



## Effect of synthesis route on the hydrogen storage properties of $2\text{MgH}_2\text{--Fe}$ compound doped with $\text{LiBH}_4$



C. Gosselin<sup>a</sup>, S. Deledda<sup>b</sup>, B.C. Hauback<sup>b</sup>, J. Huot<sup>a,\*</sup>

<sup>a</sup>Hydrogen Research Institute, Université du Québec à Trois-Rivières, 3351 des Forges, Trois-Rivières, Québec G9A 5H7, Canada

<sup>b</sup>Institute for Energy Technology, Department of Physics, P.O. Box 40, NO-2027 Kjeller, Norway

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### ABSTRACT

The hydrogen storage properties of a 2:1 mol ratio of  $\text{MgH}_2$  and Fe with or without 10 wt.% of  $\text{LiBH}_4$  were investigated. Two doping methods were used: the first one consisted of two steps: first the  $2\text{MgH}_2 + \text{Fe}$  mixture was ball milled for 10 h and subsequently  $\text{LiBH}_4$  was added and milling resumed for 1 more hour. In the second method all materials were mixed and ball milled for 10 h. The first method produced materials with an hydrogen dehydrogenation capacity of 2.69 wt.% at 623 K and that could re-absorb 2.93 wt.%  $\text{H}_2$ . The materials made by the second method presented a hydrogen dehydrogenation capacity of 2.98 wt.% at 623 K and re-absorbed 3.10 wt.%  $\text{H}_2$ . For both methods, the rehydrided sample consisted only of  $\text{MgH}_2$ . The reversibility of the reaction was enhanced with the  $\text{LiBH}_4$ , but this additive, by acting as a catalyst for the formation of  $\text{MgH}_2$ , precludes the formation of  $\text{Mg}_2\text{FeH}_6$ .

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### 1. Introduction

Because of their high hydrogen storage capacities, magnesium-based alloys have been actively considered for hydrogen storage applications [1]. However, the high temperature of operation and relatively slow kinetics drastically reduce the practicality of using this type of materials. Instead of using these alloys for hydrogen storage an elegant solution is to use them for thermal storage [2,3]. The ternary alloy  $\text{Mg}_2\text{FeH}_6$  has been discovered by Didisheim et al. who synthesized it at 450 °C under high hydrogen pressure (20–120 bar) [4]. This hydride store 5.5 wt.% of hydrogen compare to 7.6 wt.% for  $\text{MgH}_2$ . However,  $\text{Mg}_2\text{FeH}_6$  could be more suitable for heat storage applications because of its lower hydrogen dissociation pressure (66 bar compared to 104 bar at 500 °C) [5]. This means that the heat storage tank could be operated at lower pressure and thus reducing cost.

The beneficial effect of  $\text{LiBH}_4$  on hydrogen sorption kinetic of  $\text{MgH}_2$  has been well established [6,7]. Puszkiel and Gennari have shown that the composite powder  $\text{Mg}_{15}\text{Fe}$  doped with ~10 mol.%  $\text{LiBH}_4$  shows much higher capacity and faster kinetics than the undoped composite [8]. Deng et al. used  $\text{Mg}_2\text{FeH}_6$  as a catalyst for  $\text{LiBH}_4$  and found that the sorption properties of  $\text{LiBH}_4$  are improved [9]. In a recent investigation, Li et al. showed that the in the mixtures  $x\text{LiBH}_4 + (1-x)\text{Mg}_2\text{FeH}_6$  ( $x < 0.5$ ) both hydrides simultaneously release hydrogen [10].

We report here the use of  $\text{LiBH}_4$  as a catalyst for hydrogen sorption of  $\text{Mg}_2\text{FeH}_6$ . Two different synthesis pathways were studied. In one  $\text{MgH}_2$  and Fe were first milled together and  $\text{LiBH}_4$  was added for the last hour of milling. In the other method all raw materials were mixed and milled together. In this way we could test the impact of synthesis route on the final structure and hydrogen storage properties of the material.

