Dehydriding Property of LiBH$_4$ Combined with Mg$_2$FeH$_6$

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A dehydriding property of xLiBH$_4$ + (1 – x)Mg$_2$FeH$_6$ (x = 0.1–0.83) was investigated. The dehydriding reactions of pure LiBH$_4$ and Mg$_2$FeH$_6$ start at approximately 650 and 450 K, and 12.5 and 4.3 mass% hydrogen are released, respectively. The property drastically changes by combining LiBH$_4$ and Mg$_2$FeH$_6$. Within the composition range 0.1 ≤ x ≤ 0.5, LiBH$_4$ and Mg$_2$FeH$_6$ simultaneously release hydrogen. The reaction temperatures and quantities of released hydrogen alter with x. The lattice parameter of the Mg$_2$FeH$_6$ phase measured by in-situ high-resolution synchrotron diffraction measurements suggest the possibility of forming Li$_x$Mg$_2$-2x(FeH$_3$)$_x$C$_{0.5}$ with both double-cation and double-anion. [doi:10.2320/matertrans.M2013145]

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1. Introduction

A complex hydride LiBH$_4$, consisting of Li$^+$ cations and [BH$_4$]$^-$ complex anions, has high gravimetric and volumetric hydrogen densities (13.8 mass% and 121 kg H$_2$/m$^3$, respectively). The dehydriding temperature of above 673 K is higher than the required temperature for solid state hydrogen storage materials, therefore many approaches have been made to improve its dehydriding/rehydriding properties: novel additives, confinement into nanoporous materials, and reactive composite with metal hydrides. In addition, we have found that the dehydriding temperature of LiBH$_4$ can be lowered by achieving the double-cation borohydrides such as LiCa(BH$_4$)$_3$ and ZrLi(BH$_4$)$_5$ based on a linear relationship between the calculated formation enthalpy of a series of metal borohydride $M$(BH$_4$)$_n$ (n: valence of metal M) and the Pauling electronegativity of $M$. In this study, we report the unique dehydriding property of xLiBH$_4$ + (1 – x)Mg$_2$FeH$_6$ examined by thermogravimetry/differential thermal analysis/mass spectroscopy (TG-DTA-MS). The results revealed that LiBH$_4$ and Mg$_2$FeH$_6$ simultaneously release hydrogen within the composition range 0.1 ≤ x ≤ 0.5 although their individual dehydriding temperatures differ by more than 200 K. The possibility of forming Li$_x$Mg$_2$-2x(FeH$_3$)$_x$C$_{0.5}$ with both double-cation and double-anion is also briefly discussed.

2. Experimental Procedure

Mg$_2$FeH$_6$ was synthesized by mechanically milling MgH$_2$ (98%, Alfa Aesar) and Fe (99.99%, Mitsuwa) powders at a molar ratio of 2:1 for 2 h under argon and subsequent heat treatment at 673 K for 20 h under 3 MPa hydrogen. Mg$_2$FeH$_6$ was then mixed with LiBH$_4$ (95%, Aldrich) at prescribed molar ratios by mechanical milling for 5 h under argon. The dehydriding property was examined by TG-DTA-MS (Rigaku TG8120, He flow of 150 ml/min, heating rate of 5 K/min). Powder X-ray diffraction (XRD) measurements were conducted both ex-situ by a conventional X-ray diffractometer (Lab-XRD, PANalytical X’Pert-Pro, CuK$\alpha$ radiation) and in-situ by a high-resolution synchrotron radiation (SR-XRD) at the Swiss-Norwegian Beam Line (BM01B) at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. The samples were always handled in a glove box filled with purified argon or helium.

3. Results and Discussion

The TG-MS profiles of xLiBH$_4$ + (1 – x)Mg$_2$FeH$_6$ (x = 0.1–0.83) are shown in Fig. 1(a), together with those of pure Mg$_2$FeH$_6$ and LiBH$_4$. First, we note that the dehydriding reactions of pure Mg$_2$FeH$_6$ and LiBH$_4$ occur at distinctly different temperatures: their MS peaks, originated from the following reactions, appear at approximately 500 and over 730 K, respectively.

\[
\text{Mg}_2\text{FeH}_6 \rightarrow 2\text{Mg} + \text{Fe} + 3\text{H}_2
\]

(1)

\[
\text{LiBH}_4 \rightarrow \text{LiH} + \text{B} + 3/2\text{H}_2
\]

(2)

The properties change dramatically when LiBH$_4$ and Mg$_2$FeH$_6$ are combined. When x ≤ 0.5, a single peak is observed in the MS profiles. At x = 0.1, upon heating, the hydrogen is released in the temperature range 530–580 K. As x increases to 0.5, the dehydriding temperature increases while maintaining a single MS peak profile. With further increase in x (0.75 and 0.83), multistep dehydriding reactions occur at higher temperatures, as reported in former literatures. As shown in Fig. 1(b), we can see such a clear relationship between the MS peak temperature and x.

