Materials designing of metal borohydrides: Viewpoints from thermodynamical stabilities

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Abstract

Double-cation borohydrides $MLi_{m-n}(BH_4)_m$ (M = Zn, $n = 2$; M = Al, $n = 3$; M = Zr, $n = 4$; $n \leq m$) were expected to be synthesized and their thermodynamical stabilities were also examined experimentally. The samples with the compositions of $ZnLi(BH_4)_3$ and $AlLi(BH_4)_4$ disproportionate into $Zn(BH_4)_2$- (or $Al(BH_4)_3$-) and $LiBH_4$-based phases upon heating, respectively. However, no disproportionation reaction is observed in $ZrLi_{m-4}(BH_4)_m$ ($m = 5$ and 6). It should be emphasized that hydrogen desorption temperature T_d of $ZrLi_{m-4}(BH_4)_m$ continuously increases from 440 to 650 K as the composition m increases from 4 to 6, and approaches to 740 K (T_d of $LiBH_4$). The experimental results indicate that the combination of appropriate cations is an effective method to adjust the thermodynamical stabilities of metal borohydrides, similar to the conventional "alloying" method for hydrogen storage alloys.
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1. Introduction

Metal borohydrides ($M(BH_4)_n$), such as $LiBH_4$ and $Mg(BH_4)_2$ [1–19] have been attracting great interest as one of the potential candidates of advanced hydrogen storage materials, because of their high gravimetric hydrogen densities.

Recently, we have systematically investigated the thermodynamical stabilities of $M(BH_4)_n$ (M = Li, Na, K, Cu, Mg, Zn, Sc, Zr and Hf; $n = 1$–4) with a single cation by both first-principles studies and thermal desorption measurements [16]. The first-principles calculations indicated that charge transfer from M^{n+} to $[BH_4]^-$ is a key factor for the stability of $M(BH_4)_n$ [5,8,16] and also there exists a linear relationship between the calculated formation enthalpy ΔH of $M(BH_4)_n$ and the Pauling electronegativity χ_P of M [16]. Experimentally, the thermal desorption temperature T_d of $M(BH_4)_n$ examined by gas chromatography was also closely correlated with χ_P [16,17], as shown in Fig. 1. That is, T_d (closed circles) decreases with increasing the value

of χ_P. Therefore, the value of χ_P of M is concluded to be an important indicator for estimating the thermodynamical stability of $M(BH_4)_n$, i.e. T_d of $M(BH_4)_n$ might be roughly adjusted by selecting M with the appropriate value of χ_P.

However, in the case of $M(BH_4)_n$ with a single cation M^{n+}, precise adjustment of T_d might be difficult due to the inherent and discrete value of χ_P for each metal. Thus, development of $MM'(BH_4)_n$ with double-cation (or multi-cation) is expected to be quite useful to precisely adjust T_d for hydrogen storage applications [20]. This proposition is similar to the conventional "alloying" method for hydrogen storage alloys [21,22].

In the present study, we select some metals with different χ_P, whose basic information is summarized in Table 1. Among them, borohydrides composed of metals with larger χ_P, such as Zn ($\chi_P = 1.6$), Al ($\chi_P = 1.5$) and Zr ($\chi_P = 1.4$), are reported to have lower T_d, i.e. 398 [17,18], 334 [19] and 440 K [17], respectively. However, $Zn(BH_4)_2$ and $Al(BH_4)_3$ are so unstable that diborane as an impurity gas is released along with hydrogen desorption on heating [18,19]; while $Zr(BH_4)_4$ evaporates easily due to its low melting point. On the other hand, $LiBH_4$ with the smaller χ_P of Li is so stable that its T_d is approximately as high as 740 K. Therefore, their thermal stabilities are expected to be

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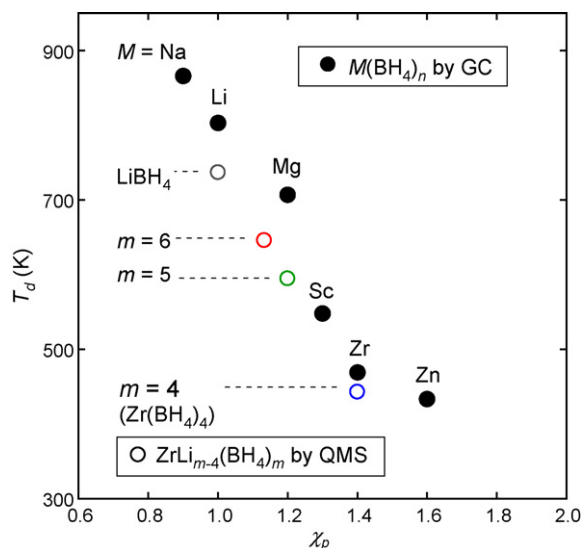 *E-mail address:* orimo@imr.tohoku.ac.jp (S. Orimo).

