Mechano-chemical synthesis of manganese borohydride (Mn(BH$_4$)$_2$) and inverse cubic spinel (Li$_2$MnCl$_4$) in the (nLiBH$_4$ + MnCl$_2$) (n = 1, 2, 3, 5, 9 and 23) mixtures and their dehydrogenation behavior

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Abstract

Manganese borohydride (Mn(BH$_4$)$_2$) was successfully synthesized by a mechano-chemical activation synthesis (MCAS) from lithium borohydride (LiBH$_4$) and manganese chloride (MnCl$_2$) by applying high energy ball milling for 30 min. For the first time a wide range of molar ratios n = 1, 2, 3, 5, 9 and 23 in the (nLiBH$_4$ + MnCl$_2$) mixture was investigated. During ball milling for 30 min the mixtures release only a very small quantity of H$_2$ that increases with the molar ratio n but does not exceed ~0.2 wt.% for n = 23. However, longer milling duration leads to more H$_2$ released. For the equimolar ratio n = 1 the principal phases synthesized are Li$_2$MnCl$_4$, an inverse cubic spinel phase, and the Mn(BH$_4$)$_2$ borohydride. For n = 2 a LiCl salt is formed which coexists with Mn(BH$_4$)$_2$. With the n increasing from 3 to 23 LiBH$_4$ is not completely reacted and its increasing amount is retained in the microstructure coexisting with LiCl and Mn(BH$_4$)$_2$. Gas mass spectrometry during Temperature Programmed Desorption (TPD) up to 450 °C shows the release of hydrogen as a principal gas with a maximum intensity around 130–150 °C accompanied by a miniscule quantity of borane B$_2$H$_6$. The intensity of the B$_2$H$_6$ peak is 200–600 times smaller than the intensity of the corresponding H$_2$ peak. In situ heating experiments using a continuous monitoring during heating show no evidence of melting of Mn(BH$_4$)$_2$ up to about 270–280 °C. At 100 °C under 1 bar H$_2$ pressure the ball milled n = 2 and 3 mixtures are capable of desorbing quite rapidly ~4 wt.% H$_2$ which is a very large amount of H$_2$ considering that the mixture also contains 2 mol of LiCl salt. The H$_2$ quantities experimentally desorbed at 100 and 200 °C do not exceed the maximum theoretical quantities of H$_2$ expected to be desorbed from Mn(BH$_4$)$_2$ for various molar ratios n. It clearly confirms that the contribution from B$_2$H$_6$ evolved is negligibly small (if any) when desorption occurs isothermally in the practical temperature range 100–200 °C. It is found that the ball milled mixture with the molar ratio n = 3 exhibits the highest rate constant k and the lowest apparent activation energy for dehydrogenation, $E_A$ ~ 102 kJ/mol. Decreasing or increasing the molar ratio n below or
An effective method of solid state hydrogen storage in hydrides and their composites [1] is one of the obstacles in transforming the present fossil fuel based economy to the hydrogen economy. The most important area for transformation from fossil fuels to hydrogen is mass transportation using cars (automotive). A most suitable for the automotive application and many others is a Proton Exchange Membrane (PEM) fuel cell stack, a potential hydride-based storage system should have the operating temperature compatible with waste heat of a PEM fuel cell. Due to the specific requirements of a Proton Exchange Membrane using cars (automotive). A most suitable for the automotive hydrogen economy. The most important area for transforming the present fossil fuel based economy to the hydrogen economy. The most important area for transforming the present fossil fuel based economy to the hydrogen economy. The most important area for transforming the present fossil fuel based economy to the hydrogen economy.

1. Introduction

An effective method of solid state hydrogen storage in hydrides and their composites [1] is one of the obstacles in transforming the present fossil fuel based economy to the hydrogen economy. The most important area for transformation from fossil fuels to hydrogen is mass transportation using cars (automotive). A most suitable for the automotive application and many others is a Proton Exchange Membrane (PEM) fuel cell stack, a potential hydride-based storage system should have the operating temperature compatible with waste heat of a PEM fuel cell stack which should not exceed 70–100 °C at a feed pressure slightly above 1 bar H₂. The most recently revised US Department of Energy (DOE) automotive hydrogen storage targets for 2015 require H₂ capacity of 5.5 wt.% for the entire storage system which includes storage medium, tank and some auxiliary devices [2]. This translates into approximately 10–11 wt.% H₂ capacity for the solid hydride-based storage material. Such large capacities can only be provided by complex light metal/nonmetal hydrides and most likely by their mixtures [1]. In this context, metal borohydrides are potentially interesting solid state hydrogen storage materials due to their very high theoretical capacities of hydrogen [1,3–8]. The most prominent among borohydrides is lithium borohydride (LiBH₄) which is easily commercially available and has a theoretical gravimetric hydrogen capacity 18.4 wt.%. Unfortunately, its dehydrogenation is not an easy task due to its relatively high enthalpy change for dehydrogenation which, in turn, results in the dehydrogenation temperatures in excess of 400 °C [3–5]. The addition of metal and non-metal catalysts accelerates the dehydrogenation rate of LiBH₄ but does not change its unfavorable thermodynamics [5–8].

