

Hydrogen storage properties of nanoconfined LiBH_4 - NaBH_4

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Abstract

In this study a eutectic melting composite of $0.62\text{LiBH}_4\text{-}0.38\text{NaBH}_4$ has been infiltrated in two nanoporous resorcinol formaldehyde carbon aerogel scaffolds with similar pore sizes (37 and 38 nm) but different BET surface areas (690 and 2358 m^2/g) and pore volumes (1.03 and 2.64 mL/g). This investigation clearly shows decreased temperature of hydrogen desorption, and improved cycling stability during hydrogen release and uptake of bulk $0.62\text{LiBH}_4\text{-}0.38\text{NaBH}_4$ when nanoconfined into carbon nanopores. The hydrogen desorption temperature of bulk $0.62\text{LiBH}_4\text{-}0.38\text{NaBH}_4$ is reduced by ~ 107 °C with the presence of carbon, although a minor kinetic variation is observed between the two carbon scaffolds. This corresponds to apparent activation energies, E_A , of $139 \text{ kJ}\cdot\text{mol}^{-1}$ (bulk) and $116 - 118 \text{ kJ}\cdot\text{mol}^{-1}$ (with carbon aerogel). Bulk $0.62\text{LiBH}_4\text{-}0.38\text{NaBH}_4$ has poor reversibility during continuous hydrogen release and uptake cycling, maintaining 22 % H_2 capacity after four hydrogen desorptions (1.6 wt.% H_2). In contrast, nanoconfinement into the high surface area carbon aerogel scaffold significantly stabilizes the hydrogen storage capacity, maintaining ~ 70 % of the initial capacity after four cycles (4.3 wt.% H_2).

Keywords

Nanoconfinement, eutectic melting composite, carbon dioxide activation, cyclic stability

1. Introduction

Our anthropogenic effect on the environment originated from utilization of fossil fuels consumption has facilitated research in alternative energy storage materials. Particularly, hydrogen is considered a suitable substitute for gasoline, due to its high energy content and non-toxic, carbon-free composition [1].

LiBH_4 is considered a potential candidate for solid state hydrogen storage due to its hydrogen storage capacity of 13.9 wt.% H_2 (excluding the decomposition of LiH) [2, 3]. However, the hydrogen desorption and absorption of LiBH_4 suffers from poor sorption kinetics and insufficient reversibility during hydrogen release and uptake cycling, not to mention its high melting point of $T_{\text{melt}} = 275 \text{ }^\circ\text{C}$ [4]. In the 1970s, Semenenko and Adams reported that LiBH_4 could be destabilized by the addition of NaBH_4 in the stoichiometric ratio of $0.62\text{LiBH}_4\text{-}0.38\text{NaBH}_4$ by forming a eutectic melting composite with a melting point of $\sim 220 \text{ }^\circ\text{C}$ [5, 6]. However, no data was presented on the hydrogen storage properties. Recently, Paskevicius et al. revealed data showing the thermal decomposition of the system, confirming a eutectic melting in the temperature range of $210 - 220 \text{ }^\circ\text{C}$ [7]. Furthermore, similar results for binary borohydride composites systems have already been published for eutectic composites comprised of LiBH_4 mixed with $\text{Mg}(\text{BH}_4)_2$, $\text{Ca}(\text{BH}_4)_2$, KBH_4 or $\text{Mn}(\text{BH}_4)_2$, respectively [7-13]. In the present study, the eutectic melting point of $\text{LiBH}_4\text{-NaBH}_4$ was exploited for nanoconfinement by melt infiltration into a high surface area nanoporous resorcinol formaldehyde carbon aerogel scaffold [14-17]. Nanoporous carbon based scaffolds may enhance hydrogen release/ uptake kinetics and improve reversibility of the nanocomposite, in addition more favorable thermodynamic properties may be achieved [18-20]. A few studies have been conducted on attempting to enhance the kinetics and reduce the temperature for hydrogen desorption of similar complex binary eutectic borohydride systems, by introducing carbon scaffolds. Several systems explore the properties of binary complex hydrides for nanoconfinement

such as $\text{LiBH}_4\text{-CaBH}_4$ [21-23], $\text{LiBH}_4\text{-Mg}_2\text{NiH}_4$ [24], $\text{LiBH}_4\text{-Mg}(\text{BH}_4)_2$ [11-13, 25], $\text{LiBH}_4\text{-LiAlH}_4$ [26] and $\text{LiBH}_4\text{-NaAlH}_4$ [27]. These systems all form eutectic melts when mixed together which makes them suitable for infiltration into porous scaffolds. As reported for the respective systems, nanoconfinements either in CAS, CMK-3, IRH-33 and NPC does facilitate hydrogen desorption and does improve the rehydrogenation of the hydride.