Fig. 1. Thermal desorption temperature T_d (main peak) as a function of the Pauling electronegativity χ_P. Closed and open circles indicate the series of single-cation borohydrides $M(BH_4)_n$ (M = Li, Na, Mg, Sc, Zr, Zn; $n = 1$–4) and double-cation ones $ZrLi_{m-4}(BH_4)_m$ ($m = 4$–6), examined by gas chromatography and quadrupole mass spectroscopy, respectively. There is a difference between T_d determined by gas chromatography and by quadrupole mass spectroscopy, owing to a longer distance between the detector and sample and also to a lower gas flow rate in gas chromatography.

adjusted for hydrogen storage application by the combination of two cations, i.e. the double-cation borohydrides $MLi_{m-n}(BH_4)_m$ (M = Zn, $n = 2$; M = Al, $n = 3$; M = Zr, $n = 4$; $n \leq m$) [23], which are expected to be synthesized according to the following reaction:

$$MCl_n + mLiBH_4 \rightarrow MLi_{m-n}(BH_4)_m + nLiCl. \qquad (1)$$
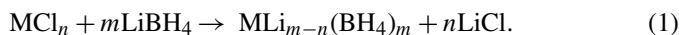
The enthalpy changes of this reaction are calculated by using the reported values of the formation enthalpies for MCl_n [24] and $LiBH_4$ [5] and the values for $MLi_{m-n}(BH_4)_m$ formed from M, Li, B and H_2, can be theoretically predicted by the equation; $248.7\chi_P - 390.8$ (χ_P is the averaged values of Pauling electronegativity described later) [16]. Any of the samples have their own negative values of $\Delta H_{milling}$ (not shown) depending on m, indicating that the reactions can occur "exothermically" in the wide composition ranges of m [20].

The purpose is to clarify whether the method to precisely adjust the hydrogen desorption temperature of metal borohydrides by the combination of two metals with different electronegativities is feasible or not. This study provides the

Table 1
Basic information of M and their borohydrides $M(BH_4)_n$

	M			
	Zn	Al	Zr	Li
χ_P	1.6	1.5	1.4	1.0
T_d (K) of $M(BH_4)_n$	398[a] [17,18]	334[a] [19]	440[b] [17]	740

[a] Diborane as a impurity gas is released along with hydrogen desorption on heating.

[b] $Zr(BH_4)_4$ has low melting point, i.e. 301.7 K.

fundamental information on the development of new metal borohydrides with appropriate thermal desorption temperature for hydrogen storage applications.

2. Experimental

Anhydrous MCl_n (M = Zn, Al and Zr) with 99.9–99.999% purities and $LiBH_4$ with 95% purity, were purchased from Aldrich Co. Ltd. The mixture of MCl_n and $mLiBH_4$ was premixed manually using an agate mortar and pestle and then mechanically milled by planetary ball milling (Fritsch P-7) in 0.1 MPa Ar for 5 h to synthesize $MLi_{m-n}(BH_4)_m$ (M = Zn, $n = 2$; M = Al, $n = 3$; M = Zr, $n = 4$; $n \leq m$) according to equation (1). The milling process was paused every 15 min to avoid an increase in temperature of the sample. The samples, thus prepared were subjected to powder X-ray diffraction measurement (Cu Kα radiation), Raman spectroscopy (532 nm-laser with back scattering geometry) and thermal desorption spectroscopy detected by quadrupole mass spectroscopy (He flow of 150 ml/min and heating rate of 5 K/min). All of the samples were always handled in a glove box filled with purified Ar/He (dew point below 183 K) gas to avoid (hydro-)oxidation.