Nakamori et al. [9,10] used the mechano-chemical activation synthesis (MCAS) which occurs during high energy ball milling of complex hydrides mixed with appropriate metal di- or tri-chlorides, MCl₃, for synthesizing a large spectrum of metal borohydrides. In essence this is a “metathesis reaction” in solid state instead of the one which uses diethyl ether as a solvent [1]. They used the mixture of metal chlorides MCl₃ and both lithium and sodium borohydride, LiBH₄ and NaBH₄, respectively, which were milled in argon for 5 h. The reaction during milling was proposed to occur as follows:

\[
\text{MCl}_3 + n\text{LiBH}_4 \rightarrow \text{M(BH}_4)_n + n\text{LiCl} \quad (M = \text{Cr, Mg, Mn, Zr, Ti, V, Zn}) \tag{1}
\]

\[
\text{MCl}_3 + n\text{NaBH}_4 \rightarrow \text{M(BH}_4)_n + n\text{NaCl} \quad (M = \text{Ca, Sc, Al}) \tag{2}
\]

The post-MCAS XRD patterns for reaction (1) with LiBH₄ showed the absence of the diffraction peaks of crystalline M(BH₄)ₙ and the presence of LiCl peaks. When NaBH₄ was used in reaction (2) then only the NaCl peaks were present while the diffraction peaks of NaBH₄ were also observed for NaBH₄ and MCl₃ where M = Ca, Sc and Al mixtures in reaction (2). This very unusual observations were interpreted by Nakamori et al. as evidence of the “disordering” of the crystal structure of M(BH₄)ₙ although this interpretation is incorrect at least in the case of the (LiBH₄–MnCl₂) mixture as will be discussed further. Nakamori et al. [9,10] concluded that reaction (1) with LiBH₄ occurred easier than reaction (2) with NaBH₄ due to similar ionic radii of Li⁺ and M⁺⁺ in solid–solid cation exchange reaction as compared to a larger ionic radius of Na⁺⁺. Indeed, soon after their reports, Varin et al. [11] reported that the MCAS of the (2NaBH₄ + MgCl₂) mixture resulted in only a partial synthesis of “disordered” magnesium borohydride Mg(BH₄)₂ accompanied by (Na, Mg)BH₄ solid solution and NaCl which somehow confirms that NaBH₄ may not be so effective as LiBH₄ in reacting with metal chloride during MCAS. Nakamori et al. [9,10] also reported that the hydrogen desorption temperature of disordered M(BH₄)ₙ (Tₜ) decreased with increasing values of the Pauling electronegativity χₚ of metal M in borohydride. They noted that the desorbed gas for M = Ca, Sc, Ti, V and Cr (χₚ ≤ 1.5) was hydrogen only, while that for M = Mn, Zn and Al (χₚ > 1.5) contained a mix of borane and hydrogen.

In the further development in the field of synthesized metal borohydrides, Choudhury et al. [12] assumed a priori that the MCAS of LiBH₄ with MnCl₂ in the ratio of 3:1 would result in the formation of new complex borohydride Mn(BH₄)₃. They did not observe diffraction peaks other than LiCl and confirmed that “disordered” LiMn(BH₄)₃ was synthesized. Subsequently, Varin et al. [13] carried out the MCAS on the (3LiBH₄ + MnCl₂) also with a presumption that LiMn(BH₄)₃ would be synthesized. Beside the LiCl diffraction peaks they observed some unidentified diffraction peaks which were later identified as belonging to Mn(BH₄)₃ as it was at the same time reported in [14–16]. Very recently, Liu et al. [17] reported limited studies of thermal decomposition behavior of LiBH₄ ball milled with MnCl₂ with the molar ratio n = 2 and 3. From Differential Scanning Calorimetry (DSC) and TG (thermogravimetric) analysis they deduced that dehydrogenation of Mn(BH₄)₃ occurs with the release of diborane (B₂H₆). They didn’t conduct any isothermal dehydrogenation tests under 1 bar H₂ pressure.

The present paper is a continuation of studies published in [13] where the MCAS of the (3LiBH₄ + MnCl₂) system was studied. In the present work a wide range of molar ratios n = 1, 2, 3, 5, 9 and 23 is used in the (nLiBH₄ + MnCl₂) mixture. The emphasis is placed on the structural development during MCAS investigated by X-ray and synchrotron diffraction, isothermal volumetric dehydrogenation under 1 bar H₂
pressure including estimates of apparent activation energy and slow hydrogen discharge during storage at room temperature and 40°C. These aspects were not reported in the previous publications.

2. Experimental

As-received commercial LiBH₄ (95% purity) and MnCl₂ (99.99% purity) from Alfa Aesar were mixed to the molar ratios (nLiBH₄ + MnCl₂) where n = 1, 2, 3, 5, 9 and 23. The effect of addition of 5 wt.% catalytic nanometric nickel (n-Ni) produced by Vale Ltd., Mississauga, Ontario, on a slow hydrogen self-discharge during long term storage at low temperatures, as already reported for LiAlH₄ [18], was also investigated for one batch with the molar ratio n = 3. Two batches of n-Ni with Specific Surface Area (SSA) of 9.5 and 60.5 m²/g which were measured in the Vale Ltd.’s laboratories by the BET (Brunauer, Emmett and Teller) method were used as possible catalytic additives. Their characteristics and effects on isothermal dehydrogenation of the n = 3 composite were already reported in [13].