### 2. Experimental

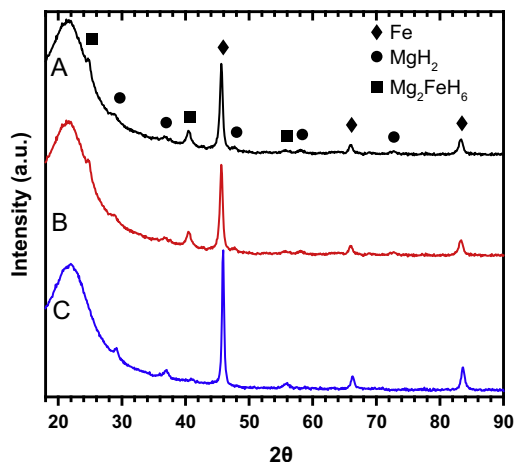
Commercial  $\text{LiBH}_4$  (95%),  $\text{MgH}_2$  (98%) and Fe (99.9%) powders were all purchased from Alfa Aesar and used without further purification. Ball milling was performed under argon using a SPEX 8000 mill. Stoichiometric amount of  $2\text{MgH}_2$  and Fe for a total of 3 g were placed in a stainless steel crucible with 4 stainless steel balls to obtain ball to powder weight ratio of 10:1. To prevent oxidation all samples were stored and handled in an argon filled glove box.

Three different composites were synthesized. For the first one, (compound A)  $2\text{MgH}_2$  and Fe powders were ball milled for 10 h. The second sample (compound B)  $2\text{MgH}_2$  and Fe powders were first milled 10 h and thereafter 10 wt.% of  $\text{LiBH}_4$  was added and milling resumed for one more hour. The third sample (compound C)  $2\text{MgH}_2$ , Fe and 10 wt.% of  $\text{LiBH}_4$  were mixed together and milled for 10 h.

Crystal structure was analyzed from X-ray powder diffraction patterns registered on a Bruker D8 Focus apparatus with  $\text{Cu K}\alpha$  radiation. To prevent reaction between sample and air during the data collection an argon-sealed sample holder was used. This sample holder is responsible for the broad amorphous-like peak below 35°. Rietveld refinements were performed using the Topas software via the fundamental parameter approach [11].

The hydrogen sorption properties of the samples were measured with a home-made Sievert-type apparatus. The dehydrogenations were made at 623 K under a pressure of 0.1 MPa. Samples were thereafter exposed to a hydrogen pressure of 3 MPa at 623 K for hydrogenation.

\* Corresponding author.



**Fig. 1.** X-ray diffraction patterns for: A-2MgH<sub>2</sub> + Fe ball milled 10 h; B-2MgH<sub>2</sub> + Fe ball milled for 10 h and further milled with LiBH<sub>4</sub> for 1 more hour; and C-2MgH<sub>2</sub> + Fe and LiBH<sub>4</sub> ball milled for 10 h.

### 3. Results and discussions

Fig. 1 shows the X-ray powder diffraction of all samples after synthesis. Phase's abundances as determined from Rietveld refinement are shown in Table 1. The slight shift of the main iron peak in pattern C compare to the other two patterns is due to zero offset. It is clear that the amount of Fe derived from these analyses is too large. For instance, if the iron in Mg<sub>2</sub>FeH<sub>6</sub> is taken into account then the total amount of iron is about 65 wt.% which is higher than the nominal stoichiometry (about 55 wt.%). The reason for such a discrepancy is likely due to the uncertainties caused by the strong fluorescence of iron caused by the incident Cu K $\alpha$  radiation. Another possible explanation is that the discrepancy is due to micro-absorption and an underestimation of the Mg-containing phases. It has been shown that Mg<sub>2</sub>FeH<sub>6</sub> is usually capped by iron [12]. Since the attenuation of Cu radiation in Fe is considerably larger than in magnesium, we expect that micro-absorption in iron will 'mask' all Mg-based phases, which in turn will be underestimated during the Rietveld refinement. Therefore, numbers given in Table 1 should only be taken as a reference. We report them here in order to have a quantitative comparison between the phase abundance of MgH<sub>2</sub> and Mg<sub>2</sub>FeH<sub>6</sub>.

It is clear from the phases abundances reported in Table 1 that adding LiBH<sub>4</sub> after 10 h of milling and continue milling for one more hour does not have any impact on the phase composition. However, milling the mixture 2MgH<sub>2</sub> + Fe + 10 wt.% LiBH<sub>4</sub> totally suppress the formation of Mg<sub>2</sub>FeH<sub>6</sub>.

The values of crystallites size are given in Table 2. It confirms that adding LiBH<sub>4</sub> after 10 h have minimal impact on the crystal structure of the material: the crystallites size is only slightly increased. On the other hand, adding LiBH<sub>4</sub> at the beginning of milling produces bigger crystallite sizes.

**Table 1**

Phase abundances in wt.% of as-milled samples as determined from Rietveld refinement. Uncertainty on each value is  $\pm 1$ .

