller (BET) method [24], and the Barret Joyner Halenda (BJH) method [25]. 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 and nanoconfined samples were characterized by temperature programmed desorption (TPD) technique using a Chemisorption Analyzer, BelCatB, Bel-Japan. The powder sample of  $\sim 50.0$  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 °C (5 °C/min) under Ar flow of 30 ml/min, dwelling at 500 °C for 20 min, and cooling to room temperature. The signal of hydrogen release was detected by a 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 hydrogen content and peak area of TPD signal produced a constant named conversion factor (CF, counts/mmol). In this work, average value of CF was obtained from 10 pulses of 5%  $\text{H}_2/\text{Ar}$  flow. The CF was used to calculate the content of hydrogen released from each sample based on the peak area of its TPD signal.

Dehydrogenation kinetics was studied by using a laboratory scale setup of a Sievert-type apparatus [26]. The powder sample of  $\sim 60\text{--}80$  mg was loaded in a stainless steel sample holder (316SS, Swagelok) under Ar atmosphere in the glove box and transferred to the apparatus. Two K-type thermocouples ( $-250$  to  $1300$  °C, SL heater) were attached to the sample holder and the furnace to measure the temperature of the system. Pressure transducers (C206, Cole Parmer) in the pressure range of 0–500 psig and 0–3000 psig were used to measure the pressure changes due to hydrogen desorption and absorption, respectively. Thermocouples and pressure transducers were connected to an AI 210I module convertor data logger (Wisco), measuring and transferring (every 1 s) the pressure and temperature changes of the sample to the computer for further evaluation. Dehydrogenation was done by heating the sample from room temperature to 360 °C (3.6 °C/min) under vacuum. For rehydrogenation, the dehydrogenated powder

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