The quantity of released hydrogen as a function of x (obtained from the TG data) is also shown in Fig. 1(b). Obviously, the quantity increases with increasing x, which is in good agreement with the calculated values (Calc. 2) based on the following reaction:

\[
x\text{LiBH}_4 + (1 - x)\text{Mg}_2\text{FeH}_6
\rightarrow x(\text{LiH} + \text{B}) + (1 - x)(2\text{Mg} + \text{Fe}) + (3 - 3/2x)\text{H}_2
\]
These results indicate that not only Mg$_2$FeH$_6$ but also LiBH$_4$ releases hydrogen from xLiBH$_4$ + (1 - x)Mg$_2$FeH$_6$ as a function of x obtained from the experimental TG data (closed circles). The dehydriding temperatures for x = 0.75 and 0.83 are defined as a temperature of the first peak. Calc. 1 (open triangles) and Calc. 2 (open squares) are the calculated values based on the hydrogen release from Mg$_2$FeH$_6$ alone and from both Mg$_2$FeH$_6$ and LiBH$_4$, respectively.

To investigate the single-step dehydriding process of xLiBH$_4$ + (1 - x)Mg$_2$FeH$_6$ when x ≤ 0.5, the samples were heated to a temperature higher than that of their MS peaks and subsequently cooled to room temperature. The representative Lab-XRD profiles for LiBH$_4$ + Mg$_2$FeH$_6$ (x = 0.5) are shown in Fig. 2. When the sample is heated to 613 K immediately following the start of hydrogen release, Mg$_2$FeH$_6$ reduces while the quantity of Fe increases. The diffraction peaks of Mg and MgB$_2$ appear along with a broad peak at around 24° (possibly indicating some amorphous phase). Following complete hydrogen release at 673 K, Mg, Fe, MgB$_2$, and the amorphous phase are confirmed in the absence of Mg$_2$FeH$_6$. These results also suggest the simultaneous dehydriding of LiBH$_4$ and Mg$_2$FeH$_6$ from xLiBH$_4$ + (1 - x)Mg$_2$FeH$_6$ (x ≤ 0.5). The diffraction peaks of LiH are not observed in Fig. 2 because of low scattering cross sections of Li and H atoms.

At this point, it seems valid to discuss the possible causes of the unique dehydriding property of xLiBH$_4$ + (1 - x)Mg$_2$FeH$_6$: reactive composite reaction and formation of Li$_x$Mg$_{2(1-x)}$(BH$_4$)$_x$(FeH$_6$)$_{1-x}$. From the formation of MgB$_2$ after the dehydriding reaction (Fig. 2), one may consider that MgH$_2$ or Mg generated after hydrogen release from Mg$_2$FeH$_6$ may have destabilized LiBH$_4$, as reported for the reactive composite reaction in 2LiBH$_4$ + MgH$_2$ as follows:

\[
\begin{align*}
2\text{LiBH}_4 + \text{MgH}_2 & \rightarrow 2\text{LiBH}_4 + \text{Mg} + \text{H}_2 \\
\rightarrow & \text{MgB}_2 + 2\text{LiH} + 4\text{H}_2 \\
\text{xLiBH}_4 + (1 - x)\text{Mg}_2\text{FeH}_6 & \rightarrow x\text{LiBH}_4 + (1 - x)(2\text{Mg} + \text{Fe} + 3\text{H}_2) \\
& \rightarrow x\text{LiH} + x/2\text{MgB}_2 + (2 - 5x/2)\text{Mg} \\
& + (1 - x)\text{Fe} + (3 - 3x/2)\text{H}_2 \\
\end{align*}
\]