The hydrogen storage properties of the nanoconfined and bulk binary metal borohydride system are investigated experimentally with powder X-ray diffraction (PXRD), temperature programmed desorption – mass spectroscopy (TPD-MS), the Sieverts' method and Fourier transformed infrared spectroscopy (FTIR). We find that $\text{LiBH}_4\text{-NaBH}_4$ can be confined inside the mesoporous carbon scaffold via melt infiltration, the presence of the scaffold reduces the temperature for hydrogen emission and improves the reversibility of hydrogen release and uptake.

2. Experimental Details

2.1 Sample Preparation.

Synthesis of resorcinol formaldehyde carbon aerogel (CA) was done by mixing 82.87 g resorcinol (Aldrich, 99 %), 113.84 mL formaldehyde, (37 wt.% stabilized by ~10-15% methanol, Merck), 113.28 mL deionized water and 0.0674 g Na_2CO_3 (Aldrich, 99.999%) during continuous stirring until complete dissolution was obtained. The pH of the final sol gel solution was 5.91. The following synthesis procedure and characterization of the aerogel was conducted as previously described [28-31]. Portions of the prepared CA were CO_2 -activated according to previous methods [28, 30, 32]. Before hydride infiltration, the CA monoliths were degassed at 400 °C under dynamic vacuum for five hours to remove adsorbed air and water from within the porous structure. All subsequent handling was performed in a glove box with purified argon atmosphere.

Commercially available LiBH_4 (Aldrich, $\geq 95\%$) and NaBH_4 (Aldrich, 99.99%) were mixed in the molar ratio $0.62\text{LiBH}_4\text{-}0.38\text{NaBH}_4$ which is reported to show eutectic melting ($\sim 220\text{ }^\circ\text{C}$) [5-7]. The mixture of bulk hydrides was ball milled according to previously published methods [13] and this sample is denoted LiNa. Briefly, a Fritsch P4 planetary mill with a tungsten carbide bowl and balls was used at a ball-to-powder (BTP) ratio of 24:1 with 2 minute milling cycles followed by 2 minute cooling cycles. The sample was milled for a total of 60 minutes at 250 rpm. The theoretical hydrogen content of bulk LiNa, based on the stoichiometric composition $0.62\text{LiBH}_4\text{-}0.38\text{NaBH}_4$, was calculated to be $\rho_m(\text{LiNa}) = 12.2\text{ wt.\% H}_2$.

The added amount of hydride was selected in order to obtain a degree of pore filling corresponding to $\sim 60\text{ vol\%}$, calculated based on the total pore volume, V_{tot} , of the scaffold and the average bulk densities $\rho(\text{LiNa}) = 0.787\text{ g/mL}$. Melt infiltration was performed using gas handling components and a stainless steel pressure cell that heated the sample to $T = 240\text{ }^\circ\text{C}$ ($\Delta T/\Delta t = 2\text{ }^\circ\text{C/min}$) under a H_2 pressure of 140 – 168 bar at $240\text{ }^\circ\text{C}$ for 30 min. The furnace was then turned off and the sample allowed to cool to room temperature.

2.2 Sample Characterization

Synchrotron radiation powder X-ray diffraction (SR-PXD) data were collected at beamline I711 at MAX-lab in Lund, and at PETRA III beamline P07 of DESY in Hamburg. While in the glovebox, the samples were mounted in a sapphire capillary tube (0.79 mm. I.D.), in an airtight sample holder inside an argon filled glovebox [33]. The sample holder was removed from the glovebox and attached to a gas control system at the synchrotron diffractometer. The data was collected using a CCD detector with a selected wavelength of $\lambda = 0.99185\text{ \AA}$ (MAX-lab) and $\lambda = 0.23088\text{ \AA}$ (PETRA III).

A Perkin Elmer STA 6000 coupled with a Hiden Analytical quadrupole mass spectrometer was used to perform thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) mass spectroscopy (MS) measurements. Thus, temperature-programmed desorption mass spectroscopy (TPD-MS) data is provided. The measurements were performed in constant flow (64 mL/min) of argon (99.99%). A powdered sample (< 5 mg), was placed in an Al₂O₃ crucible with lid and were heated in the temperature range of 40 to 500 °C ($\Delta T/\Delta t = 2$ °C/min). The MS signals at $m/e = 2$, 18 and 34 were monitored so as to detect the presence of H₂, H₂O and B₂H₆. Kissinger plots were obtained from the DSC data by heating selected samples at 2, 5 10 and 15 °C/min from which the temperature for maximum DSC signal of hydrogen desorption is utilized.

Sieverts' measurements were conducted on nanoconfined and bulk 0.62LiBH₄-0.38NaBH₄ during four hydrogen release and uptake cycles. Hydrogen desorption data was collected on a PCTPro 2000 Sieverts' apparatus in the temperature range of RT to 500 °C ($\Delta T/\Delta t = 2$ °C/min), with the temperature maintained at 500 °C for 10 h, at $p(\text{H}_2) = 1$ bar. Hydrogen absorption was performed in the pressure range of 140 to 150 bar, at a temperature of 400 °C ($\Delta T/\Delta t = 5$ °C/min) during 10 h, and then the sample was cooled naturally to RT.