3. Results and discussion

3.1. Syntheses of $MLi_{m-n}(BH_4)_m$

Fig. 2 shows the powder X-ray diffraction profiles of the samples after mechanical milling of (a) $ZnCl_2 + mLiBH_4$ ($m = 2$ and 3), (b) $AlCl_3 + mLiBH_4$ ($m = 3$ and 4) and (c) $ZrCl_4 + mLiBH_4$ ($m = 4$–6). The profiles of starting materials $ZnCl_2$, $AlCl_3$, $ZrCl_4$
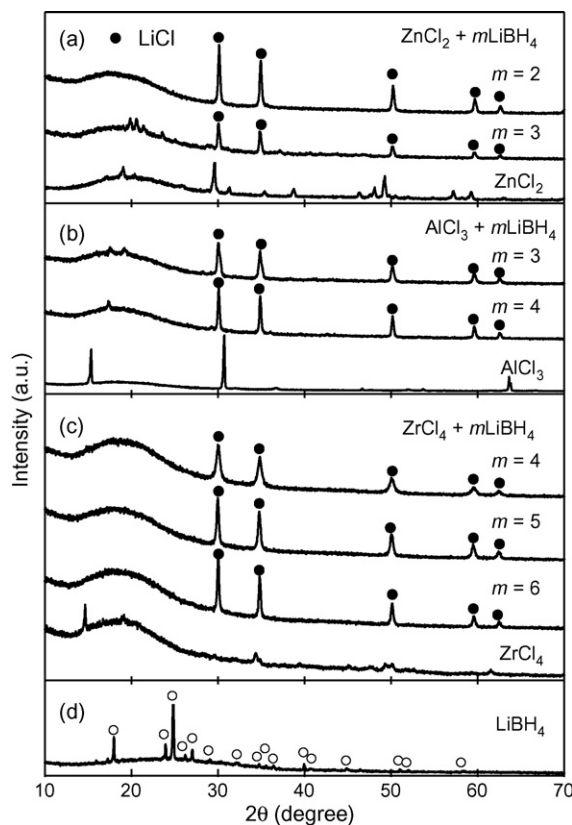

Fig. 2. Powder X-ray diffraction profiles of the samples after mechanical milling of (a) $ZnCl_2 + mLiBH_4$ ($m = 2$, 3), (b) $AlCl_3 + mLiBH_4$ ($m = 3$, 4), (c) $ZrCl_4 + mLiBH_4$ ($m = 4$–6) and (d) the purchased $LiBH_4$. The profiles of starting materials $ZnCl_2$, $AlCl_3$ and $ZrCl_4$ are also shown for references.

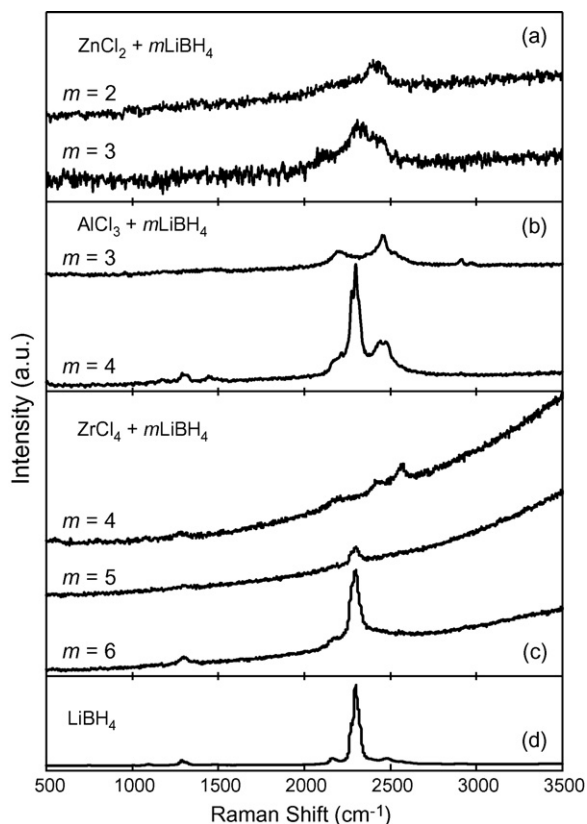Fig. 3. Raman spectra of the samples after mechanical milling of (a) $ZnCl_2 + mLiBH_4$ ($m = 2, 3$), (b) $AlCl_3 + mLiBH_4$ ($m = 3, 4$), (c) $ZrCl_4 + mLiBH_4$ ($m = 4$–6) and (d) the purchased $LiBH_4$.

and $LiBH_4$ are also shown for references. The broad diffraction peaks at around 20° in all the profiles, result from the diffraction of tape covered samples to avoid exposing to air. LiCl, one of the products of Eq. (1), is identified in all the diffraction profiles for the samples after mechanical milling. Furthermore, no diffraction peaks of the starting materials of MCl_n and $LiBH_4$ are observed. Thus, the X-ray diffraction results suggest the progression of reaction of Eq. (1), i.e. the possible formation of $MLi_{m-n}(BH_4)_m$ and LiCl.