Controlled Mechanical Milling (CMM) of all mixtures was carried out for 30 min in ultra-high purity hydrogen gas atmosphere (purity 99.999%: O₂ < 2 ppm; H₂O < 3 ppm; CO₂ < 1 ppm; N₂ < 6 ppm; CO < 1 ppm; THC < 1 ppm) at ~600 kPa pressure in the magneto-mill Uni-Ball-Mill 5 manufactured by A.O.C. Scientific Engineering Pty Ltd., Australia [1,19–21]. The milling was carried out under a strong impact mode (IMP68) with two magnets positioned at 6 and 8 o’clock, at the distance from the vial of ~10 and ~2 mm, respectively [13]. The ball-to-powder weight ratio (R) was 132 and the rotational speed of milling vial was ~200 rpm. After loading with powder, an air-tight milling vial with an O-ring, equipped with a pressure valve mounted in the lid, was always first evacuated and then purged several times with ultra-high purity argon (Ar) gas (99.999% purity) before final pressurization with H₂. During milling the vial was continuously cooled by an air fan and the milling process was stopped every 10 min for an additional cool off. The release of hydrogen during ball milling was monitored and estimated from the pressure increase in the milling vial measured by a pressure gage using an ideal gas law [1] and expressed in weight % with respect to the total weight of powder sample with the accuracy ±0.1 wt.% H₂.

The powder 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) in order to minimize any possible contamination by moisture or oxygen from air.

The hydrogen thermal desorption/absorption was evaluated using a second generation volumetric Sieverts-type apparatus custom-built by A.O.C. Scientific Engineering Pty Ltd., Australia [1]. The details of the measurements can be found in [13]. Sieverts’ volumetric dehydrogenation tests were carried out shortly after completion of milling process to avoid a prolonged storage as will be discussed later. The amount of desorbed hydrogen was calculated from the ideal gas law as described in detail in [1] and expressed in weight % with respect to the total weight of powder sample. The calibrated accuracy of desorbed hydrogen capacity is 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 from the obtained Sieverts’ dehydrogenation curves using the Arrhenius plot of k values with

where k is the rate of hydrogen desorption (wt.%H₂/s), Eₐ is the apparent activation energy (kJ/mol), R is the gas constant (8.314472 J/mol K) and T is absolute temperature (K). The rate constant k was determined using the Johnson-Mehl-Avrami-Kolmogorov (JMAK) equation [1]:

where η is the reaction exponent which is related to transformation mechanism and α is the desorption fraction at time t. The standard error for the apparent activation energy estimation is about ±5 kJ/mol. More details on the apparent activation energy measurements can be found in [22–24].

X-ray powder diffraction (XRD) analysis was performed on a Bruker D8 diffractometer using a monochromated CuKα₁ radiation (λ = 0.15406 nm) produced at an accelerating voltage of 40 kV and a current of 30 mA. The scan range was from 2θ = ~10 to ~90° and the rate was ~1.2 min⁻¹ with a step size of ~0.02. Powder was loaded in a glove box filled with Ar into a home-made environmental brass holder with a Cu/glass plates for powder support. Upper and lower part of the environmental holder is sealed through a soft-rubber O-ring and tightened using threaded steel bolts with nuts. The upper part of the holder contains a Kapton window transmittable to X-rays. For additional confirmation of the phases present synchrotron powder diffraction was used. The data were collected at the Swiss-Norwegian Beam Lines in Grenoble using the radiation wavelength of 0.73065 Å (more details can be found in [14]).

Temperature programmed desorption (TPD) experiments were performed with the use of HTP1-S Sieverts-type apparatus coupled with a quadrupole mass spectrometer (Hiden Inc.). Sample of about 25 mg was loaded into 100 µl (microliters) alumina crucible (with no contact with atmospheric air) to prevent reaction with copper sample holder. During loading procedure each sample was evacuated down to 1–10⁻⁵ mbar pressure. Experiment was carried out under constant helium (99.999% purity) flow of 100 ml/min. Constant heating rate of 2 and ~10°C/min was used to register desorption spectra containing both hydrogen and diborane (B₂H₆) signal.

3. Results and discussion

3.1. Microstructure of ball milled composites

A number of complex hydrides and their mixtures containing various additives can partially decompose during highly energetic ball milling desorbing varying amounts of hydrogen [24–26]. In order to find out if the (nLiBH₄ + MnCl₂) mixture exhibits similar behavior the pressure change in the milling
vial was continuously monitored during the entire length of the milling process and then converted to wt.% H₂ as mentioned earlier. Fig. 1 shows a trend of increasing amount of desorbed H₂ with increasing molar ratio n of LiBH₄ in the mixture during high energy ball milling for 30 min. The amount of H₂ desorbed during 30 min of ball milling even for the n = 23 mixture is still very small and does not exceed 0.2 wt.% which is close to the experimental error of measurements. However, when the milling duration was extended to 1 h for the (3LiBH₄ + MnCl₂) molar ratio then the H₂ desorption was more substantive reaching about 1 wt.% after completion of milling. Therefore, it is not recommended to exceed 30 min of mechanical milling for which in all practical terms the mechanical dehydrogenation phenomenon can be neglected. We are now investigating the mechanical dehydrogenation phenomenon for Mn(BH₄)₂ and other complex hydrides in more detail.