The Fourier transform infrared spectrometry (FTIR) analyses were carried out on a NICOLET 380 FT-IR from Thermo- Electronic Corporation with a permanently aligned optics and proprietary diamond-turned pinned-in-place mirror optics. A small amount of sample was placed on the base plate and subsequently the diamond pin was pressed on to the sample, forming a thin film. The samples were examined within the wave number range of 4000 - 400 cm⁻¹.

3. Results and Discussion

The structural parameters of pristine carbon aerogel (CA) are determined from nitrogen adsorption analysis using the BET, BJH and t-plot method [34, 35] and are given in Table 1. CA has a specific BET surface area of $S_{\text{BET}} = 690$ m²/g, a total pore volume of $V_{\text{tot}} = 1.03$ mL/g and a pore size

distribution centered around $D_{\max} = 37$ nm. CO₂-activation of CA for 4 hours (CA-4) results in significant increase of structure parameters; $S_{\text{BET}} = 2358$ m²/g, $V_{\text{tot}} = 2.64$ mL/g and $D_{\max} = 38$ nm. The amount of LiNa added to the scaffold is also provided in gravimetric and volumetric quantities, corresponding to a pore filling of ~60 vol% which ensures complete infiltration of the hydride. After infiltration of LiNa, the structure parameters of the carbon composite are significantly reduced (see supporting information) suggesting infiltration into the pores of the scaffold.

3.1 In situ SR-PXD study of nanoconfined LiBH₄-NaBH₄

The eutectic melting composite prepared by mechanical ball milling of LiBH₄-NaBH₄ forms a physical mixture of the two hydrides. *In-situ* synchrotron radiation powder X-ray diffraction (SR-PXD) is used to follow the melt infiltration process of LiNa into scaffold CA under hydrogen pressure, as shown in Figure 1. Initially, the diffraction patterns of the low temperature polymorphs NaBH₄ and *o*-LiBH₄ are present, which during heating to 110 °C gives rise to a phase transition to *h*-LiBH₄. The melting of the eutectic composite occurs at ~225 °C. As expected, at 240 °C, the Bragg peaks of NaBH₄ and *h*-LiBH₄ almost completely disappears, which is associated with the eutectic melting regime. After 15 min at 240 °C the sample is cooled to RT allowing the eutectic hydride composite to recrystallize inside the pores of the carbon aerogel. During cooling, *h*-LiBH₄ transforms to *o*-LiBH₄ and the diffraction pattern at RT also exhibit NaBH₄ peaks, as shown in Figure 1. This indicates that no reaction occurs between LiBH₄ and NaBH₄ but miscibility results in formation of a molten phase. The Bragg peaks are significantly reduced and broadened, indicating nano crystallite formation of LiNa inside the pores of CA. Unfortunately, ball milling of 0.62LiBH₄-0.38NaBH₄ resulted in contamination by the ball-milling media, tungsten carbide WC, as indicated by three distinct diffraction peaks at 2θ values 21°, 23° and 31°.

3.2 Hydrogen Desorption

Thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and temperature programmed desorption mass spectroscopy (TPD-MS), has been used to investigate the first hydrogen desorption of bulk $0.62\text{LiBH}_4\text{-}0.38\text{NaBH}_4$ (LiNa) and LiNa physically mixed with CA (CA mix) and melt infiltrated in CA (CA melt), see Figure 2. The TPD-MS of bulk LiNa exhibits two minor hydrogen release peaks with onset at 200 and 270 °C *i.e.* peak **a** and **b**, respectively. The first desorption peak may be assigned to the eutectic melting of LiNa, which is expected to occur around 224 °C [5, 6]. The major hydrogen desorption event begins at 350 °C and the release of hydrogen continues until 500 °C with two local maxima observed at 380 and 440 °C (denoted **c** and **d**, respectively). The total amount of released hydrogen from the bulk LiNa hydride is only 7.56 wt.% in the temperature range of 50 to 500 °C and corresponds to 62 % of the available hydrogen in the sample content, possibly due to partial decomposition of both LiBH_4 and NaBH_4 .

