

## ***Original***

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### **Simultaneous desorption behavior of M borohydrides and Mg<sub>2</sub>FeH<sub>6</sub> reactive hydride composites**

**(M = Mg, then Li, Na, K, Ca)**

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## Simultaneous desorption behavior of M borohydrides and Mg<sub>2</sub>FeH<sub>6</sub> reactive hydride composites (M = Mg, then Li, Na, K, Ca)

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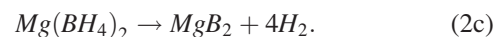
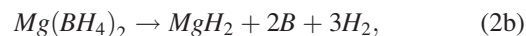
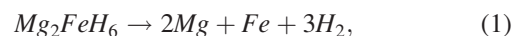
Combinations of complex metal borohydrides ball milled with the transition metal complex hydride, Mg<sub>2</sub>FeH<sub>6</sub>, are analysed and compared. Initially, the Reactive Hydride Composite (RHC) of Mg<sup>2+</sup> cation mixtures of Mg<sub>2</sub>FeH<sub>6</sub> and γ-Mg(BH<sub>4</sub>)<sub>2</sub> is combined in a range of molar ratios and heated to a maximum of 450 °C. For the molar ratio of 6 Mg<sub>2</sub>FeH<sub>6</sub> + Mg(BH<sub>4</sub>)<sub>2</sub>, simultaneous desorption of the two hydrides occurred, which resulted in a single event of hydrogen release. This single step desorption occurred at temperatures between those of Mg<sub>2</sub>FeH<sub>6</sub> and γ-Mg(BH<sub>4</sub>)<sub>2</sub>. Keeping this anionic ratio constant, the desorption behavior of four other borohydrides, Li-, Na-, K-, and Ca-borohydrides was studied by using materials ball milled with Mg<sub>2</sub>FeH<sub>6</sub> applying the same milling parameters. The mixtures containing Mg-, Li-, and Ca-borohydrides also released hydrogen in a single event. The Mass Spectrometry (MS) results show a double step reaction within a narrow temperature range for both the Na- and K-borohydride mixtures. This phenomenon, observed for the RHC systems at the same anionic ratio with all five light metal borohydride mixtures, can be described as simultaneous hydrogen desorption within a narrow temperature range centered around 300 °C. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4929340>]

Solid state hydrogen storage materials provide continuous energy storage solutions for intermittent renewable energy systems. Over the last decade, complex hydrides have proved to have enormous potential for hydrogen storage systems.<sup>1–5</sup> Metal boron systems are capable of forming complex hydrides and can be synthesised using lightweight elements resulting in high gravimetric hydrogen capacity. Lightweight borohydrides including Mg, Li, Na, K, and Ca borohydrides are good examples of high hydrogen capacity systems, with theoretical hydrogen capacities of 14.9, 18.5, 10.7, 7.5, and 11.6 wt. % of hydrogen respectively (M(BH<sub>4</sub>)<sub>n</sub> → M+nB+2nH<sub>2</sub>). The decomposition products are too stable to cycle under moderate temperatures and pressures making it difficult for practical use<sup>3,6,7</sup> (for example, reactions in Eqs. (2a)–(2c)).

One way to alter the behavior of the desorption properties of borohydrides is to form a reactive hydride composite (RHC). Such systems have gained increased importance in recent years as some of these RHCs have lower reaction enthalpies whilst maintaining relatively high storage capacities. Examples of such systems include, LiBH<sub>4</sub> + MgH<sub>2</sub>,<sup>8,9</sup> NaBH<sub>4</sub> + MgH<sub>2</sub>,<sup>10,11</sup> Ca(BH<sub>4</sub>)<sub>2</sub> + MgH<sub>2</sub>,<sup>12</sup> and more recently LiBH<sub>4</sub> + Mg<sub>2</sub>FeH<sub>6</sub> (Ref. 13) and NaBH<sub>4</sub> + Mg<sub>2</sub>FeH<sub>6</sub>.<sup>14</sup> Combinations of RHC systems, Mg(BH<sub>4</sub>)<sub>2</sub>, Ca(BH<sub>4</sub>)<sub>2</sub>, and KBH<sub>4</sub> each with Mg<sub>2</sub>FeH<sub>6</sub> are presented in this letter in two parts. First, a detailed analysis of Mg(BH<sub>4</sub>)<sub>2</sub> + Mg<sub>2</sub>FeH<sub>6</sub> desorption behavior is given followed by an interesting desorption comparison between each of the five light metal

borohydrides (Li, Na, Mg, K, and Ca) mixed with Mg<sub>2</sub>FeH<sub>6</sub> at the same anionic ratio.

