

Article

Dehydriding Process and Hydrogen–Deuterium Exchange of LiBH₄–Mg₂FeD₆ Composites

Guanqiao Li ¹, Motoaki Matsuo ^{2,*}, Katsutoshi Aoki ², Tamio Ikeshoji ² and Shin-ichi Orimo ^{1,2}

¹ WPI-Advanced Institute for Materials Research (WPI-AIMR), Tohoku University, Sendai 980-8577, Japan; E-Mails: likk@imr.tohoku.ac.jp (G.L.); orimo@imr.tohoku.ac.jp (S.-i.O.)

² Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan; E-Mails: k-aoki@eqchem.s.u-tokyo.ac.jp (K.A.); ikeshoji@imr.tohoku.ac.jp (T.I.)

* Author to whom correspondence should be addressed; E-Mail: mmatsuo@imr.tohoku.ac.jp; Tel.: +81-22-215-2094; Fax: +81-22-215-2091.

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Abstract: The dehydriding process and hydrogen–deuterium exchange (H–D exchange) of $x\text{LiBH}_4 + (1 - x)\text{Mg}_2\text{FeD}_6$ ($x = 0.25, 0.75$) composites has been studied in detail. For the composition with $x = 0.25$, only one overlapping mass peak of all hydrogen and deuterium related species was observed in mass spectrometry. This implied the simultaneous dehydriding of LiBH₄ and Mg₂FeD₆, despite an almost 190 °C difference in the dehydriding temperatures of the respective discrete complex hydrides. *In situ* infrared spectroscopy measurements indicated that H–D exchange between [BH₄][−] and [FeD₆]^{4−} had occurred during ball-milling and was promoted upon heating. The extent of H–D exchange was estimated from the areas of the relevant mass signals: immediately prior to the dehydriding, more than two H atoms in [BH₄][−] was replaced by D atoms. For $x = 0.75$, H–D exchange also occurred and about one to two H atoms in [BH₄][−] was replaced by D atoms immediately before the dehydriding. In contrast to the situation for $x = 0.25$, firstly LiBH₄ and Mg₂FeD₆ dehydrided simultaneously with a special molar ratio = 1:1 at $x = 0.75$, and then the remaining LiBH₄ reacted with the Mg and Fe derived from the dehydriding of Mg₂FeD₆.

Keywords: complex hydride; borohydride; isotopic exchange; hydride composites; hydrogen storage

1. Introduction

The complex hydride LiBH_4 , consisting of Li^+ cations and $[\text{BH}_4]^-$ complex anions, has a high gravimetric hydrogen density of 18.4 mass% and a volumetric hydrogen density of $121 \text{ kg H}_2/\text{m}^3$ [1]. The main issues to be resolved for developing LiBH_4 as a hydrogen storage material are lowering of its high dehydrating temperature of $>420 \text{ }^\circ\text{C}$ and moderating the harsh rehydrating conditions of 35 MPa H_2 and high temperatures above $600 \text{ }^\circ\text{C}$ [2]. Many attempts have been made to improve the dehydrating properties of LiBH_4 by incorporating various additives, confining within nanoporous materials, or by preparing reactive composites with metal hydrides, and so on [3–12].

Recently, we reported that the dehydrating temperature of LiBH_4 is distinctly decreased upon combination with the complex hydride Mg_2FeH_6 composed of Mg^{2+} cations and $[\text{FeH}_6]^{4-}$ complex anions [13]. For example, the dehydrating temperature of LiBH_4 in $x\text{LiBH}_4 + (1 - x)\text{Mg}_2\text{FeH}_6$ composite with $x = 0.5$ is $350 \text{ }^\circ\text{C}$, which is $100 \text{ }^\circ\text{C}$ lower than that of pure LiBH_4 .

