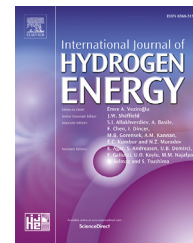




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Dehydrogenation and rehydrogenation of a 0.62LiBH₄-0.38NaBH₄ mixture with nano-sized Ni

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ABSTRACT

The dehydrogenation reaction pathway of a 0.91 (0.62LiBH₄-0.38NaBH₄)-0.09Ni mixture in the temperature range of 25–650 °C in flowing Ar and the cycling stability in H₂ are presented. No H₂ is released immediately after melting at 225 °C. The major dehydrogenation occurs above 350 °C. Adding nano-sized Ni reduces the dehydrogenation peak temperatures by 20–25 °C, leading to three decomposition steps where Ni₄B₃ and Li_{1.2}Ni_{2.5}B₂ are found in the major dehydrogenation products for the 1st and the 3rd step; whilst the Ni-free mixture decomposes through a two-step decomposition pathway. A total of 8.1 wt% of hydrogen release from the 0.91 (0.62LiBH₄-0.38NaBH₄)-0.09Ni mixture is achieved at 650 °C in Ar. This mixture has a poor hydrogen cycling stability as its reversible hydrogen content decreases from 5.1 wt% to 1.1 wt% and 0.6 wt% during three complete desorption-absorption-cycles. However, the addition of nano-sized Ni facilitates the reformation of LiBH₄.

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Introduction

Due to its high energy content, hydrogen is considered one of the most promising energy vectors for use in establishing sustainable energy systems [1,2]. One of the main challenges for the use of hydrogen as a fuel is the safe and efficient storage of hydrogen [3]. Hydrogen can be stored in several different ways, among which the solid-state storage approach has received extensive attention [4–7].

Metal borohydrides, such as LiBH₄ or Mg(BH₄)₂, chemically store the hydrogen atoms by covalently bonding

hydrogen to boron in the complex anion [BH₄]⁻. Such compounds have been considered as promising solid-state hydrogen storage media since 2003, due to their high volumetric hydrogen content and low operating pressures (<12 bar) [5,8–14]. For instance, the volumetric hydrogen density of LiBH₄ is 121 kg H₂ m⁻³ [8], which is about four times higher than the 40 kg H₂ m⁻³ for gaseous H₂ compressed at 700 bar [15]. However, the hydrogen release and uptake properties of metal borohydrides are often hindered by poor thermodynamics (e.g. high temperatures are required) and sluggish kinetics, which has prevented their use as reversible hydrogen stores [5].

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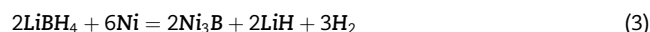
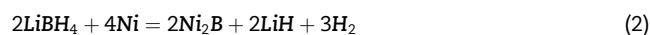
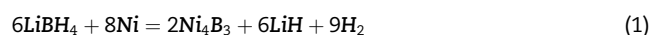
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One of the potential approaches to decrease the hydrogen sorption temperatures of borohydrides is to form low-melting-point borohydride mixtures, such as $\text{LiBH}_4\text{-NaBH}_4$, $\text{LiBH}_4\text{-KBH}_4$, $\text{LiBH}_4\text{-Mg}(\text{BH}_4)_2$, $\text{LiBH}_4\text{-Ca}(\text{BH}_4)_2$ and $\text{NaBH}_4\text{-KBH}_4$ [16–22]. These mixtures are often called eutectic borohydrides and have lower fusion temperatures than their pure constituents, leading to dehydrogenation at relatively low temperatures through kinetic effects [11]. In fact, the nature of molten salts is critical in utilizing H_2 release from borohydrides, especially from alkali-metal borohydrides that often melt before their major H_2 desorption begin [11]. In addition, the dehydrogenation of borohydrides from the liquid rather than the solid state may lead to less unwanted phases in the reaction products, such as $[\text{B}_{10}\text{H}_{10}]^{2-}$ and $[\text{B}_{12}\text{H}_{12}]^{2-}$ phases [23]. Since metal dodecaborates act as boron sinks that hinder the rehydrogenation of decomposed borohydrides [24,25], the formation of such compounds is not favorable and needs to be avoided in solid-state hydrogen storage systems. Moreover, the low melting point is beneficial for the nanoconfinement-by-infiltration approach, in which molten borohydrides are infiltrated into a porous material to reduce the decomposition temperature as well as to improve the reversibility [26–32].