Mg<sub>2</sub>FeH<sub>6</sub> was synthesized using the method described in Li *et al.*<sup>13</sup> Once synthesized, Mg<sub>2</sub>FeH<sub>6</sub> was ball milled (Fritsch Pulverisette, Germany) with the γ-polymorph of Mg(BH<sub>4</sub>)<sub>2</sub> (98.7%, Sigma Aldrich) in Ar atmosphere at varying stoichiometric molar ratios, 1:0, 6:1, 2:1, 2:5, and 0:1 (x:y = xMg<sub>2</sub>FeH<sub>6</sub> + yMg(BH<sub>4</sub>)<sub>2</sub>), with theoretical hydrogen capacities of 5.47%, 6.2%, 10.7%, and 14.9%, respectively. The desorption reaction for Mg<sub>2</sub>FeH<sub>6</sub> (Eq. (1)) is well documented;<sup>15,16</sup> however, the hydrogen release for Mg(BH<sub>4</sub>)<sub>2</sub> is more complex as it undergoes several polymorph transitions as well as produce intermediate compounds such as B<sub>12</sub>H<sub>12</sub> (Refs. 17 and 18) during decomposition. Several suggested end products of the Mg(BH<sub>4</sub>)<sub>2</sub> hydrogen desorption reaction are given in Eqs. (2a)–(2c)



Ball milling was used to mix Mg<sub>2</sub>FeH<sub>6</sub> with four other metal borohydrides, LiBH<sub>4</sub> (95%, Sigma Aldrich), NaBH<sub>4</sub> (98%, Sigma Aldrich), KBH<sub>4</sub> (99.9%, Sigma Aldrich), and Ca(BH<sub>4</sub>)<sub>2</sub> (98.8%, Sigma Aldrich). All of the ball milling parameters such as rotation speed (400 rpm), ball to powder ratio (40:1), and milling time (300 min) were kept constant when preparing the mixtures. To observe dehydrogenation

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behavior, coupled differential thermal analysis (DTA), thermal gravimetric (TG) analysis, and mass spectroscopy (MS) were employed (Rigaku Thermoplus, TG8120, Japan) in He atmosphere. Thermal events were observed from room temperature to 450 °C at a heating rate of 5 °C/min. Powder X-ray diffraction (PXRD) was undertaken on a PANalytical instrument (X'Pert<sup>3</sup> Powder, The Netherlands) with the following operating parameters: Cu K $\alpha$  radiation,  $\lambda = 1.5418$  Å range 10°–90° 2 $\theta$  and *in situ* PXRD measurements were done at the Swiss-Norwegian Beam Lines (SNBL, BM01A ESRF, France),  $\lambda = 0.80607$  Å.

The MS results from hydrogen release for Mg<sub>2</sub>FeH<sub>6</sub>–Mg(BH<sub>4</sub>)<sub>2</sub> mixtures are shown in Figure 1(a). Changing molar ratios between the two hydride systems resulted in a sequential hydrogen release relative to the amounts of phases present. The onset desorption temperature for the mixtures all appeared within the onset temperature range of the individual compounds (between ca. 180 °C for Mg<sub>2</sub>FeH<sub>6</sub> and ca. 280 °C for  $\gamma$ -Mg(BH<sub>4</sub>)<sub>2</sub>). Hydrogen release from the borohydride rich mixture (2:5 sample) behaved in a similar manner to pure  $\gamma$ -Mg(BH<sub>4</sub>)<sub>2</sub>; however, there was increased amount