In that case, however, two peaks should appear in the MS profiles because the dehydriding reactions of Mg$_2$FeH$_6$ and LiBH$_4$ occur individually at different temperatures. In fact, the MS profile of LiBH$_4$ + 2MgH$_2$ also shown in Fig. 1(a), which was examined to compared with that of LiBH$_4$ + Mg$_2$FeH$_6$ (x = 0.5), exhibits two desorption peaks at approximately 580 and 660 K, assigned to the dehydriding from MgH$_2$ and LiBH$_4$, respectively. LiBH$_4$ in LiBH$_4$ + 2MgH$_2$ releases hydrogen at higher temperature than that in LiBH$_4$ + Mg$_2$FeH$_6$, indicating that the reactive composite reaction is not feasible.

The possibility of forming Li$_x$Mg$_{2(1-x)}$(BH$_4$)$_x$(FeH$_6$)$_{1-x}$ is also considered. As shown in Fig. 2, the diffraction peaks of Mg$_2$FeH$_6$ alone are observed without those of LiBH$_4$. The
temperature change in the lattice parameter $a$ for Mg$_2$FeH$_6$ in LiBH$_4$ + Mg$_2$FeH$_6$ ($x = 0.5$), obtained from the in-situ SR-XRD data (not shown), is plotted in Fig. 3. Clearly, the lattice expansion of Mg$_2$FeH$_6$ in LiBH$_4$ + Mg$_2$FeH$_6$ differs from pure Mg$_2$FeH$_6$; the lattice parameter is smaller in LiBH$_4$ + Mg$_2$FeH$_6$ than in pure Mg$_2$FeH$_6$ across the whole temperature range, and the slopes seem different from each other presumably due to the different thermal expansion coefficients. These results imply the possible formation of $\text{Li}_x\text{Mg}_{2-2x}(\text{BH}_4)_x(\text{FeH}_6)_{1-x}$ after mechanical milling via the following reaction:

$$x\text{LiBH}_4 + (1-x)\text{Mg}_2\text{FeH}_6 \rightarrow \text{Li}_x\text{Mg}_{2-2x}(\text{BH}_4)_x(\text{FeH}_6)_{1-x} \quad (6)$$

Such a complex hydride with both double-cation (Li$^+$ and Mg$^{2+}$) and double-anion ([BH$_4$]$^-$ and [FeH$_6$]$^{8-}$) has not been reported to date although combinations of either cation or anion have been known to exist as LiM(BH$_4$)$_n$\textsuperscript{15,16} LiBH$_4$–LiNH$_2$,\textsuperscript{21-24} NaBH$_4$–NaNH$_2$,\textsuperscript{25-27} and Mg$_2$FeH$_6$–MgCoH$_5$ systems.\textsuperscript{28,29} It needs further consideration to prove the validity of reaction (6). Detailed structural analysis will be conducted both experimentally (by neutron diffraction) and theoretically (by first-principles calculations).

4. Conclusions

In summary, we have investigated the dehydriding property of $\text{xLiBH}_4 + (1-x)\text{Mg}_2\text{FeH}_6$ ($x = 0.1$–0.83) by TG-DTA-MS. The dehydriding reactions of pure LiBH$_4$ and Mg$_2$FeH$_6$ start at approximately 650 and 450 K, and 12.5 and 4.3 mass% hydrogen are released, respectively. The property drastically changes by combining LiBH$_4$ and Mg$_2$FeH$_6$. Within the composition range $0.1 \leq x \leq 0.5$, LiBH$_4$ and Mg$_2$FeH$_6$ simultaneously release hydrogen. The reaction temperatures and quantities of released hydrogen alter between those of Mg$_2$FeH$_6$ and LiBH$_4$ with $x$. The lattice parameter of the Mg$_2$FeH$_6$ phase measured by the in-situ SR-XRD measurements suggests that Li$_x$Mg$_{2-2x}$(BH$_4$)$_x$(FeH$_6$)$_{1-x}$ with both double-cation and double-anion may be formed during the mechanical milling of LiBH$_4$ and Mg$_2$FeH$_6$, with consequent enhancement of hydrogen release from LiBH$_4$.

These experimental findings provide a fundamental basis for developing complex hydrides for advanced hydrogen storage.

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REFERENCES

2) S. Orimo, Y. Nakamori, J. R. Eliseo, A. Züttel and C. M. Jensen: Chem. Rev. 107 (2007) 4111.