Sample	Fe	MgH <sub>2</sub>	Mg <sub>2</sub> FeH <sub>6</sub>
Nominal 2MgH <sub>2</sub> + Fe	49	51	–
Nominal 2MgH <sub>2</sub> + Fe + 10 wt.% LiBH <sub>4</sub>	44	46	–
2MgH <sub>2</sub> + Fe ball milled 10 h	50	23	27
2MgH <sub>2</sub> + Fe ball milled 10 h + 10 wt.% LiBH <sub>4</sub> ball milled 1 more hour	52	22	26
2MgH <sub>2</sub> + Fe + 10 wt.% LiBH <sub>4</sub> ball milled 10 h	64	36	–

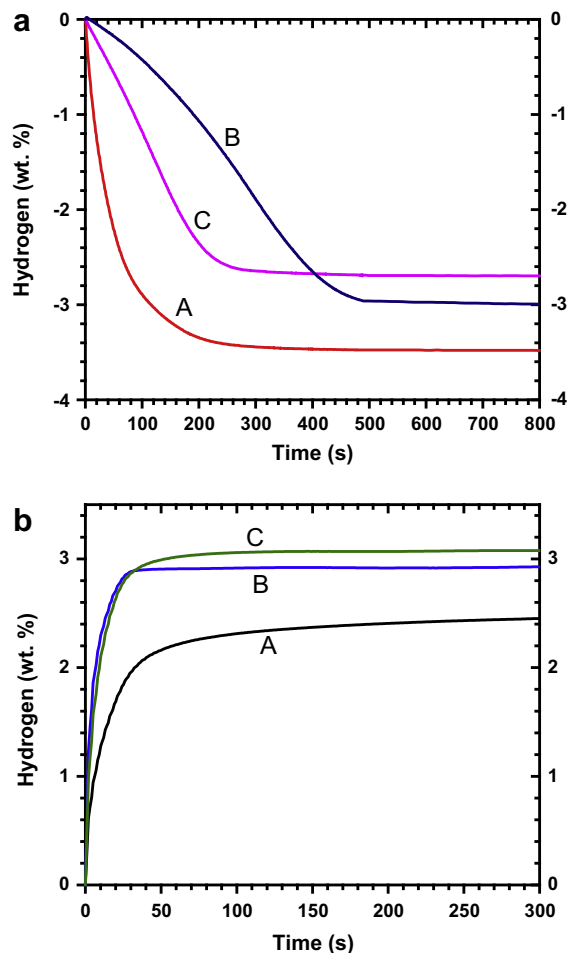
**Table 2**

Crystallites size in nm of different phases in as-milled samples as determined from Rietveld refinement. Uncertainty on last significant digit each value is given in parenthesis.

Sample	Fe	MgH <sub>2</sub>	Mg <sub>2</sub> FeH <sub>6</sub>
2MgH <sub>2</sub> + Fe milled 10 h	14.4(3)	5.7(8)	8.6(5)
2MgH <sub>2</sub> + Fe milled 10 h + 10 wt.% LiBH <sub>4</sub> and milled 1 more hour	15.3(2)	6.1(7)	9.6(5)
2MgH <sub>2</sub> + Fe + 10 wt.% LiBH <sub>4</sub> milled 10 h	24.6(5)	8.3(7)	–

After milling, the samples were first desorbed at 623 K under an initial pressure of 0.1 MPa. The dehydrogenation curves are shown in Fig. 2a. It is clear that these samples have different kinetics and capacities. As ball milling was performed under argon, the nominal capacity should be 3.8 wt.%, not taking into account LiBH<sub>4</sub>. We see that the only sample having a capacity close to the nominal one is the undoped sample. Doping has the effect of reducing the capacity and dehydrogenation kinetic.

The first hydrogenation kinetics are shown in Fig. 2b. Here the trend is reversed: the undoped sample has a lower capacity than the doped ones. Kinetics are quite fast but the capacities are far from the nominal value (5.6 wt.% assuming full hydrogenation to Mg<sub>2</sub>FeH<sub>6</sub>). Such variation of capacities between the first dehydrogenation and hydrogenation is somewhat expected because the



**Fig. 2.** Sorption kinetics at 623 K of (a) first dehydrogenation under initial pressure of 0.1 MPa and (b) first hydrogenation under 3 MPa. The single curves refer to: A-2MgH<sub>2</sub> + Fe ball milled 10 h; B-2MgH<sub>2</sub> + Fe ball milled for 10 h and further milled with LiBH<sub>4</sub> for 1 more hour; and C-2MgH<sub>2</sub> + Fe + LiBH<sub>4</sub> ball milled for 10 h.

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