of hydrogen released at higher temperatures. The 2:1 mixture also showed multiple thermal transitions together with hydrogen release and it can be seen that as the content of Mg<sub>2</sub>FeH<sub>6</sub> increased, the number of thermal transitions for desorption decreased. This behavior is in agreement with Li *et al.*<sup>13,14</sup> where similar mixtures of Mg<sub>2</sub>FeH<sub>6</sub> + LiBH<sub>4</sub> and Mg<sub>2</sub>FeH<sub>6</sub> + NaBH<sub>4</sub> were decomposed under the same conditions and this resulted in the desorption temperatures occurring between that of the individual hydrides. It is important to note that TG data (Figure 1(b)), associated with the thermal events of the Mg(BH<sub>4</sub>)<sub>2</sub> mixtures in this letter, indicated that each of the ball milled molar ratio combinations was able to desorb close to the aforementioned theoretical capacities, confirming that complete desorption of both the Mg(BH<sub>4</sub>)<sub>2</sub> and Mg<sub>2</sub>FeH<sub>6</sub> had taken place.

From Figure 1, an unexpected result was the simultaneous desorption of both the Mg<sub>2</sub>FeH<sub>6</sub> and Mg(BH<sub>4</sub>)<sub>2</sub> from the 6:1 sample. The literature shows that it is more common to find multiple desorption steps for any borohydride system.<sup>6,8,10,12</sup> This is also true for RHC systems that contain borohydrides with either MgH<sub>2</sub><sup>12,19</sup> or CaH<sub>2</sub><sup>20</sup> where no mutual desorption behavior was observed. The 6:1 sample showed a single transition, attributed to hydrogen release, with an onset at ca. 280 °C and a peak temperature centered around 300 °C.

To further investigate the occurrence of this single desorption event, four RHC systems containing Mg<sub>2</sub>FeH<sub>6</sub> with four other light metal borohydrides (Li, Na, K, and Ca-BH<sub>4</sub>) were ball milled with a constant anionic ratio, 3[FeH<sub>6</sub>]<sup>4-</sup>:1[BH<sub>4</sub>]<sup>-</sup> and then compared to the Mg borohydride RHC. A direct comparison of these desorption reactions was made: (i) 3Mg<sub>2</sub>FeH<sub>6</sub> + LiBH<sub>4</sub>, (ii) 3Mg<sub>2</sub>FeH<sub>6</sub> + NaBH<sub>4</sub>, (iii) 6Mg<sub>2</sub>FeH<sub>6</sub> + Mg(BH<sub>4</sub>)<sub>2</sub>, (iv) 3Mg<sub>2</sub>FeH<sub>6</sub> + KBH<sub>4</sub>, and (v) 6Mg<sub>2</sub>FeH<sub>6</sub> + Ca(BH<sub>4</sub>)<sub>2</sub>. The stoichiometric ratios were adjusted for Mg and Ca borohydride reactions to ensure that the anionic ratio remained constant.

Figure 2(a) shows the resultant PXRD data of these all of the RHC mixtures immediately after ball milling. The peaks identified the presence of Mg<sub>2</sub>FeH<sub>6</sub> with some remaining Fe, inherent from the Mg<sub>2</sub>FeH<sub>6</sub> synthesis process. Different batches of Mg<sub>2</sub>FeH<sub>6</sub> were synthesised with various levels of Fe impurities; therefore, the PXRD of the ball milled mixtures shows varying degrees of Fe intensities before and after desorption (Figure 2). There were no new crystalline phases present; however, PXRD amorphicity of the metal borohydrides was apparent. The synthesis of non-equilibrium states during ball milling is a well-known phenomenon.<sup>21</sup>

For direct comparison, DTA-TG-MS analysis was used for each of the borohydride-magnesium iron hydride mixes with the same anionic ratio (Figure 3). For all samples, Mg<sub>2</sub>FeH<sub>6</sub> appeared to undergo thermodynamic stabilization when mixed with any of the metal borohydrides as indicated by an increase in desorption temperatures. Similar to the Mg based RHC, the TG results showed that all the mixtures had undergone complete desorption (data not shown). For the mixtures containing LiBH<sub>4</sub>, Mg(BH<sub>4</sub>)<sub>2</sub> and Ca(BH<sub>4</sub>)<sub>2</sub> single step desorption behaviour are observed. However, for the samples containing NaBH<sub>4</sub> and KBH<sub>4</sub>, broader overlapping double peaks appear. This could be the result of Na and K melting immediately after hydrogen release, as this temperature is higher