There is no traces of $MLi_{m-n}(BH_4)_m$ in the X-ray diffraction profiles, which is due to the absence of any long range ordering in the structure, similar to other $M(BH_4)_n$ synthesized by mechanical milling [16,17]. Therefore, Raman spectra were examined to obtain information on the B−H bonding to confirm the existence of $MLi_{m-n}(BH_4)_m$ in the samples prepared by mechanical milling. The Raman spectra of the samples after mechanical milling are shown in Fig. 3. The spectrum of $LiBH_4$ is also shown as a reference, where the B−H stretching (ν_1) and bending (ν_1 and also ν'_2) modes in the $[BH_4]^-$ complex anion are observed at around 2300 and 1300 cm^{-1}, respectively. Since $ZnLi_{m-2}(BH_4)_m$ ($m = 2$ and 3) is easily scorched by laser irradiation for Raman spectroscopy, only a small and weak peak at about 2400 or 2300 cm^{-1} is observed, respectively, which are expected to correspond to the stretching modes of the B−H bonding. There are two or three stretching modes at around 2200–2580 cm^{-1} in the Raman spectra of the synthesized

$Al(BH_4)_3$ and $Zr(BH_4)_4$, as shown in Fig. 3(b and c), respectively [25,26]. On the other hand, the similar vibration modes in the $[BH_4]^-$ complex anion to that of $LiBH_4$ are observed in the Raman spectra of the samples with double-cation, i.e. $ZnLi(BH_4)_3$, $AlLi(BH_4)_4$, $ZrLi(BH_4)_5$ and $ZrLi_2(BH_4)_6$. The varieties in the Raman spectra depending on the sample compositions, which are expected to be due to the change of the condition surrounding the $[BH_4]^-$ anion, indirectly indicate the progression of Eq. (1).

3.2. Thermal desorption properties of $MLi_{m-n}(BH_4)_m$

Fig. 4 shows the hydrogen desorption profiles of the mixture of $MCl_n + mLiBH_4$ after mechanical milling, detected by quadrupole mass spectroscopy. Though the samples synthesized by mechanical milling is mixtures of $MLi_{m-n}(BH_4)_m$ and LiCl, the thermal desorption profiles originate only from $MLi_{m-n}(BH_4)_m$, because LiCl decomposes at the temperature higher than 878 K. The result of $LiBH_4$ is also shown as a reference. Both $Zn(BH_4)_2$ and $Al(BH_4)_3$ have lower T_d as shown in Fig. 4(a and b), i.e. 393 and 334 K, respectively; but impurity gases of diborane, were released along with the desorption of hydrogen (not shown) [18,19]. On the other hand, the thermal desorption profiles of the samples with the compositions of $ZnLi(BH_4)_3$ and $AlLi(BH_4)_4$ indicate that both
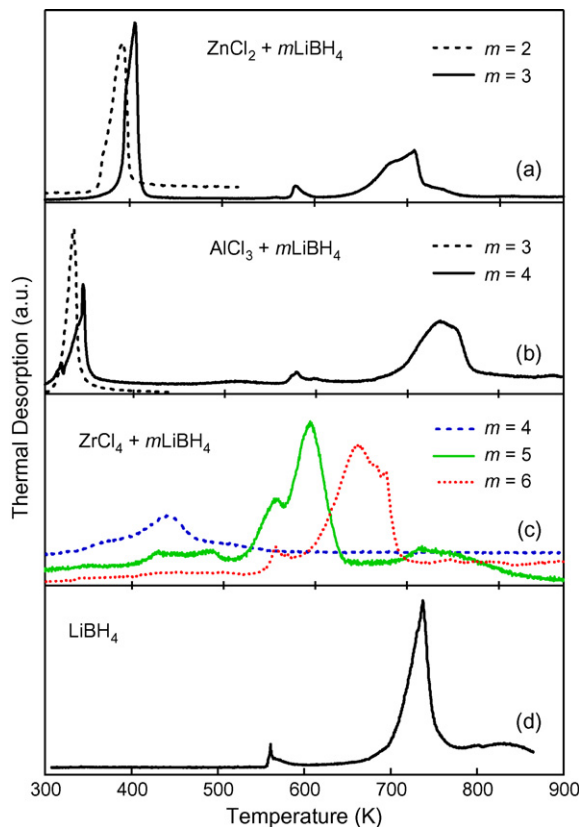