The addition of carbon aerogel (CA), whether as physically mixed with LiNa or melt infiltrated into the scaffold, significantly improves the hydrogen release kinetics compared to that of bulk LiNa *i.e.* the major hydrogen desorption rate of sample CA occurs at 333 °C (**d'** is 107 °C lower than for that of bulk, **d**). The reduced temperature is elucidated in Figure 2C, as peaks **a'**, **c'** and **d'**, in which these peaks are equivalent to those presented in the bulk desorption profile. Furthermore, the onset temperature for hydrogen release is as low as 150 °C, possibly assigned to the effect induced by nanoconfinement or the presence of the carbon surface, acting as a catalyst for hydrogen desorption [18]. Comparing the mixed and nanoconfined samples, it is worth noting that the hydrogen desorption profile of the physical mixed sample displays an intense peak at 232 °C (**a'**), which is not present in the nanoconfined sample. This is due to the pretreated process during melt infiltration and states that a fraction of hydrogen is desorbed during the melting of $\text{LiBH}_4\text{-NaBH}_4$. The weight loss fraction of hydrogen release for the melt infiltrated sample (CA melt) is 3.95 wt.%, upon heating from 50 to 500 °C, corresponding to 98 % of the samples theoretical available hydrogen

content (4.0 wt.% H₂). However, the physical mixed sample only releases 2.73 wt.% H₂, in the same temperature range, corresponding to 66 % of the available hydrogen content. This demonstrates that the nanoconfined sample facilitate destabilization of LiNa and larger hydrogen loss, in contrast to the physically mixed sample. From the DSC curve (Figure 2B) of bulk LiNa, the polymorphic transformation from *o*- to *h*-LiBH₄ ($T = 98$ °C) and the endothermic signal of the eutectic melting ($T = 224$ °C) is observed. In the case of the physically mixed sample the signal for the melting occur at significantly lower temperature and in addition, a subsequent exothermic peak ($T = 226$ °C) is observed which could possibly be assigned to the wetting of CA by molten LiNa [8]. The DSC signals of the melt infiltrated sample, CA-LiNa, are also shifted towards lower temperatures compared to bulk LiNa. Three endothermic signals are displayed at 96, 214 and 316 °C, see Figure 2B. The first signal corresponds to the polymorphic transformation of LiBH₄ and is shifted 2 °C lower than for bulk LiNa. The second corresponds to the melting of the eutectic mixture and occurs 10 °C lower than the bulk. Finally, the third broad peak is assigned to the major hydrogen desorption of LiNa.

The TPD peaks **c** and **d** seems to relate to the decomposition of LiBH₄ and NaBH₄, respectively. However, it is not clear from the data collected which peak corresponds to which borohydride. The temperature difference between **c'** and **d'** compared to **c** and **d** may be due to the difference in the interaction between the carbon scaffold and the respective borohydrides, *i.e.* a possible catalytic effect [18].

Employing the high surface area scaffold (CA-4), for nanoconfinement of LiNa, does not facilitate major alterations in hydrogen desorption kinetics compared to the as prepared scaffold (CA), *i.e.* the temperature for maximum hydrogen release rate is 336 °C, see Figure S3 in supporting information. Interestingly, sample CA-4 rehydrogenated for 10 hours at 140 bar H₂ pressure (after 4 desorption cycles) shows reduced hydrogen release temperatures compared to the nanoconfined sample CA-4,

with the maximum temperature for hydrogen released reduced to 315 °C. However, in the first hydrogen desorption, the binary hydride composite possibly reacts to the scaffold facilitating an earlier release of hydrogen.

The kinetics for hydrogen release of LiNa, CA and CA-4 is further analyzed the Kissinger approach, see Figure 3. A significant decrease in apparent activation energy, E_A , for hydrogen release of nanoconfined LiNa compared to bulk LiNa is observed. The apparent activation energies (E_A) of hydrogen desorption of bulk and nanoconfined LiNa, in CA and CA-4 and are estimated to be 139, 116 and 118 $\text{kJ}\cdot\text{mol}^{-1}$, respectively (see Figure 3). Thus, CO_2 -activation has no significant effect on the activation energy. Nanoconfinement and different carbon materials have previously been shown to have a significant improvement of kinetics and a reduction of the apparent activation energy for hydrogen release reactions [18].

3.3 Cyclic stability and reversibility

Sieverts' measurements have been conducted to investigate the stability of the hydrogen capacity over four desorption/absorption cycles. The four desorption profiles of bulk $0.62\text{LiBH}_4\text{-}0.38\text{NaBH}_4$ (LiNa) and LiNa nanoconfined in 'as-prepared' (CA) and CO_2 -activated (CA-4) carbon aerogels are displayed in Figure 4. The amount of hydrogen released is presented relative to the gravimetric amount of $0.62\text{LiBH}_4\text{-}0.38\text{NaBH}_4$ in the samples (wt.% H_2 / LiNa), as a function of time and temperature.

Bulk LiNa releases 7.2 wt.% H_2 / LiNa during the first desorption that corresponds to 59 % of the available hydrogen content in the sample, $\rho_m(\text{LiNa}) = 12.2$ wt.% H_2 . This compares well with the result obtained from the TGA measurement. A significant decrease of more than 70 % is observed during the second, third and fourth desorption *i.e.* 2.1, 1.6 and 1.6 wt.% H_2 , corresponding to 29.2, 22.2 and 22.2 % of the calculated hydrogen content of the LiNa, respectively, see Table 2.