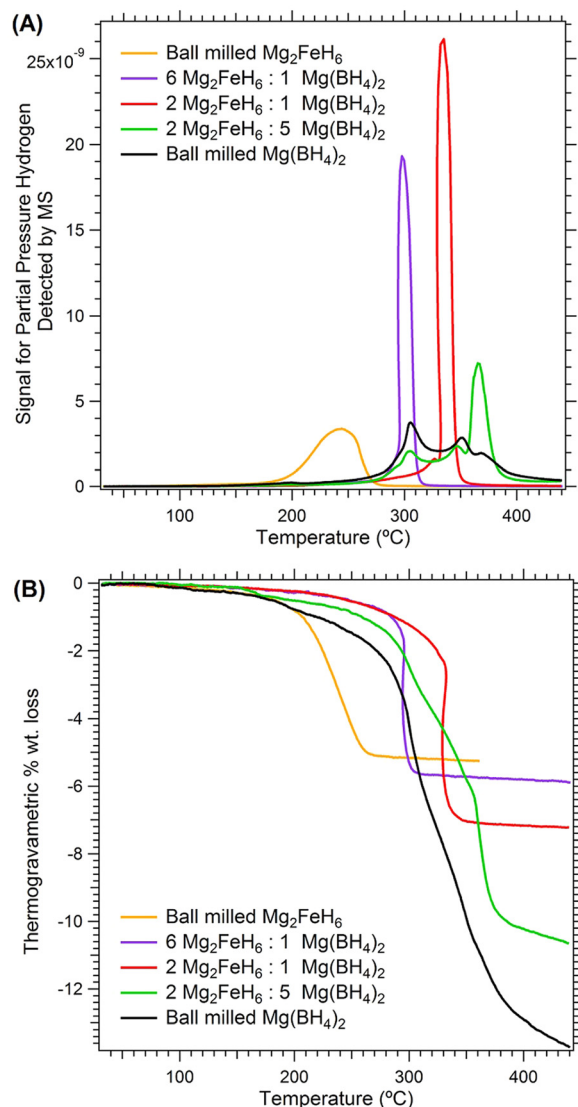


FIG. 1. (a) H<sub>2</sub> detected from mass spectroscopy, (b) thermogravimetric analysis during the desorption reaction of Mg<sub>2</sub>FeH<sub>6</sub> + Mg(BH<sub>4</sub>)<sub>2</sub> with varying stoichiometric ratios.