Fig. 2a and b shows X-ray and synchrotron diffraction pattern, respectively, for mixtures with varying molar ratio n after high energy ball milling. The X-ray results which are supported by the synchrotron results clearly show that in all mixtures the Mn(BH₄)₂ hydride has been synthesized by the mechano-chemical “metathesis” reaction. The identification of this hydride was based on data reported in [14–16] which show that Mn(BH₄)₂ has a hexagonal lattice structure with a = 10.435(1) Å and c = 10.835(2) Å.

However, depending on the exact value of the molar ratio n there are some differences with respect to the presence of other phases after ball milling. A majority phase in the equimolar n = 1 mixture is an inverse cubic spinel phase Li₂MnCl₄ (file # 1984-ICSD) while a minority phase is Mn(BH₄)₂. It should also be noted that Li₂MnCl₄ has its diffraction peaks shifted to slightly bigger d-values which suggests that there is a solid solution between Cl and BH₄ anions. This spinel has been extensively studied for its ionic conductivity as a potential solid electrolyte for lithium-ion batteries [27–29]. The present work clearly shows that this important compound can be relatively easily synthesized by ball milling.

For n = 2 the pattern is changed where instead of Li₂MnCl₄ a LiCl salt appears. The presence of the latter was also proposed by Nakamori et al. [9,10]. Obviously, a minority phase in the n = 2 mixture is Mn(BH₄)₂. With the n increasing from 3 to 23 both XRD and synchrotron patterns (Fig. 2a and b) show steadily increasing intensity of LiBH₄ diffraction peaks.

This confirms that LiBH₄ is not completely reacted and an increasing amount of LiBH₄ is retained in the microstructure. The identification of LiBH₄ peaks was based on our own standard XRD pattern for ball milled LiBH₄ compared with a diffraction pattern reported in [30]. Therefore, the results of diffraction studies in Fig. 2a and b clearly indicate that the reaction paths in the mechano-chemical metathesis depend on the molar ratio n of LiBH₄ to MnCl₂ according to the following reactions:

\[
\text{LiBH}_4 + \text{MnCl}_2 \rightarrow 0.5\text{Mn}(/\text{BH}_4)_2 + 0.5\text{Li}_2\text{MnCl}_4 \quad (n = 1) \tag{5}
\]

\[
n\text{LiBH}_4 + \text{MnCl}_2 \rightarrow \text{Mn}(/\text{BH}_4)_2 + 2\text{LiCl} + (n - 2)\text{LiBH}_4 \quad (n = 2–23) \tag{6}
\]

### 3.2. Thermal behavior

Fig. 3 shows TPD gas desorption spectra combined with a mass spectroscopy analysis for ball milled n = 3 (Fig. 3a and b) and n = 5 mixtures (Fig. 3c and d), for two heating rates of 2 °C/min and 10 °C/min. The primary H₂ release peak from Mn(BH₄)₂ is centered around 130–150 °C depending on the heating rate. The second smaller and very broad H₂ release peak occurs in a wide temperature range 300–450 °C. This second peak corresponds to the decomposition of retained LiBH₄ which is a very volatile process as evidenced by sharp random peaks appearing at 300–450 °C in Fig. 3c and d for the n = 5 mixture which are related to the melting of excess LiBH₄. In Fig. 3a around 130 °C there is also a miniscule peak corresponding to the release of diborane B₂H₆. The intensity of the borane peak increases with increasing heating rate from 2 to 10 °C/min (Fig. 3b). For n = 5 at the heating rate 2 °C/min the B₂H₆ peak does not appear (Fig. 3c) while it re-appears again when the heating rate increases to 10 °C/min (Fig. 3d). It seems that B₂H₆ is released in the gas mixture with H₂ only at higher heating rates and for low molar ratios n ≤ 5 although this phenomenon should be studied more thoroughly to arrive at a definite conclusion. Furthermore, the intensity of the B₂H₆ peak even if it is observed is 200–600 times smaller than the intensity of the corresponding H₂ peak. The obtained results mean that the quantity of released diborane is minuscule being barely on the verge of the resolution of the Hiden Sieverts apparatus-quadrupole mass spectrometric experimental system. It must be pointed out that Liu et al. [17] reported that the relatively low intensity of diborane peaks they observed in their thermogravimetric experimental setup was due to the fact that large quantities of diborane did not reach the mass spectrometer. They observed some borate deposits on the piping system. They measured a high mass loss of 8.4 wt.% which possibly indicated a release of diborane. However, this is not the case in the present work as will be shown later.

Therefore, in accord with the gas thermal analysis results obtained in this work the decomposition reaction of Mn(BH₄)₂ can be written as follows neglecting minutiae quantities of B₂H₆ (if any):

\[
\text{Mn}(/\text{BH}_4)_2 \rightarrow \text{Mn} + 2\text{B} + 4\text{H}_2 \tag{7}
\]

Our mass spectroscopy results of released gas are in agreement with Choudhury et al. [12] who reported that for

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**Fig. 1** – The amount of H₂ desorbed during high energy ball milling for 30 min of (nLiBH₄ + MnCl₂) vs. the molar ratio n.
Fig. 2 – (a) X-ray diffraction pattern and (b) synchrotron diffraction pattern (the radiation wavelength $\lambda = 0.73065$ Å) for the (nLiBH$_4$ + MnCl$_2$) mixtures where $n = 1, 2, 3, 5, 9$ and 23, synthesized for 30 min by mechano-chemical synthesis under high energy impact milling mode (IMP68). ICDD and ICSd file numbers for peak identification of LiCl and Li$_2$MnCl$_4$ are shown in the legend.
a ball milled (3LiBH₄ + MnCl₂) mixture a gas chromatography analysis showed only H₂ desorbed without any other gases upon repeated sampling.