Besides this decreased dehydrating temperature of LiBH_4 , a unique dehydrating process was identified. In thermal gravimetry–mass spectrometry measurements (TG–MS) of $x\text{LiBH}_4 + (1 - x)\text{Mg}_2\text{FeH}_6$ ($0.1 \leq x \leq 0.83$) composites, when $x \leq 0.5$, only one MS peak was observed. When $x > 0.5$, more than two MS peaks were observed. Moreover, over the entire composition range, the dehydrating temperature of LiBH_4 decreased almost linearly with the proportion of Mg_2FeH_6 . These results suggested that when $x \leq 0.5$, Mg_2FeH_6 and LiBH_4 dehydrated simultaneously, despite the almost $190 \text{ }^\circ\text{C}$ difference in the dehydrating temperatures of the respective discrete complex hydrides. Conversely, when $x > 0.5$, firstly Mg_2FeH_6 dehydrated to Mg and Fe, and then LiBH_4 dehydrated by reacting with the Mg and/or Fe formed.

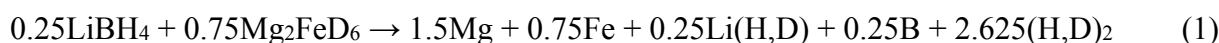
Several studies on LiBH_4 -rich compositions of $x\text{LiBH}_4 + (1 - x)\text{Mg}_2\text{FeH}_6$ ($x > 0.65$) composites have been published. The dehydrating process of $0.8\text{LiBH}_4 + 0.2\text{Mg}_2\text{FeH}_6$ was investigated by Langmi *et al.* [14] and Deng *et al.* [15]. Both of them reported that the dehydrating temperature of LiBH_4 was decreased by combining with Mg_2FeH_6 by the following two-step dehydrating process. Firstly, Mg_2FeH_6 dehydrated to Mg and Fe, and then LiBH_4 reacted with the Mg and Fe formed. The boron in LiBH_4 was stabilized by Mg and Fe to form MgB_2 and FeB . Ghaani *et al.* [16] reported the destabilized thermodynamics of $2/3\text{LiBH}_4 + 1/3\text{Mg}_2\text{FeH}_6$ composites when compared with that of the respective discrete complex hydrides. In these studies, neither the linear variation in the dehydrating temperature with changing composition nor the evidence of simultaneous dehydrating of LiBH_4 and Mg_2FeH_6 has apparently been noticed. Therefore, clarifying the unique dehydrating process is important to gain a deep knowledge of such composites of complex hydrides.

Because the hydrogen released from LiBH_4 and Mg_2FeH_6 cannot be differentiated in MS measurements, the evidence for simultaneous dehydrating when $x \leq 0.5$ was not conclusive and the assignment of the multiple MS peaks observed to the dehydrating of LiBH_4 and Mg_2FeH_6 when $x > 0.5$ was not unequivocal. In this study, instead of Mg_2FeH_6 we have used Mg_2FeD_6 to prepare $x\text{LiBH}_4 + (1 - x)\text{Mg}_2\text{FeD}_6$ composites with two compositions, $x = 0.25$ and 0.75 , in the expectation of distinguishing the dehydrating processes of the respective components by the MS signals of H_2 and D_2 . During the actual measurement, H–D exchange between LiBH_4 and Mg_2FeD_6 was observed, and the relationship between this H–D exchange and the simultaneous dehydrating processes is discussed herein.

2. Results and Discussion

2.1. Dehydrating Property of $0.25\text{LiBH}_4 + 0.75\text{Mg}_2\text{FeD}_6$

The TG–MS profile of $0.25\text{LiBH}_4 + 0.75\text{Mg}_2\text{FeD}_6$ is shown in Figure 1. The dehydrating profile was almost the same as that of $0.25\text{LiBH}_4 + 0.75\text{Mg}_2\text{FeH}_6$, in which only one MS peak was observed, implying that both LiBH_4 and Mg_2FeH_6 were dehydrated, as explained in the Introduction. Taking the purity of Mg_2FeD_6 into consideration, the experimental weight loss of 9.5 wt% was in reasonable agreement with the theoretical weight loss (10.5 wt%) for full dehydrating of LiBH_4 and Mg_2FeD_6 and the general reaction equation may be as follows:



Actually, XRD analysis of the sample collected after TG measurement (400 °C), as illustrated in Figure S1 in the Supplementary Material, showed that the dehydrated products contained Mg, Fe, Fe_2B , and LiH(D) .