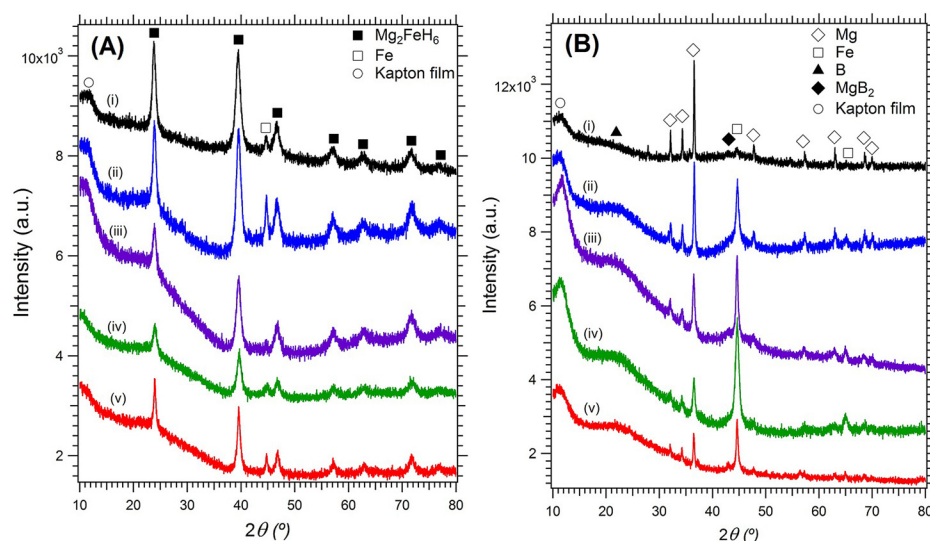


FIG. 2. PXD data of  $\text{Mg}_2\text{FeH}_6$  with M borohydride mixtures of (a) as ball milled and (b) after heating to  $450^\circ\text{C}$  in the DTA-TG-MS (i)  $3\text{Mg}_2\text{FeH}_6 + \text{LiBH}_4$ , (ii)  $3\text{Mg}_2\text{FeH}_6 + \text{NaBH}_4$ , (iii)  $6\text{Mg}_2\text{FeH}_6 + \text{Mg}(\text{BH}_4)_2$ , (iv)  $3\text{Mg}_2\text{FeH}_6 + \text{KBH}_4$ , (v)  $6\text{Mg}_2\text{FeH}_6 + \text{Ca}(\text{BH}_4)_2$ .

than their melting temperatures; therefore, hydrogen release of the remaining sample is affected. The desorption products are labelled in the PXD diffractogram as shown in Figure 2(b). All RHC mixtures were reduced to elemental Mg and Fe, with the possibility of small amounts of amorphous boron ( $24^\circ 2\theta$ ) and  $\text{MgB}_2$  ( $43^\circ 2\theta$ ) formation. There was little evidence of any Fe-B containing phases.

Borohydrides undergo several steps decomposition and this is usually reflected in the DTA-MS with multiple thermal transitions.<sup>6</sup> The Pauling electronegativities of the cations are strongly correlated with thermodynamic stability<sup>22</sup> and therefore reflected in the onset temperatures for hydrogen release (Table I). In contrast, the desorption behavior of the RHC mixtures at this particular anionic ratio, displayed mutual hydrogen release, all occurring within a narrow temperature range centred around  $300^\circ\text{C}$  (Table I). The results show a phenomenon of all of the RHC mixtures desorbing within this narrow temperature range even for the

borohydrides with relatively high thermodynamic stability ( $\text{NaBH}_4$  and  $\text{KBH}_4$ ).

The single desorption behavior observed in these experiments is unique in that it appears to be independent of the cation present, and therefore independent of the Pauling electronegativity. There are several possibilities for this behavior. Although the elemental Fe remaining from  $\text{Mg}_2\text{FeH}_6$  synthesis does not appear to catalyze the borohydride desorption,<sup>23</sup> the Fe produced after  $\text{Mg}_2\text{FeH}_6$  desorption may act as an activation trigger. Another possibility is the formation of solid solution upon heating. *In situ* PXD measurements demonstrated that the lattice expansion of the RHCs was different to that of  $\text{Mg}_2\text{FeH}_6$  alone (Figure 4). Physical proximity of the two mixes that occurred after ball milling them together may lead to desorption occurring at an enthalpy between the individual components, thus leading to a single or near single transition. Another likely explanation for mutual desorption behavior is the hydrogen exchange of each of the components prior to desorption similar to the system  $\text{LiBH}_4\text{-Mg}_2\text{FeD}_6$ .<sup>24</sup> Hydrogen exchange has been shown in the  $\text{MgH}_2 + \text{LiBH}_4$  system therefore increasing the desorption temperature of  $\text{MgH}_2$ .<sup>25</sup>

In conclusion, RHC compounds containing  $\text{Mg}_2\text{FeH}_6$  and  $\text{Mg}(\text{BH}_4)_2$  in various stoichiometric ratios underwent complete desorption within a temperature range of the individual components. At the ratio of 6:1,  $\text{Mg}_2\text{FeH}_6$  and  $\text{Mg}(\text{BH}_4)_2$  in a single decomposition event were observed. Keeping this anionic ratio constant,  $\text{Mg}_2\text{FeH}_6$  was ball milled with four other light metal hydrides, Li, Na, K, and Ca, and the desorbed under the same conditions as the Mg based system. It was shown that a unique phenomenon of