As mentioned above, decomposition of retained LiBH₄ also occurs at the 350–450 °C range but it has no practical meaning due to very high temperatures involved.

We also investigated melting behavior of the n = 2 and 3 ball milled mixtures. According to reactions (6) and (7) after completion of ball milling the n = 2 and 3 mixture consists of (Mn(BH₄)₂ + LiCl) and (Mn(BH₄)₂ + LiCl + LiBH₄), respectively. A small amount of mixture powder was placed on a pure copper button which, in turn, was placed on a hot plate. A thermocouple was attached to the copper button. This experimental set up was located in a glove box which was purged several times using high purity argon gas. The temperature was slowly increased to 274 and 286 °C for the n = 2 and 3 mixture, respectively. The behavior of powder was continuously filmed with a digital camera during heating. No evidence of melting of Mn(BH₄)₂ was observed. We only observed that the milled powder changed its color from gray to black most likely due to a local sintering. After heating the powder was slightly sintered but it could be easily broken loose into a fine dry powder. Černý et al. [14] reported that in a mixture with LiCl the Mn(BH₄)₂ hydride melted at about 177 °C (450 K). Apparently, the present experiments do not confirm such a low melting temperature of Mn(BH₄)₂ which is observed to be stable at least up to about 270–280 °C.

3.3. Isothermal dehydrogenation

Fig. 4 shows the examples of isothermal dehydrogenation curves at temperatures from 100 °C to 200 °C in 1 bar H₂.
pressure for the ball milled \((2\text{LiBH}_4 + \text{MnCl}_2)\) mixture. It can be seen that the \(n = 2\) mixture containing \(\text{Mn(BH}_4)_2\) and \(2\text{LiCl}\) after synthesis desorbs quite rapidly about 4 wt.% \(\text{H}_2\) at 100 \(^\circ\text{C}\) under 1 bar \(\text{H}_2\) pressure (Fig. 4a). This quantity of desorbed \(\text{H}_2\) is not measurably changed during desorption up to 200 \(^\circ\text{C}\) (Fig. 4b–d). The desorbed \(\text{H}_2\) quantity is nearly a half of \(\text{Mn(BH}_4)_2\) theoretical \(\text{H}_2\) capacity which is, indeed, a very large quantity of desorbed \(\text{H}_2\), keeping in mind that the ball milled mixture contains 2 mol of \(\text{LiCl}\) (Eq. (6)) which is simply a “dead-weight”. As mentioned in [13] a complete removal of \(\text{LiCl}\) from the microstructure could be achieved in the well-known Soxhlet extractor which was already successfully used for extracting \(\text{LiCl}\) and \(\text{NaCl}\) from solid mixtures with alanates [31,32]. Such an additional \(\text{LiCl}\) extraction processing could definitely substantially boost the \(\text{H}_2\) desorption capacity from a nearly single-phase \(\text{Mn(BH}_4)_2\) having a theoretical capacity of 9.5 wt.% \(\text{H}_2\) for the composites with \(n = 2\) and 3 molar ratios.

![Fig. 4](image-url) – Examples of isothermal volumetric dehydrogenation curves at (a) 100 \(^\circ\text{C}\), (b) 120 \(^\circ\text{C}\), (c) 140 \(^\circ\text{C}\) and (d) 200 \(^\circ\text{C}\), under 1 bar \(\text{H}_2\) pressure for the ball milled \((2\text{LiBH}_4 + \text{MnCl}_2)\) mixture.

<table>
<thead>
<tr>
<th>Molar ratio (n)</th>
<th>(\text{Mn(BH}_4)_2) after ball milling</th>
<th>No. moles (\text{H}) from reaction (7)</th>
<th>Molar mass (\text{H}) from reaction (7) (g/mol)</th>
<th>(\text{Mn(BH}_4)_2 + \text{MnCl}_2)</th>
<th>Theoretical (\text{H}_2) content from reaction (7) (wt.%)</th>
<th>Experimental hydrogen desorbed at 100 and 200 (^\circ\text{C}) (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.5</td>
<td>4</td>
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<td>147.628</td>
<td>2.73</td>
<td>0.9 and 2.4</td>
</tr>
<tr>
<td>2</td>
<td>1.0</td>
<td>8</td>
<td>8.064</td>
<td>169.412</td>
<td>4.76</td>
<td>3.8 and 4.2</td>
</tr>
<tr>
<td>3</td>
<td>1.0</td>
<td>8</td>
<td>8.064</td>
<td>191.196</td>
<td>4.22</td>
<td>4.2 and 4.5</td>
</tr>
<tr>
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<td>1.0</td>
<td>8</td>
<td>8.064</td>
<td>234.764</td>
<td>3.43</td>
<td>2.6 and 2.7</td>
</tr>
<tr>
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<td>1.0</td>
<td>8</td>
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<td>321.900</td>
<td>2.50</td>
<td>2.1 and 2.2</td>
</tr>
<tr>
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<td>8.064</td>
<td>626.876</td>
<td>1.29</td>
<td>1.3 and 1.3</td>
</tr>
</tbody>
</table>

Note: Molar masses (g/mol) taken for computing are as follows: \(\text{H} = 1.008\); \(\text{Li} = 6.941\); \(\text{B} = 10.811\); \(\text{Mn} = 54.938\); \(\text{Cl} = 35.453\).
Even without catalytic additives, the rate of dehydrogenation in Fig. 4 is very reasonable since 4 wt.% H₂ can be obtained within about 12 h at 100 °C (Fig. 4a). At only slightly higher temperature of 120 °C the dehydrogenation time for the same quantity of H₂ is reduced by half to just 4–6 h (Fig. 4b) and is proportionally shorter at 140 and 200 °C.