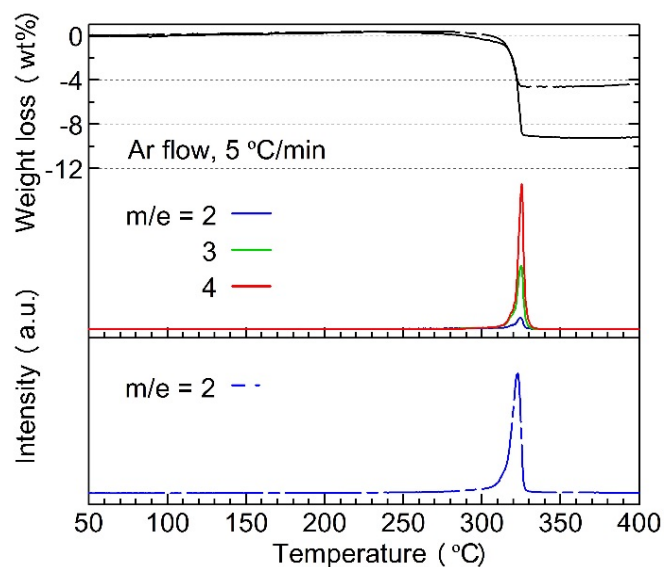


Figure 1. TG–MS profile of $0.25\text{LiBH}_4 + 0.75\text{Mg}_2\text{FeD}_6$ (solid line) and $0.25\text{LiBH}_4 + 0.75\text{Mg}_2\text{FeH}_6$ (dash line). $m/e = 2, 3,$ and 4 are signals of H_2 , HD , and D_2 , respectively.

In the MS measurement, peaks due to H_2 and D_2 were observed at the same temperature of 325 °C. This proved our expectation that LiBH_4 and Mg_2FeD_6 dehydrated simultaneously. Besides the H_2 and D_2 peaks, a peak due to HD was also observed, indicative of H–D exchange between LiBH_4 and Mg_2FeD_6 .

To prove this H–D exchange, *in situ* IR spectra were recorded, and the results are shown in Figure 2. As shown in the spectrum at 25 °C, H–D exchange has already occurred during ball-milling process. Referring to theoretical data, for isotopically pure LiBH_4 , a BH stretching peak at $\nu \approx 2350 \text{ cm}^{-1}$ and bending peaks at $\nu \approx 1300$ and 1100 cm^{-1} should be observed [17]; for isotopically pure Mg_2FeD_6 , an FeD stretching peak should appear at $\nu \approx 1260 \text{ cm}^{-1}$ [18]. The experimentally observed peak at $\nu = 2340 \text{ cm}^{-1}$ at 25 °C was assigned to the BH stretching mode, and that at $\nu = 1310 \text{ cm}^{-1}$ was assigned to the FeD stretching mode. The missing BH bending peak and the broadened peak of the BH

stretching mode indicate that the symmetry of $[\text{BH}_4]^-$ had been broken owing to the part replacement of H atoms by D atoms [19]. The peak at $\nu \approx 1840 \text{ cm}^{-1}$ was assigned as the FeH stretching mode in $\text{Mg}_2\text{FeD}_5\text{H}$ [18]. A very broad peak in the region $\nu = 1600\text{--}1900 \text{ cm}^{-1}$ was considered to be due to merged FeH and BD stretching peaks [18,20]. It was difficult to distinguish the FeH stretching peak at $\nu = 1794 \text{ cm}^{-1}$ and the BD stretching peak at $\nu = 1775 \text{ cm}^{-1}$ within the spectral resolution.