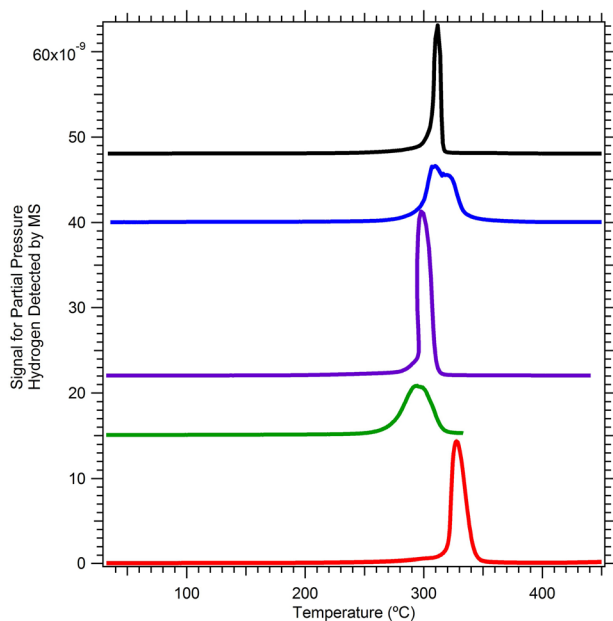


FIG. 3. Hydrogen signal taken from the MS whilst heating to  $450^\circ\text{C}$  in the DTA for (i)  $3\text{Mg}_2\text{FeH}_6 + \text{LiBH}_4$ , (ii)  $3\text{Mg}_2\text{FeH}_6 + \text{NaBH}_4$ , (iii)  $6\text{Mg}_2\text{FeH}_6 + \text{Mg}(\text{BH}_4)_2$ , (iv)  $3\text{Mg}_2\text{FeH}_6 + \text{KBH}_4$ , (v)  $6\text{Mg}_2\text{FeH}_6 + \text{Ca}(\text{BH}_4)_2$ .

TABLE I. Comparison of desorption temperatures of borohydrides vs RHC mixtures.

Borohydride	$\text{MBH}_4^6$ ( $^\circ\text{C}$ )	RHC with $\text{Mg}_2\text{FeH}_6$ ( $^\circ\text{C}$ )
$\text{LiBH}_4$	340	290
$\text{NaBH}_4$	530	290
$\text{Mg}(\text{BH}_4)_2$	280	280
$\text{KBH}_4$	680	270
$\text{Ca}(\text{BH}_4)_2$	350	310

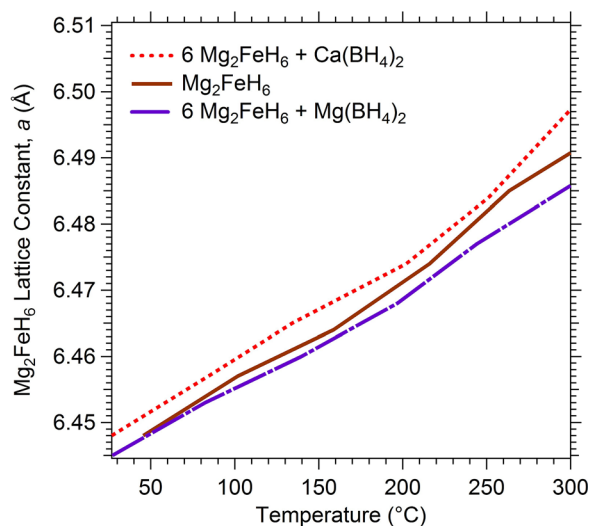


FIG. 4. Lattice constant expansion upon heating,  $a$ , for  $\text{Mg}_2\text{FeH}_6$ , pure (solid line), with  $\text{Mg}(\text{BH}_4)_2$  (red dotted line), and with  $\text{Ca}(\text{BH}_4)_2$  (purple dotted dashed line). Data were taken from SNBL and ESRF.

simultaneous hydrogen release from all of the RHCs occurred within a narrow temperature release with a single or near single transition. This behavior could potentially lead to a more simple system of hydrogen storage due to the narrow operating temperature and high hydrogen capacities.

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