Table 1 shows the H₂ quantities experimentally desorbed at 100 and 200 °C compared to the maximum theoretical

![XRD patterns for all mixtures after full dehydrogenation at (a) 100 °C and (b) 200 °C. ICDD and ICSD file numbers for peak identification of LiCl, Li₂MnCl₄ and Mn are shown in the legend.](image)

Fig. 5 - XRD patterns for all mixtures after full dehydrogenation at (a) 100 °C and (b) 200 °C. ICDD and ICSD file numbers for peak identification of LiCl, Li₂MnCl₄ and Mn are shown in the legend.
quantities of H₂ expected to be desorbed from Mn(BH₄)₂ for various molar ratios n calculated according to reaction (7). It is observed that at 100 and 200 °C the quantities of H₂ desorbed from Mn(BH₄)₂ do not exceed the theoretical H₂ quantities expected to be desorbed from a mixture with n = const according to reaction (7). It clearly confirms the fact, already observed in Fig. 3, that the contribution from B₂H₆ is negligibly small (if any) when desorption occurs isothermally in the practical temperature range 100–200 °C. As mentioned above, Liu et al. [17] proposed that a decomposition of Mn(BH₄)₂ could occur via formation of B₂H₆ according to the following reaction:

\[ \text{Mn(BH₄)₂} \rightarrow \text{Mn} + \text{H₂} + \text{B₂H₆} \] (8)

However, reaction (8) requires that the quantities of desorbed (H₂ + B₂H₆) gas to be several times larger than those experimentally observed in the present work as listed in Table 1. The obtained results allow us to conclude that the isothermal dehydrogenation of Mn(BH₄)₂ mechano-chemically synthesized by ball milling occurs at the temperature range of 100–200 °C. As mentioned above, Liu et al. [17] proposed that a decomposition of Mn(BH₄)₂ could occur via formation of B₂H₆ according to reaction (7) rather than reaction (8).

In order to monitor the microstructural evolution occurring during isothermal dehydrogenation the XRD tests were carried out on mixtures fully desorbed at 100 °C (Fig. 5a) and 200 °C (Fig. 5b). Full desorption means that dehydrogenation was carried out to the end of each desorption curve in Fig. 4. The peaks of Li₂MnCl₄, LiCl and LiBH₄ remain essentially unchanged after desorption by comparison with their counterparts for the ball milled structure in Fig. 2a. The peaks of Mn(BH₄)₂ disappeared. Very weak peaks of Mn appear on a few but not all XRD patterns indicating that Mn could be partially crystalline and possibly partially amorphous. The microstructure observed after desorption is in a qualitative agreement with reaction (7) occurring during dehydrogenation. No peaks of crystalline B from reaction (7) are present after dehydrogenation which indicates that B must be fully amorphous.

The apparent activation energy was estimated and the examples of the Arrhenius plots of rate constant k with temperature according to Eq. (3) for the mixtures with the molar ratios n = 1, 2, 3 and 5 are presented in Fig. 6a–d, respectively. Corresponding temperatures for which estimates were done are also shown in the plots. Excellent coefficients of fit R² give a testimony to the accuracy of the method. Fig. 7a shows a plot of rate constant k in Eq. (3) vs. the molar ratio n for all ball milled mixtures, calculated for dehydrogenation at 120 °C. It is observed that the k values achieve a maximum for n = 3. Correspondingly, Fig. 7b shows that the apparent activation energy for dehydrogenation plotted vs. the molar ratio n, exhibits a minimum value of \( \sim 102 \text{ kJ/mol} \) for n = 3. This value was already reported by Varin et al. [13] and it was also reported that the apparent activation energy was reduced to \( \sim 92 \text{ kJ/mol} \) with added 5 wt.% nanometric Ni having SSA = 60.5 m²/g [13].

With the molar ratio n < 3 and n > 3 the apparent activation energy for the Mn(BH₄)₂ dehydrogenation is larger than that for n = 3. This effect is very pronounced in Fig. 7b. According to reaction (7) for a mixture having n = 3 a small quantity of LiBH₄ is retained after mechano-chemical synthesis while there is no retained LiBH₄ for n < 3 and the LiBH₄ quantity increases for n > 3. It is hypothesized that that a small quantity of retained LiBH₄ may accelerate the hydrogen desorption rate from

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**Fig. 6** – Examples of the Arrhenius plots of rate constant k with temperature for estimation of the apparent activation energy of hydrogen desorption for the mechano-chemically synthesized (nLiBH₄ + MnCl₂) mixtures. (a) n = 1, (b) n = 3, (c) n = 3 and (d) n = 5. The three temperatures used for each plot are shown.
Mn(BH4)_2 whereas both decrease and increase in the quantity of retained LiBH4 with decreasing/increasing n eliminates this effect. However, the exact atomistic mechanism is not clear at the moment. Apparently, the mixture with n = 3 exhibits the highest rate constant k and correspondingly the lowest apparent activation energy. This is a very interesting results showing that the molar ratio n = 2 may not be the optimal one.