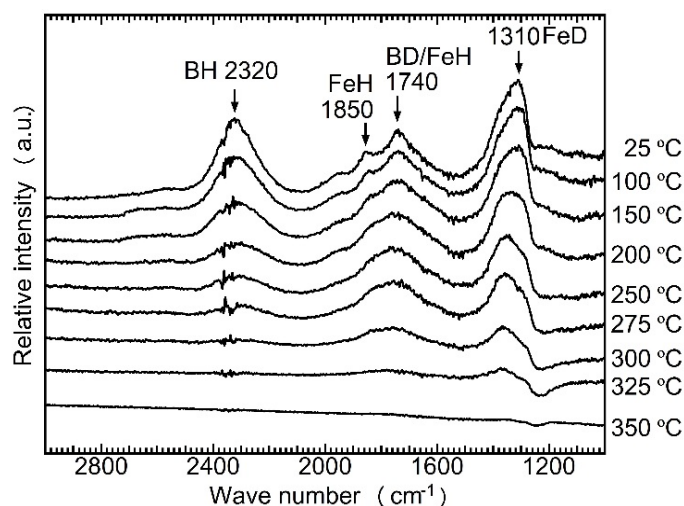


Figure 2. *In situ* IR spectra of ball-milled $0.25\text{LiBH}_4 + 0.75\text{Mg}_2\text{FeD}_6$. The heating rate was $5 \text{ }^\circ\text{C}/\text{min}$. The atmosphere in the sample holder was 0.1 MPa Ar without gas flow.

When we take a look at the IR spectra during the heating process, the area of the BD/FeH stretching peak did not change discernibly when compared to that of the steadily diminishing BH stretching peak, although the whole peak intensities weakened upon heating due to deterioration of the optical focusing by the thermally expanding sample. In addition, the FeD stretching peak at $\nu = 1310 \text{ cm}^{-1}$ was shifted to higher wavenumber and broadened significantly during the heating process. Referring to previous H–D exchange studies of LiBH_4 and $\text{Mg}(\text{BH}_4)_2$ [19–21], these results suggest that H–D exchange was promoted during the heating process. At $325 \text{ }^\circ\text{C}$, all of the peaks faded as a result of the dehydriding reaction, consistent with the TG–MS measurements shown in Figure 1. The peaks disappeared and the spectrum did not change further at $350 \text{ }^\circ\text{C}$, suggesting completion of the dehydriding reaction.

To further assess the extent of H–D exchange, we attempted a quantitative analysis based on the areas of MS signals that directly related to the amount of gas released. If it is supposed that H and D atoms are firstly released from H–D exchanged $\text{Mg}_2\text{FeH}_{y/3}\text{D}_{6-y/3}$ and $\text{LiBH}_{4-y}\text{D}_y$, and then mix and combine freely to form H_2 , HD, and D_2 gas molecules, then statistically the area ratio of the MS signals of H_2 , HD, and D_2 should be 25:12:1. In fact, the experimentally measured area ratio of these MS signals was 9:5:1, quite different from the statistical distribution. Thus, the processes of H–D exchange and dehydriding need to be interpreted differently. Here, we suppose that:

- H–D exchange occurred during ball-milling and the heating process but stopped as soon as the dehydriding started;
- H_2 , HD, or D_2 molecules were directly released from either $\text{Mg}_2\text{FeH}_{y/3}\text{D}_{6-y/3}$ or $\text{LiBH}_{4-y}\text{D}_y$; H or D atoms derived from the two different complex hydrides cannot combine to form gas molecules.

Based on this assumption, the extent of H–D exchange was estimated from the area ratio of MS signals. The result shows that the extent of H–D exchange, y , was around 2.5 immediately prior to the onset of dehydriding:



According to the estimation, less than one D atom in $[\text{FeD}_6]^{4-}$ was replaced by H atom before the dehydriding and more than two H atoms in $[\text{BH}_4]^-$ were replaced by D atoms. This result is in good agreement with the IR spectra: even though a shift to higher wavenumber was observed, the area of the FeD stretching peak did not decrease markedly because the replacement in $[\text{FeD}_6]^{4-}$ was slight. Conversely, the BH stretching peak at $\nu \approx 2320 \text{ cm}^{-1}$ was weakened and the BD stretching peak at $\nu \approx 1740 \text{ cm}^{-1}$ was significantly intensified since the symmetry of $[\text{BH}_4]^-$ was severely disrupted.