The eutectic $\text{LiBH}_4\text{-NaBH}_4$ mixture has received attention owing to its relatively low cost among known eutectic borohydride mixtures and a high theoretical gravimetric hydrogen storage capacity of approximately 15 wt% [17]. According to experimental measurements and theoretical calculations, two eutectic compositions have been proposed in the past: 0.62 $\text{LiBH}_4\text{-0.38NaBH}_4$ [17,28] and 0.71 $\text{LiBH}_4\text{-0.29NaBH}_4$ [33]. The melting of this kind of mixtures occurs at around 216–225 °C [28,33], which is about 60 °C lower than that of LiBH_4 [34] and about 280 °C lower than that of NaBH_4 [35,36]. The dehydrogenation of 0.62 $\text{LiBH}_4\text{-0.38NaBH}_4$ mixture starts at 287 °C with a total of 10.8 wt% hydrogen release upon heating to 650 °C in Ar [37]. In general, the decomposition of borohydrides is complex and usually involves the formation of a series of intermediate phases as a function of temperature and pressure [38–41]. Under an Ar atmosphere, the dehydrogenation pathways of the 0.62 $\text{LiBH}_4\text{-0.38NaBH}_4$ mixture are mainly accompanied by the precipitation of LiH , $\text{Li}_2\text{B}_{12}\text{H}_{12}$ and B from 287 °C to 520 °C and the formation of Na and B from 520 °C to 650 °C [37]. These high dehydrogenation temperatures are indeed above the US DOE (department of energy) target of on-board H_2 storage for light-duty vehicles [42] and therefore need to be further reduced with the help of a detailed understanding of the dehydrogenation pathways.

Many attempts to tailor the temperature required for dehydrogenation and to improve the cycling stability of borohydrides have been made, such as adding additives/catalysts [9,19,43–47], forming reactive hydride composites [48–55] and confining into nano-porous scaffolds [56–59]. Furthermore, adding Ni to LiBH_4 forms an interesting $\text{LiBH}_4\text{-Ni}$ system, which has received attention due to the low dehydrogenation enthalpy values (18–34 $\text{kJ mol}^{-1} \text{H}_2$) of the possible chemical reactions (Equations (1)–(3)), generating nickel borides (i.e. Ni_4B_3 , Ni_2B , Ni_3B) [60], which have been described as valuable additives [60–62]. The addition of 25 wt% nano-sized Ni to LiBH_4 reduces the dehydrogenation peak temperature by 50 °C, and improves the reversible hydrogen content from 4.3 wt%

for Ni-free sample to 10.8 wt% as a consequence of the effect of the Ni_4B_3 [60].



Thus, to reduce the dehydrogenation temperature of the 0.62 $\text{LiBH}_4\text{-0.38NaBH}_4$ mixture, this work used 18 wt% (9 mol%) nano-sized Ni particles as additive. In addition, the modified decomposition pathway was studied by determining the phases and the structural evolution as a function of temperature, using a series of samples heat-treated at selected temperatures through a combination of experimental techniques, i.e. powder X-ray diffraction (PXRD), Raman spectroscopy, Fourier-transform infrared spectroscopy (FTIR), Thermogravimetry differential scanning calorimetry (TG-DSC) and temperature programmed desorption – mass spectrometry (TPD-MS). The rehydrogenation of this $\text{LiBH}_4\text{-NaBH}_4\text{-Ni}$ mixture was also investigated using a Sieverts type apparatus.

Materials and methods

Synthesis

LiBH_4 ($\geq 95.0\%$), NaBH_4 ($\geq 99.99\%$) and nano-sized Ni powder (average size < 100 nm, $\geq 99.9\%$) were received from Sigma-Aldrich, stored and handled solely in an Ar glovebox.

The 0.62 $\text{LiBH}_4\text{-0.38NaBH}_4$ and 0.91 (0.62 $\text{LiBH}_4\text{-0.38NaBH}_4$)-0.09Ni mixtures were prepared using a Retsch PM 400 planetary ball mill in 1 bar Ar for 10 h (in total) at 175 rpm. The ball milling process used 250 mL stainless steel milling pots and 13 mm (diameter) stainless steel balls. The ball-to-sample mass ratio was 66:1. To avoid sample overheating during milling, this process was set to rest for 5 min in between every 5 min of operation.

The milled samples were heat-treated by heating at 2 °C min^{-1} in Ar (flowing at 160 mL min^{-1}) to different target temperatures: 250, 468, 515, 586 and 650 °C. These samples were cooled to room temperature (RT) before further characterization.

Characterization

Powder X-ray diffraction

Powder X-ray diffraction (PXRD) measurements were performed using a Bruker D8 Advance X-Ray Diffractometer with Cu K_α radiation ($\lambda = 1.5418$ Å). Samples were loaded and sealed inside a PMMA airtight dome-shaped sample holder inside an Ar glovebox, before transfer to the PXD. The surface of sample was flattened and smoothed to ensure a well-defined geometry. The measurements were performed in the range $2\theta = 5\text{--}90^\circ$ at a scanning rate of 2° min^{-1} using a 9 position multi-changer stage. In case of relatively small amount of powder samples, these samples were loaded into rotating glass capillaries (inner diameter = 0.5 mm) and sealed with silicone grease, then measured in 10–70° 2θ at a scanning rate of 1° min^{-1} .

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