Hydrogen release of LiNa nanoconfined into CA is significantly enhancing the cyclic stability compared to bulk LiNa. During the first desorption 10.5 wt.% H₂ / LiNa (corresponding to 86 % of the theoretical available hydrogen content). In the second, third and fourth desorption 6.3, 5.8 and 5.4 wt.% H₂ / LiNa is released which is equivalent to 60, 55 and 51 % of the initial hydrogen content, respectively. The amount of hydrogen released relative to the total mass of LiNa-CA nanoconfined is 3.4 wt.% H₂ during the first desorption and is in good agreement with the TGA data (Figure 2). The increased amount of released hydrogen during the second to fourth cycle may be due to facilitated hydrogen absorption for the nanoconfined sample.

The gravimetric hydrogen storage capacity and the cyclic stability of LiNa nanoconfined into CO₂ activated carbon aerogel CA-4 are further improved compared to sample CA-LiNa, in well agreement with previous studies [13, 23, 32]. The first desorption releases 11.5 wt.% H₂ / LiNa (~94 % of the theoretical available hydrogen content), corresponding to 6.4 wt.% H₂ / sample. During the second, third and fourth desorption cycles, sample CA-4 releases 7.9, 7.8 and 7.7 wt.% H₂ / LiNa *i.e.* ~67 % of the initial hydrogen capacity is retained during four cycles.

In general the employment of CA for nanoconfinement of LiNa is associated with 51 % retention of hydrogen capacity after four desorption cycles, in contrast to only 22 % for bulk LiNa under the selected physical conditions for hydrogen release and uptake. However, further enhancement in cyclic stability is obtained using the high surface area scaffold CA-4 maintaining 67 % of the total capacity after four desorption cycles. This is considered a significant enhancement of the hydrogen storage properties of eutectic nano composite of LiBH₄-NaBH₄, which is a rather unexplored system.

The FTIR spectra indicate reversible hydrogen storage of $0.62\text{LiBH}_4\text{-}0.38\text{NaBH}_4$ and formation of metal borohydrides during rehydrogenation. In Figure 5, bulk LiBH_4 and NaBH_4 both demonstrates three characteristic B-H stretching modes in the range of $2000 - 2500 \text{ cm}^{-1}$ as well as B-H bending bands at 1093 , 1236 and 1298 cm^{-1} in LiBH_4 and a single signal at 1095 cm^{-1} for that of NaBH_4 . The bulk eutectic LiNa mixture evidently exhibits a combination of the previously mentioned B-H bending and stretching bands (red spectrum), however after nanoconfinement, these signals are significantly reduced due to the presence of the carbon scaffold (green spectra). As the nanoconfined sample has been completely dehydrogenated *i.e.* heated to $500 \text{ }^\circ\text{C}$ for 10 hours, the FTIR spectrum (blue) only displays a single B-H stretch at 2345 cm^{-1} . This stretch is at a slightly higher wave number than for the stretch originating from the borohydrides, and therefore could be assigned to another borohydride compound e.g. *closo*-borane, though it is amorphous as demonstrated with PXD in Figure 6. The FTIR spectra closely resemble that of $\text{Li}_2\text{B}_{12}\text{H}_{12}$ [36]. Furthermore, rehydrogenation of the decomposed sample at $400 \text{ }^\circ\text{C}$ for 10 hours at a hydrogen pressure of 140 bar (orange spectra) results in the observation of low intensity B-H stretching in the wave number range between $2000 - 2500 \text{ cm}^{-1}$. The sharp signals in this range can be clearly assigned to the B-H stretching of NaBH_4 . From powder diffraction it is confirmed that NaBH_4 is formed during rehydrogenation at $400 \text{ }^\circ\text{C}$, 140 bar hydrogen after 10 hours. Decomposition of nanoconfined LiNa facilitates the formation of the product Li_3BO_3 and the lack of B-H stretching modes for LiBH_4 in the rehydrogenated FTIR spectrum (orange spectrum) may be due to the oxidation of a significant proportion of the initial LiBH_4 . However, once this reaction has taken place and all of the framework oxygen has been converted to stable Li_3BO_3 , the remaining nanoconfined $\text{LiBH}_4\text{-NaBH}_4$ is reversible. These results suggest that the reversible source may be an amorphous compound of LiBH_4 and NaBH_4 . Weak LiH diffraction peaks are observed after rehydrogenation of the nanoconfined sample (see Figure 6). This implies that metallic Li should be

formed after decomposition, which is converted to LiH after rehydrogenation under the applied conditions. However, the lack of metallic Li diffraction peaks in the decomposed sample might suggest that Li nanoparticles are present, and combined with the fact that even having the theoretical amount of Li in the carbon aerogel means that it is only a small proportion of the sample.