2.2. Dehydriding Property of $0.75\text{LiBH}_4 + 0.25\text{Mg}_2\text{FeD}_6$

In contrast to the situation for $0.25\text{LiBH}_4 + 0.75\text{Mg}_2\text{FeD}_6$, multiple MS peaks were observed for the dehydriding process of $0.75\text{LiBH}_4 + 0.25\text{Mg}_2\text{FeD}_6$. The TG–MS profile is shown in Figure 3, together with that of $0.75\text{LiBH}_4 + 0.25\text{Mg}_2\text{FeH}_6$ as a reference. The total weight loss was 9.0 wt%, which suggests full dehydriding of both LiBH_4 and Mg_2FeD_6 . The dehydrided products were confirmed as Mg, FeB_2 , and LiH(D) by XRD analysis, as shown in Figure S2 in the Supplementary Material.

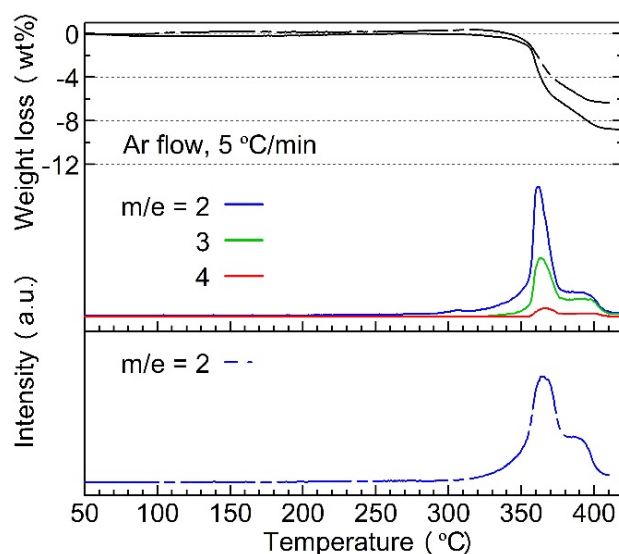


Figure 3. TG–MS profile of $0.75\text{LiBH}_4 + 0.25\text{Mg}_2\text{FeD}_6$ (solid line) and $0.75\text{LiBH}_4 + 0.25\text{Mg}_2\text{FeH}_6$ (dash line).

For the $0.25\text{LiBH}_4 + 0.75\text{Mg}_2\text{FeD}_6$ composition, *In situ* IR confirmed that H–D exchange between LiBH_4 and Mg_2FeD_6 occurred during ball-milling and was promoted during the heating process, as shown in Figure S3 in the Supplementary Material. With the same premises as in the case of the $0.25\text{LiBH}_4 + 0.75\text{Mg}_2\text{FeD}_6$ composition, the extent of H–D exchange immediately prior to dehydriding was estimated as $y \approx 4.5$ from the area ratio of the MS signals (sum of the two peaks) of H_2 , HD, and D_2 . This result shows that more than one H atom in $[\text{BH}_4]^-$ was replaced by D:



The slope of the TG profile changed and the MS curves separated at around 370 °C. The weight loss was 5.4 wt% before the inflection temperature followed by 3.6 wt% until completion of the dehydriding. Considering the estimated extent of HD exchange, the weight loss indicated that $0.25\text{LiBH}_4 - y/3\text{D}_{y/3} + 0.25\text{Mg}_2\text{FeH}_y\text{D}_{6-y}$ dehydrided before the inflection temperature and then the residue $0.5\text{LiBH}_4 - y/3\text{D}_{y/3}$ dehydrided. The area ratio of the first MS peak was 14:7:1, and this changed to 8:6:1 for the second MS peak. This result supports the interpretation that the first MS peak corresponds to the simultaneous dehydrogenation of isotopically exchanged LiBH_4 and Mg_2FeD_6 and the second MS peak corresponds to the dehydriding of $\text{LiBH}_4 - y/3\text{D}_{y/3}$. Therefore, it is evident that even though multiple MS peaks were observed, LiBH_4 and Mg_2FeD_6 were still dehydrided simultaneously. Following on from our previous report on the dehydriding properties of other compositions of $x\text{LiBH}_4 + (1-x)\text{Mg}_2\text{FeH}_6$ composites, when $x \leq 0.5$ (molar ratio of $\text{LiBH}_4:\text{Mg}_2\text{FeD}_6 = 1:1$), only one MS peak is observed [13]. It can be surmised that the molar ratio 1:1 is a special composition: LiBH_4 can dehydride simultaneously with $\text{Mg}_2\text{FeH}_6/\text{Mg}_2\text{FeD}_6$ up to this molar ratio; if there is more LiBH_4 in the composite, the residual LiBH_4 will subsequently dehydride by reacting with Mg and Fe derived from the dehydriding of $\text{Mg}_2\text{FeH}_6/\text{Mg}_2\text{FeD}_6$.