Fig. 4. Thermal desorption profiles of the samples after mechanical milling of (a) $ZnCl_2 + mLiBH_4$ ($m = 2, 3$), (b) $AlCl_3 + mLiBH_4$ ($m = 3, 4$), (c) $ZrCl_4 + mLiBH_4$ ($m = 4$–6) and (d) the purchased $LiBH_4$ detected by quadrupole mass spectroscopy. T_d of $ZrCl_4 + mLiBH_4$ ($m = 4$–6) after mechanical milling is summarized in Fig. 1 with open circles.

of them disproportionate into $Zn(BH_4)_2$- (or $Al(BH_4)_3$-) and $LiBH_4$-based phases during heating process, respectively. The peaks below 400 K for $ZnLi_{m-4}(BH_4)_m$ and $AlLi_{m-4}(BH_4)_m$ shift slightly to higher temperature side about 10 K with the increasing value of m, probably originating from the partial combination effect of Zn or Al with Li, respectively.

However, it is worth emphasizing that hydrogen desorption profiles of $ZrLi(BH_4)_5$ and $ZrLi_2(BH_4)_6$ do not show obvious disproportionation reaction into $Zr(BH_4)_4$- and $LiBH_4$-based phases upon heating, although some additional reactions with small peaks are detected. Only hydrogen was detected in the thermal desorption measurement of $ZrLi_{m-4}(BH_4)_m$. Moreover, T_d for $ZrLi_{m-4}(BH_4)_m$, i.e. 440 K ($m = 4$), 595 K ($m = 5$) and 650 K ($m = 6$), shifts gradually to higher temperature with increasing composition ratio of Li/Zr and continuously approaches to 740 K which is T_d for $LiBH_4$.

The relationship between T_d and the averaged value of χ_P of $ZrLi_{m-4}$ is expressed in Fig. 1. Here, the averaged value of χ_P for $ZrLi_{m-4}$ depending on m is simply calculated as follows:

$$\chi_P = \frac{1.4 + 1.0(m-4)}{1 + (m-4)}. \qquad (2)$$

Apparently, T_d of $ZrLi_{m-4}(BH_4)_m$, namely $MM'(BH_4)_n$ with double-cation, is closely related to the averaged χ_P as what have been observed in the $M(BH_4)_n$ with a single cation [16]. This experimental feature highly suggests that the hydrogen desorption temperature of metal borohydrides can be precisely adjusted by the appropriate combination of cations. The criteria for the selection of appropriate cations which can effectively and precisely adjust hydrogen desorption temperature are expected to be clarified in near future.

Some additional reactions with small peaks in Fig. 4 are possibly resulted from small amounts of residual $LiBH_4$ as the starting material and Zr-rich borohydrides in the milled samples. The origin of these peaks cannot be well clarified due to the absence of diffraction peaks of other phases except for LiCl, as shown in Fig. 2. New synthesis processes of well-crystallized $ZrLi_{n-4}(BH_4)_n$ are now being developed, which seems to be indispensable for the further study.

4. Summary

A series of double-cation borohydrides $MLi_{m-n}(BH_4)_m$ (M = Zn, $n = 2$; M = Al, $n = 3$; M = Zr, $n = 4$; $n \leq m$) were expected to be synthesized by mechanical milling of MCl_n and $mLiBH_4$. Their thermodynamical stabilities were examined by quadrupole mass spectroscopy. Thermal desorption measurement results indicate that the samples with the compositions of $ZnLi(BH_4)_3$ and $AlLi(BH_4)_4$ disproportionate into $Zn(BH_4)_2$- (or $Al(BH_4)_3$-) and $LiBH_4$-based phases upon heating, respectively. However, no disproportionation reaction into $Zr(BH_4)_4$- and $LiBH_4$-based phases is confirmed in the case of $ZrLi_{m-4}(BH_4)_m$. The hydrogen desorption temperature T_d of $ZrLi_{m-4}(BH_4)_m$ increases from 440 K ($m = 4$) to 650 K ($m = 6$) and continuously approaches to 740 K (T_d of $LiBH_4$). That is, T_d of $ZrLi_{m-4}(BH_4)_m$, namely $MM'(BH_4)_n$ with double-cation is closely related to the averaged χ_P as what have been observed

in the $M(BH_4)_n$ with a single cation. Consequently, the above-mentioned results indicate that the appropriate combination of cations is an effective method to adjust the thermodynamical stability of metal borohydrides, similar to the conventional "alloying" method for hydrogen storage alloys.

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