So far, the only paper reporting the apparent activation energy of dehydrogenation for Mn(BH4)_2 is published by Choudhury et al. [12] for the ball milled (3LiBH4 + MnCl2) mixture. For the undoped system they report the value of 130.6 kJ/mol. This value is higher than ~102 kJ/mol obtained in [13] and the present work. However, Choudhury et al. used the Kissinger plots from the TPD data for their assessment of the apparent activation energy in contrast to the JMAK/Arrhenius method used in the present work for the direct volumetric hydrogen desorption data. We have found that these two diverse methodologies can give results differing within a 10–20% range.

3.4. Self-discharge of hydrogen at low temperatures

Recently, it has been reported for the first time by Varin et al. that a few ball milled LiAlH4-based mixtures combined with nanometric-size metal catalysts [18,24], complex hydride LiNH2 [25] and a MnCl2 catalytic precursor [33] continuously self-discharge H2 when stored for a prolonged time in glass vials at a temperature range from room temperature (RT) to 80 °C under slight overpressure of high purity argon. In order to find out if the same phenomenon occurs for the present (nLiBH4 + MnCl2) mixtures, first of all, a ball milled (2LiBH4 + MnCl2) mixture, which according to reaction (6) and Fig. 2a contains Mn(BH4)_2 and 2 mol of LiCl, was dehydrogenated in a Sieverts-type apparatus at 100 °C under 1 bar H2 pressure immediately after ball milling (0 days storage) and after storage for 11 days at RT under a slight overpressure of high purity argon. The pertinent desorption curves are shown in Fig. 8. It is clearly seen that the desorption curve after 11 days of storage shows a capacity deficiency of about 1.2 wt.% H2 with respect to the desorption curve obtained immediately after ball milling. Apparently, the Mn(BH4)_2 hydride present in this composite slowly desorbed that quantity of H2 within 11 days of storage.

Further studies of this phenomenon were conducted on the ball milled (3LiBH4 + MnCl2) mixture which according to reaction (6) and Fig. 2a contains mainly Mn(BH4)_2, 2 mol LiCl and 1 mol of retained LiBH4. Following procedures reported in [18,24,33] after a pre-determined length of time small samples stored at RT and 40 °C were extracted from the vial and fully dehydrogenated isothermally at a temperature of 140 °C in a Sieverts-type apparatus under 1 bar H2 pressure, registering the quantity of H2 desorbed. It was already reported in [13] that the addition of nanometric Ni (n-Ni) to (3LiBH4 + MnCl2) slightly accelerated dehydrogenation and reduced the apparent activation energy for dehydrogenation. In order to investigate the effect of nano-metal catalyst on the slow self-discharge during storage two batches of nanometric nickel (n-Ni) catalytic additive used in [13], having Specific Surface Area (SSA) = 9.5 and 60.5 m²/g, were incorporated in the quantity of 5 wt.% into (3LiBH4 + MnCl2) by ball milling.

Fig. 9 shows the quantities of H2 desorbed at 140 °C after long storage at room temperature (RT) and 40 °C of samples without and with the catalytic additive of nanometric Ni (n-Ni). It is seen in Fig. 9a and b that the n = 3 mixture without any additive discharges only a small amount of ~0.7 and 1.4 wt.% H2 after storage for 70–80 days at RT and 40 °C, respectively. The addition of n-Ni does not measurably change the rate of self-discharge at RT (Fig. 9c and e) although the n-Ni additive...
visibly accelerates it at 40 °C (Fig. 9d and f). Particularly effective is n-Ni with SSA = 60.5 m²/g which allows discharge of 2.5 wt.% H₂ within 63 days of storage at 40 °C (Fig. 9f). However, it should be pointed out that the rates of H₂ self-discharge observed for LiAlH₄ ball milled with nanometric Ni and Fe additives reported in [18,24] are much higher than that for ball milled (3LiBH₄ + MnCl₂) containing n-Ni with SSA = 9.5 m²/g; stored at 40 °C, (e) with 5 wt.% n-Ni SSA = 60.5 m²/g; stored at RT and (f) with 5 wt.% n-Ni SSA = 60.5 m²/g; stored at 40 °C. SSA-specific surface area. Storage in a glass vial under high purity argon.

Fig. 9 – The quantities of hydrogen desorbed at 140 °C in 1 bar H₂ pressure after long term storage of ball milled (3LiBH₄ + MnCl₂) (microstructure consisting of Mn(BH₄)₂ + 2LiCl + LiBH₄) at low temperatures. (a) No additive; stored at room temperature (RT), (b) no additive; stored at 40 °C, (c) with 5 wt.% n-Ni SSA = 9.5 m²/g; stored at RT, (d) with 5 wt.% n-Ni SSA = 9.5 m²/g; stored at 40 °C, (e) with 5 wt.% n-Ni SSA = 60.5 m²/g; stored at RT and (f) with 5 wt.% n-Ni SSA = 60.5 m²/g; stored at 40 °C. SSA-specific surface area. Storage in a glass vial under high purity argon.