4. Conclusion

The eutectic melting composite $0.62\text{LiBH}_4\text{-}0.38\text{NaBH}_4$ (LiNa) is a physical mixture of the respective borohydrides with a melting point of $T_{\text{melt}} \sim 225$ °C. This composite has been successfully melt infiltrated into a pristine carbon aerogel scaffold (CA) and a CO_2 -activated high surface area carbon aerogel scaffold (CA-4). The effect of CO_2 -activated carbon aerogel allows infiltration of larger quantities of hydride. Furthermore, the activation procedure appears to make the carbon more inert, thereby reducing the amount of possible formed borates and oxides which could contribute to the improved reversibility. The employment of CA significantly improves the hydrogen desorption kinetics compared to bulk $0.62\text{LiBH}_4\text{-}0.38\text{NaBH}_4$ and facilitates a reduction in hydrogen release temperature of ~ 107 °C. There is no substantial impact on the kinetics between the two types of carbon. This is also illustrated by the apparent activation energies (E_A) of hydrogen desorption of bulk and nanoconfined LiNa, in CA and CA-4 which is estimated to be 139, 116 and 118 $\text{kJ}\cdot\text{mol}^{-1}$, respectively. However, the reversible hydrogen storage capacity during hydrogen release and uptake is significantly improved by nanoconfinement into the high surface area scaffold CA-4, releasing 6.4 wt% H_2 relative to the sample mass, using only 60 vol% pore filling. In fact considering 100 vol% pore filling of $0.62\text{LiBH}_4\text{-}0.38\text{NaBH}_4$ into CA-4, would give rise to an available hydrogen storage capacity of ~ 11 wt.% H_2 after the first desorption and possibly ~ 7 wt.% H_2 after four desorption cycles.

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6. Table and Figure Captions

Table 1 Structural parameters; BET surface area, (S_{BET}), micro, meso and total pore volume, (V_{micro} , V_{meso} , V_{tot}), and pore size (D_{max}) of as prepared carbon aerogel scaffold (CA) and CO_2 -activated scaffold (CA-4). The added amount of $0.62\text{LiBH}_4\text{-}0.38\text{NaBH}_4$, in the samples is also provided gravimetrically and volumetrically.

Table 2 The theoretical hydrogen content, $\rho_{\text{m}}(\text{H}_2)$ relative to the amount of hydrogen storage material $0.62\text{LiBH}_4\text{-}0.38\text{NaBH}_4$ (LiNa). The measured hydrogen release during the first desorption calculated relative to the mass of the sample, and in percentage of the relative theoretical content (in

brackets). The amount of released hydrogen relative to the amount of added $\text{LiBH}_4\text{-NaBH}_4$ during desorption cycles one to four. The data is extracted from Figure 4.

Figure 1 *In-situ* synchrotron radiation powder X-ray diffraction (SR-PXD) of CA mixed with $0.62\text{LiBH}_4\text{-}0.38\text{NaBH}_4$ measured between RT and $240\text{ }^\circ\text{C}$ ($\Delta T/\Delta t = 2\text{ }^\circ\text{C}/\text{min}$) with the temperature held constant at $240\text{ }^\circ\text{C}$ for 15 min at $p(\text{H}_2) = 120\text{ bar}$ ($\lambda = 0.99185\text{ \AA}$). Afterwards the sample was naturally cooled to RT.

Figure 2 Thermal analysis of bulk $0.62\text{LiBH}_4\text{-}0.38\text{NaBH}_4$, LiNa (red), a physical mixture of LiNa with CA (pink) and LiNa melt infiltrated into CA (blue). A) shows TGA data, B) DSC data and C) TPD-MS profiles of H_2 signals ($m/e = 2$). Samples are heated from 50 to $500\text{ }^\circ\text{C}$ ($\Delta T/\Delta t = 2\text{ }^\circ\text{C}/\text{min}$).

Figure 3 Kissinger plot obtained from DSC data at heating rates of 2, 5, 10 and $15\text{ }^\circ\text{C}/\text{min}$ for bulk $0.62\text{LiBH}_4\text{-}0.38\text{NaBH}_4$ (LiNa) and LiNa nanoconfined in CA and CA-4.

Figure 4 Sieverts' measurement showing hydrogen release for cycles 1 to 4 for bulk $0.62\text{LiBH}_4\text{-}0.38\text{NaBH}_4$ (LiNa) (top), LiNa infiltrated into CA (middle) and into CA-4 (bottom). Hydrogen desorption was performed at a fixed temperature of $500\text{ }^\circ\text{C}$ ($\Delta T/\Delta t = 2\text{ }^\circ\text{C}$) for 10 hours and at $p(\text{H}_2) = 1\text{ bar}$. Hydrogen absorption was performed at $400\text{ }^\circ\text{C}$ and $p(\text{H}_2) = 140\text{ bar}$ for 10 hours.

