



The effects of filamentary Ni, graphene and lithium amide (LiNH₂) additives on the dehydrogenation behavior of mechano-chemically synthesized crystalline manganese borohydride (Mn(BH₄)₂) and its solvent filtration/extraction

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ABSTRACT

Dehydrogenation properties of mechano-chemically synthesized crystalline Mn(BH₄)₂ hydride without and with ultrafine filamentary carbonyl nickel (Ni), graphene and LiNH₂ were investigated. It is reported for the first time that all additives suppressed the release of B₂H₆ with the filamentary Ni additive being the most effective suppressor of B₂H₆. In DSC, the decomposition peak of Mn(BH₄)₂ was endothermic. The estimated apparent activation energy for isothermal dehydrogenation was dramatically reduced to 44.9 ± 4.3 kJ/mol for the 5 wt. % LiNH₂ additive from about 76–81 kJ/mol range for the additive-free sample and 5 wt.% filamentary Ni and graphene additives. The most striking finding, that has never been reported in the literature, is that the process of solvent filtration and extraction of the mechano-chemically synthesized (Mn(BH₄)₂/LiCl) sample, resulted in the crystallization of a dimetallic borohydride solvate [Li(Et₂O)₂]Mn₂(BH₄)₅ instead of crystalline Mn(BH₄)₂. Its dehydrogenation behavior was investigated isothermally and by TGA/DSC.

1. Introduction

Hydrogen (H₂) plays a vital role in the decisive shift from economies dependent on fossil fuels to the ones based on renewable and clean resources. The solid-state metal hydrides are deemed promising as H₂ sources due to their high volumetric hydrogen capacity and the fact that they do not suffer the drawbacks experienced by compressed gaseous and liquid hydrogen, such as large thermal losses and safety problems [1]. Solid hydrides can be used for supplying very clean gaseous H₂ to fuel cell (FC) stacks for automotive sector [1–3]. Unfortunately, solid-state H₂ storage in hydrides has serious constraints for the automotive sector, the most important of which is the inability to meet the need for “on board” rehydrogenation. So far, this and other very serious constraints preclude a full implementation of solid state H₂ storage in the automotive sector [3]. However, some commercial market applications for solid-state hydrogen storage systems may not critically require “on board” rehydrogenation. Such H₂ storage/generation systems can

utilize disposable H₂ cartridges of various sizes whose thermal decomposition products could be either regenerated “off board”, after dehydrogenation, or converted into other useful chemicals. A number of potential, non-automotive applications exist, such as portable electronic devices, stationary auxiliary power systems, off road vehicles, drones, bulk hydrogen storage, air transportation and many others [2,3].

Lithium borohydride, LiBH₄, which is a relatively expensive hydride, exhibits the highest theoretical hydrogen capacity of about 18 wt. % of all solid hydrides. Unfortunately, its decomposition temperature, higher than 400 °C, is too high for any practical application. The pertinent hydrides should be capable of desorbing H₂ from a hydride reservoir within the coolant temperature range provided by the waste heat generated by the FC stack, usually not exceeding about 80–100 °C, under H₂ pressure slightly above 1 bar [2,3].

Therefore, since LiBH₄ in its pure form is practically useless, it is more convenient to convert it into another hydride that would be able

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to desorb H₂ at a much lower temperature range than that for LiBH₄. An interesting candidate hydride for potential non-automotive hydrogen generation/storage, which can be synthesized from LiBH₄, is manganese borohydride (Mn(BH₄)₂) exhibiting a still impressive theoretical gravimetric H₂ capacity of 9.5 wt.%. It can be synthesized in solid state by mechano-chemical activation synthesis (MCAS) [4–10] according to the following reaction:



The presence of LiCl which is formed as a “dead weight” salt by-product, reduces the practical capacity of H₂ in the synthesized product. The capacity of hydrogen for $n = 2$ (no retained LiBH₄) is 4.76 wt.% H₂, a nearly half of its theoretical H₂ capacity. Therefore, an efficient removal of LiCl from the mixture with Mn(BH₄)₂ (Eq. (1)) is of great importance. Another problem with Mn(BH₄)₂, upon its decomposition, is a release of varying quantities of diborane (B₂H₆), simultaneously with hydrogen [6–11], which reduces the purity of H₂ gas and could be damaging to the membrane of a Proton Exchange Membrane (PEM) fuel cell. Previous studies have not identified any efficient way to suppress B₂H₆ formation during the decomposition process.