Fig. 10 shows a comparison of the XRD pattern for as-milled (3LiBH₄ + MnCl₂) (a phase mixture of Mn(BH₄)₂ + 2LiCl + LiBH₄) containing n-Ni with SSA = 60.5 m²/g and the XRD pattern of the same mixture after storage for 95 days at 40 °C (~2.5 wt.% H₂ discharged). In the ball milled sample the diffraction peaks of Mn(BH₄)₂ are well developed whereas in the sample stored for 95 days the Mn(BH₄)₂ peaks are more diffuse and their intensity is reduced. A clear peak of Mn is also observed. This confirms that Mn(BH₄)₂ was gradually decomposing as experimentally observed by the H₂ release according to reaction (7) without any release of B₂H₆. Since no peaks of crystalline B are observed, which is required by reaction (7), it is most likely that B is in an amorphous state.

Finally, it should be pointed out that a phenomenon of H₂ self-discharge from hydride composites during their storage
at low temperatures is not only very interesting scientifically but also has some practical implications. Sandrock et al. [34,35] pointed out the significance of such a behavior for long-duration, low-demand devices that use H2 such as low power remote fuel cells or portable gas analyzers. Materials slowly discharging H2 can also be used in a number of chemical processes where a continuously reducing atmosphere is needed for a completion of the process. They can also have an application in a military sector for long-term cartridges supplying hydrogen to portable devices for soldiers on a mission.

4. Conclusions

The present paper reports the results of the mechanochemical activation synthesis (MCAS) of manganese borohydride (Mn(BH4)2) from mixtures of lithium borohydride (LiBH4) and manganese chloride (MnCl2) and its thermal dehydrogenation behavior. For the first time a wide range of molar ratios \( n = 1, 2, 3, 5, 9 \) and 23 is used in the \((n\text{LiBH}_4 + \text{MnCl}_2)\) mixtures. The main conclusions can be summarized as follows:

1. During ball milling up to 30 min the \((n\text{LiBH}_4 + \text{MnCl}_2)\) mixtures desorb very small quantities of H2 which increase with increasing molar ratio \( n \) but do not exceed 0.2 wt.% even for \( n = 23 \). However, when the milling duration was extended to 1 h for the \((3\text{LiBH}_4 + \text{MnCl}_2)\) mixture then the H2 desorption was more substantive reaching about 1 wt.% after completion of milling.

2. XRD and synchrotron diffraction studies confirm that for the molar ratio \( n = 1 \) the principal phases synthesized by the MCAS are Li2MnCl4 (cubic spinel) and Mn(BH4)2 according to following reaction:

   \[
   \text{LiBH}_4 + \text{MnCl}_2 \rightarrow 0.5\text{Mn(BH}_4)_2 + 0.5\text{Li}_2\text{MnCl}_4.
   \]

   For \( n = 2 \) a LiCl salt and Mn(BH4)2 are formed according to following reaction: 2LiBH4 + MnCl2 → Mn(BH4)2 + 2LiCl. With the \( n \) increasing from 3 to 23, LiBH4 is not completely reacted and its increasing amount is retained in the microstructure coexisting with LiCl and Mn(BH4)2 according to following reaction: \( n\text{LiBH}_4 + \text{MnCl}_2 \rightarrow \text{Mn(BH}_4)_2 + 2\text{LiCl} + (n - 2)\text{LiBH}_4 \).

3. Mass spectrometry of evolving gas during TPD tests shows a strong H2 release peak and a miniscule borane (B2H6) peak at around \( 150 \) °C with the intensity of the borane peak being 200–600 times smaller than the intensity of the corresponding H2 peak.

4. In situ continuous heating experiments confirm that no evidence of melting of Mn(BH4)2 is observed at least up to \( \sim 280 \) °C.

5. Volumetric dehydrogenation tests show that the \((n\text{LiBH}_4 + \text{MnCl}_2)\) mixture with the molar ratios \( n = 2 \) and 3 consisting mostly of Mn(BH4)2 and LiCl desorb quite rapidly about 4 wt.% H2 at 100 °C under 1 bar H2 pressure. This quantity of desorbed H2 is not measurably changed during desorption up to 200 °C. This is a very large quantity of desorbed H2 considering the presence of LiCl dead-weight in the microstructure. It suggests that after extraction of LiCl a single-phase Mn(BH4)2 would be able to desorb about 9 wt.% H2 at a 100–200 °C temperature range.

6. Evolving gas mass spectrometry analysis and volumetric dehydrogenation tests show quite convincingly that the decomposition of Mn(BH4)2 occurs at the temperature range 100–200 °C with a non-existent or negligibly small contribution from borane gas (B2H6).

7. The ball milled mixture with \( n = 3 \) exhibits the highest rate constant \( k \) and the lowest apparent activation energy for dehydrogenation, \( E_A \sim 102 \) kJ/mol. Decreasing or increasing the molar ratio \( n \) below or above 3 increases the apparent activation energy.
Ball milled n = 2 and 3 mixtures discharge slowly H2 during storage at room temperature and 40 °C. The addition of 5 wt.% nano-Ni with a specific surface area of 60.5 m2/g substantially enhances the rate of discharge at 40 °C.

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