Figure 5 FTIR spectra of bulk LiBH_4 and NaBH_4 , and (a) ball milled $0.62\text{LiBH}_4\text{-}0.38\text{NaBH}_4$, (b) sample CA-4 post melt infiltration of LiNa, (c) CA-4-LiNa after being dehydrogenated at $500\text{ }^\circ\text{C}$ for the fourth time and (d) CA-4-LiNa rehydrogenated for 10 h at $400\text{ }^\circ\text{C}$ after four desorption cycles. The intensity of spectrum d has been upscaled corresponding to added amount of LiNa for better comparison.

Figure 6 *Ex-situ* SR-PXD of bulk 0.62LiBH₄-0.38NaBH₄ (LiNa) (red), nanoconfined into CA-4 (green), CA-4 after being dehydrogenated at 500 °C in 10 h for the fourth time (blue) and CA-4 rehydrogenated at $p(\text{H}_2) = 140$ bar and 400 °C in 10 h after being desorbed four times (orange). The unknown compound in the dehydrogenated and rehydrogenated samples could possibly be an oxide ($\lambda = 0.23088$ Å).

7. References

- [1] Ley MB, Jepsen LH, Lee YS, Cho YW, von Colbe JMS, Dornheim M, et al. Complex hydrides for hydrogen storage - new perspectives. *Mater Today* 2014;17:122-8.
- [2] Schlesinger HI, Brown HC. Metallo borohydrides. III. Lithium borohydride. *J Am Chem Soc* 1940;62:3429-35.
- [3] Orimo SI, Nakamori Y, Eliseo JR, Züttel A, Jensen CM. Complex hydrides for hydrogen storage. *Chem Rev* 2007;107:4111-32.
- [4] Mauron P, Buchter F, Friedrichs O, Remhof A, Bielmann M, Zwicky CN, et al. Stability and reversibility of LiBH₄. *J Phys Chem B* 2008;112:906-10.
- [5] Adams RM. In BORAX TO BORANES. *Advances in Chemistry*. American Chemical Society, Washington, DC, 1961
- [6] Semenenko KN, Chavgun AP, Surov VN. Interaction of sodium tetrahydroborate with potassium and lithium tetrahydroborates. *Russ J Inorg Chem*. 1971;16:271-3.
- [7] Paskevicius M, Ley MB, Sheppard DA, Jensen TR, Buckley CE. Eutectic Melting in Metal Borohydrides. *Phys Chem Chem Phys* 2013;15:19774-89.
- [8] Lee HS, Lee YS, Suh JY, Kim M, Yu JS, Cho YW. Enhanced Desorption and Absorption Properties of Eutectic LiBH₄-Ca(BH₄)₂ Infiltrated into Mesoporous Carbon. *J Phys Chem C* 2011;115:20027-35.
- [9] Lee JY, Ravnsbæk D, Lee YS, Kim Y, Cerenius Y, Shim JH, et al. Decomposition Reactions and Reversibility of the LiBH₄-Ca(BH₄)₂ Composite. *J Phys Chem C* 2009;113:15080-6.
- [10] Bardaji EG, Zhao-Karger Z, Boucharat N, Nale A, van Setten MJ, Lohstroh W, et al. LiBH₄-Mg(BH₄)₂: A Physical Mixture of Metal Borohydrides as Hydrogen Storage Material. *J Phys Chem C* 2011;115:6095-101.
- [11] Sartori S, Knudsen KD, Hage FS, Heyn RH, Bardaji EG, Zhao-Karger Z, et al. Influence of nanoconfinement on morphology and dehydrogenation of the Li¹¹BD₄-Mg(¹¹BD₄)₂ system. *Nanotechnology* 2012;23:25.
- [12] Zhao-Karger Z, Witter R, Bardaji EG, Wang D, Cossement D, Fichtner M. Altered reaction pathways of eutectic LiBH₄-Mg(BH₄)₂ by nanoconfinement. *J Mater Chem A* 2013;1:3379-86.
- [13] Javadian P, Jensen TR. Enhanced hydrogen reversibility of nanoconfined LiBH₄-Mg(BH₄)₂. *Int J Hydrogen Energy* 2014;39:9871-6.
- [14] de Jongh PE, Adelhelm P. Nanosizing and Nanoconfinement: New Strategies Towards Meeting Hydrogen Storage Goals. *Chem Sus Chem* 2010;3:1332-48.