A solvent-mediated synthesis (wet) method has been reported in the literature for the synthesis of various complex hydrides. Mg(AlH₄)₂ was obtained based on the metathesis reaction of NaAlH₄ and MgCl₂ in diethyl ether (Et₂O) and subsequent purification using Soxhlet extraction [12]. Using the same method, Eu(BH₄)₂ and Sm(BH₄)₂, free from solvent (dimethyl sulfide) and LiCl were also achieved [13]. Pure Mg(BH₄)₂ was obtained using the reaction of Et₃NBH₃ and MgH₂ [14]. Richter et al. [15] successfully synthesized Mn(BH₄)₂ through reaction of MnCl₂ with LiBH₄ in a toluene/dimethylsulfide mixture at room temperature which yielded halide and solvent-free manganese borohydride after extraction with dimethylsulfide (DMS) and subsequent removal of residual solvent. Tumanov et al. [16] studied the reaction of MnCl₂ with MBH₄ (M = Li⁺, Na⁺, K⁺) in Et₂O. They synthesized new intermediates [M(Et₂O)₂]Mn₂(BH₄)₅ (M = Li⁺, Na⁺) identified by X-ray diffraction. The solvent removal in a vacuum from the [Li(Et₂O)₂]Mn₂(BH₄)₅ dimetallic borohydride solvate led to Mn(BH₄)₂ contaminated with LiCl, presumably due to an efficient trapping of the latter salt by the [Mn(BH₄)₂-Et₂O] system, while the solvent removal from the [Na(Et₂O)₂]Mn₂(BH₄)₅ dimetallic borohydride solvate produced chlorine-free Mn(BH₄)₂ accompanied with NaBH₄. Using KBH₄ led to the formation of K₂Mn(BH₄)₄ as a second phase.

The attempt to remove the NaCl salt from the product of MCAS from a (Mg(AlH₄)₂ + 2NaCl) mixture and the LiCl from a (Ca(AlH₄)₂-2LiCl) mixture, in both cases using Et₂O and THF in a Soxhlet apparatus, was reported by Mamatha et al. [17]. They also reported that complex removal of THF could not be achieved.

Most recently, we reported [18] that NaCl could be effectively removed by diethyl ether (Et₂O) solvent extraction from a mixture with an amorphous Mn(BH₄)₂-type hydride which transformed to crystalline Mn(BH₄)₂ during a solvent extraction process.

The current work has the following objectives: (1) to study the effects of additives such as ultrafine filamentary nickel (Ni), graphene (graphene oxide) and LiNH₂ on suppressing the formation of B₂H₆ during decomposition, (2) to study the possible effects of those additives on the mechanical and thermal dehydrogenation of mechano-chemically synthesized Mn(BH₄)₂, (3) to employ a simple diethyl ether (Et₂O)-based solvent filtration/extraction method to remove, at least partially, the LiCl salt from a solid mixture with Mn(BH₄)₂ (Eq. (1)) and finally, (4) to investigate the dehydrogenation behavior of LiCl-free solvent extracted material.