3. Experimental Section

Mg_2FeD_6 was synthesized by pressing a $2\text{Mg} + \text{Fe}$ mixture into pellets and subjecting it to heat treatment at 400 °C for 20 h under 3 MPa D_2 . The product yield was 91% according to TG measurement and the isotopic purity was almost 100% according to the MS measurement. Mg_2FeD_6 was then mixed with LiBH_4 (95%, Aldrich, St. Louis, MO, USA) and $x\text{LiBH}_4 + (1-x)\text{Mg}_2\text{FeD}_6$ composites with compositions $x = 0.25$ and 0.75 were prepared by planetary ball-milling (Fritsch P-5, Fritsch, Idar-Oberstein, Germany) for 5 h under argon.

The dehydriding properties were examined by TG–MS measurements (TG8120, Rigaku, Tokyo, Japan, Ar flow of 150 mL/min, heating rate of 5 °C/min). Powder X-ray diffraction (XRD) measurements were conducted on an X'Pert-Pro diffractometer ($\text{Cu-K}\alpha$ radiation, PANalytical, Almelo, The Netherlands). *In situ* infrared spectroscopy measurements were performed on a iZ10 infrared spectrometer (diffuse-reflectance mode, heating rate 5 °C/min, resolution 4 cm^{-1} , Thermo Nicolet, Thermo Fisher Scientific, Waltham, MA, USA). The samples were always handled in a glove box filled with purified argon.

4. Conclusions

We have investigated the dehydriding processes of $x\text{LiBH}_4 + (1-x)\text{Mg}_2\text{FeD}_6$ ($x = 0.25, 0.75$) composites in detail. For both of these compositions, H–D exchange between LiBH_4 and Mg_2FeD_6 occurred during ball-milling and was promoted during the heating process, as confirmed by *in situ* infrared spectroscopy and mass spectrometry measurements. The extent of H–D exchange immediately prior to the dehydriding reaction was estimated from the area ratio of MS signals. For the composition with $x = 0.25$, more than two H atoms in $[\text{BH}_4]^-$ were replaced by D atoms and for that with $x = 0.75$, one to two H atoms in $[\text{BH}_4]^-$ were replaced by D atoms.

For the composition with $x = 0.25$, only one MS peak was observed, which resulted from the simultaneous dehydriding of isotopically exchanged LiBH_4 and Mg_2FeD_6 . For the composition with

$x = 0.75$, two MS peaks were observed, which resulted from partial simultaneous dehydriding of isotopically exchanged LiBH_4 and Mg_2FeD_6 , and subsequent dehydriding of the residue isotopically exchanged LiBH_4 . A special molar ratio of 1:1 has been identified as the limit for simultaneous dehydriding of LiBH_4 with $\text{Mg}_2\text{FeH}_6/\text{Mg}_2\text{FeD}_6$. Experiments aimed at delineating the detailed thermodynamics of the dehydriding process based on pressure–composition isotherm analysis is underway and the kinetics of the H–D exchange is being investigated by *in situ* Raman spectroscopy.

Supplementary Materials

Supplementary materials can be accessed at: <http://www.mdpi.com/1996-1073/8/6/5459/s1>.

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Author Contributions

All of the authors contributed to this work. Guanqiao Li and Motoaki Matsuo designed and conducted the experiments, and wrote the paper. Katsutoshi Aoki, Tamio Ikeshoji and Shin-ichi Orimo helped analyze the data and revise the paper.

Conflicts of Interest

The authors declare no conflict of interest.

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