- [15] Vajo JJ. Influence of nano-confinement on the thermodynamics and dehydrogenation kinetics of metal hydrides. *Curr Opin Solid St M* 2011;15:52-61.
- [16] Nielsen TK, Besenbacher F, Jensen TR. Nanoconfined hydrides for energy storage. *Nanoscale* 2011;3;2086-98.
- [17] Fichtner M. Nanoconfinement effects in energy storage materials. *Phys Chem Chem Phys* 2011;13:21186-95.
- [18] Ward PA, Teprovich JA, Peters B, Wheeler J, Compton RN, Zidan R. Reversible Hydrogen Storage in a LiBH₄-C₆₀ Nanocomposite. *J Phys Chem C* 2013;117:22569-75.
- [19] Chumphongphan S, Filsø U, Paskevicius M, Sheppard DA, Jensen TR, Buckley CE. Nanoconfinement degradation in NaAlH₄/CMK-1. *Int J Hydrogen Energy* 2014;39:11103-9.
- [20] Gosalawit-Utke R, Milanese C, Javadian P, Girella A, Laipple D, Puzskiel J, et al. 2LiBH₄-MgH₂-0.13TiCl₄ confined in nanoporous structure of carbon aerogel scaffold for reversible hydrogen storage. *J Alloy Compd* 2014;599:78-86.
- [21] Lee H S, Hwang SJ, Kim HK, Lee YS, Park J, Yu JS, Cho YW. In Situ NMR Study on the Interaction between LiBH₄-Ca(BH₄)₂ and Mesoporous Scaffolds. *J Phys Chem Letters* 2012;3:2922-2927.
- [22] Ampoumogli A, Charalambopoulou G, Javadian P, Richter B, Jensen TR, Steriotis Th. Hydrogen desorption and cycling properties of composites based on mesoporous carbons and a LiBH₄-Ca(BH₄)₂ eutectic mixture. *J Alloy Compd* 2015;645:480-484
- [23] Javadian P, Sheppard DA, Buckley CE, Jensen TR. Hydrogen storage properties of nanoconfined LiBH₄-Ca(BH₄)₂. *Nano Energy* 2015;11:96-103.
- [24] Javadian P, Zlotea C, Ghimbeu CM, Latroche M, Jensen TR. Hydrogen Storage Properties of Nanoconfined LiBH₄-Mg₂NiH₄ Reactive Hydride Composites. *J Phys Chem C* 2015;119:5819-5826.
- [25] Liu X, Peaslee D, Sheehan TP, Majzoub EH. Decomposition Behavior of Eutectic LiBH₄-Mg(BH₄)₂ and Its Confinement Effects in Ordered Nanoporous Carbon. *J Phys Chem C* 2014;118:27265-27271
- [26] Xia G, Meng Q, Guo Z, Gu Q, Liu H, Liu Z, Yu X. Nanoconfinement significantly improves the thermodynamics and kinetics of co-infiltrated 2LiBH₄-LiAlH₄ composites: Stable reversibility of hydrogen absorption/resorption. *Acta Materialia* 2013;61:6882-6893.
- [27] Thiangviriya S, Plerdsranoy P, Wiset N, Javadian P, Jensen TR, Utke R. Hydrogen sorption and reaction mechanisms of nanoconfined 2LiBH₄-NaAlH₄. *J Alloy Compd* 2015;633:484-493.
- [28] Baumann TF, Worsley MA, Han TYJ, Satcher Jr JH. High surface area carbon aerogel monoliths with hierarchical porosity. *J Non-Cryst Solids* 2008;354:3513-5.
- [29] Al-Muhtaseb SA, Ritter JA. Preparation and properties of resorcinol-formaldehyde organic and carbon gels. *Adv Mater* 2003;15:101-14.
- [30] Lin C, Ritter JA. Carbonization and activation of sol-gel derived carbon xerogels. *Carbon* 2000;38:849-61.
- [31] Nielsen TK, Javadian P, Polanski M, Besenbacher F, Bystrzycki J, Jensen TR. Nanoconfined NaAlH₄: Determination of Distinct Proliferative Effects from Pore Size, Crystallite Size, and Surface Interactions. *J Phys Chem C* 2012;116:21046-51.
- [32] Nielsen TK, Javadian P, Polanski M, Besenbacher F, Bystrzycki J, Skibsted, et al. Nanoconfined NaAlH₄: prolific effects from increased surface area and pore volume. *Nanoscale* 2014;6:599-607.
- [33] Jensen TR, Nielsen TK, Filinchuk Y, Jørgensen JE, Cerenius Y, Gray EM, et al. Versatile in situ powder X-ray diffraction cells for solid-gas investigations. *J Appl Crystallogr* 2010;43:1456-63.

- [34] Barrett EP, Joyner LG. Determination of Nitrogen Adsorption-Desorption Isotherms - Estimation of Total Pore Volumes of Porous Solids. *Anal Chem* 1951;23:791-2.
- [35] Brunauer S, Emmett PH, Teller E. Adsorption of gases in multimolecular layers. *J Am Chem Soc* 1938;60:309-19.
- [36] Pitt MP, Paskevicius M, Brown DH, Sheppard DA, Buckley CE. Thermal Stability of $\text{Li}_2\text{B}_{12}\text{H}_{12}$ and its Role in the Decomposition of LiBH_4 . *J Am Chem Soc*. 2013;135:6930-41.