2. Experimental

In total, four mixtures were synthesized from the as-received powders. The first mixture was composed of the commercial lithium

borohydride (LiBH₄) (95% purity) and MnCl₂ (99.99% purity), both from Alfa Aesar (Canada) in the molar ratio of 2 to 1. The second mixture with the same 2:1 M ratio of (LiBH₄) and MnCl₂ was made with the addition of 5 wt.% ultrafine filamentary carbonyl nickel supplied by Cnem Corp (Canada), referred to as “filamentary Ni” in the text. The third mixture contained the addition of 5 wt.% flake-reduced graphene oxide (FL-rGO), referred to as “graphene”, obtained from Nanomaterials (<http://www.nanomaterials.pl>). The FL-rGO product consists of 2–3 stacked nanostructure graphene layers and contains ~9.6 wt.% of oxygen and ~1 wt.% H₂ (the exact chemical elemental analysis can be found at (<http://www.nanomaterials.pl>)). The graphene product is amorphous and contains 26–30 at. % of oxygen. The fourth mixture contained 5 wt.% LiNH₂ that was ordered from Sigma Aldrich with a purity of 95%.

In order to avoid reactions between the powder samples and moisture or oxygen from air, all processes during preparation of the samples were handled in a glove box containing a moisture-absorbing Drierite granulated compound. Before handling, the glove box was purged a few times with high purity argon gas (99.999% purity).

Mechano-chemical activation synthesis (MCAS) of the powder mixtures was carried out for 1h in an ultra-high purity hydrogen gas atmosphere (purity 99.999%) at ~300 kPa pressure in the magnetoball mill, Uni-Ball-Mill 5, manufactured by A.O.C. Scientific Engineering Pty Ltd, Australia [1,19–21]. Strong impact mode (IMP68) was used for milling, with two magnets positioned at 6 and 8 o'clock, at the distances from the vial of ~10 and ~2 mm, respectively. The milling media consisted of four 25-mm diameter steel balls, each with a mass of 65 g. The mill rotation speed and the ball-to-powder weight ratio (R) were ~200 rpm and 132, respectively.

During milling, the vial was continuously cooled by an air fan. The release of hydrogen during ball milling was monitored and estimated from the pressure increase in the milling vial measured by a pressure gauge, using ideal gas law [1] and expressed in wt.% with respect to the total weight of the powder sample. The accuracy was ± 0.1 wt.% H₂.

The hydrogen thermal desorption/absorption was evaluated by means of a second-generation volumetric Sieverts-type apparatus custom-built by A.O.C. Scientific Engineering Pty Ltd., Australia [22]. An approximately 30–40 mg sample was used in a desorption test. Before starting this test, the inner tubing of the apparatus was evacuated and purged four times with hydrogen. The furnace of the apparatus was heated separately to the desired test temperature and subsequently inserted into a tightly sealed powder sample reactor, inside which an atmospheric pressure of 1 bar H₂ was maintained. The powder sample in the reactor took ~400 s to reach the furnace temperature of 100–200 °C, which is negligible compared to the desorption completion time. Hence, the test can be considered as “isothermal”. Desorption curves were corrected for the hydrogen gas expansion due to the increase in temperature. The amount of desorbed hydrogen was calculated from the ideal gas law, as described in details in [1], and expressed in wt.% with respect to the *total weight* of the powder sample. The calibrated accuracy of the desorbed hydrogen capacity was about ± 0.1 wt.% H₂ and that of temperature reading and stabilization ± 0.1 °C.

The apparent activation energy for volumetric hydrogen desorption was estimated using the registered dehydrogenation curves by applying a simple Arrhenius equation [1] following Sandrock et al. [23]

$$k = k_0 e^{-E_A/RT} \quad (2)$$

where k is the rate of hydrogen desorption, in the convenient engineering term of wt.%H₂/h measured from the slope of the volumetric hydrogen desorption curves registered by the Sieverts-type apparatus (the selected linear portion of each pertinent dehydrogenation curve was fitted by a linear equation used to obtain its slope) [23,24], where E_A is the activation energy in kJ/mol, R is the gas constant (8.314472 J/mol K), and T is the absolute temperature (K). The measured rates were plotted in the Arrhenius form as $\ln k$ vs. 1000/RT.

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