

Synthesis of novel complex hydrides with mixed non-metal-based and metal-based complex anions

A dehydrating reaction of LiBH_4 is drastically promoted by combining with Mg_2FeH_6 . The dehydrating reaction of pure LiBH_4 starts at approximately 650 K, which decreases with increasing the amount of Mg_2FeH_6 added. The lattice parameter of Mg_2FeH_6 measured by *in-situ* high-resolution synchrotron diffraction measurements suggests the possibility of forming a solid solution $\text{Li}_{1-x}\text{Mg}_{2x}(\text{BH}_4)_{1-x}(\text{FeH}_6)_x$ with mixed non-metal-based $[\text{BH}_4]^-$ and metal-based $[\text{FeH}_4]^{4-}$ complex anions.

A complex hydride LiBH_4 , consisting of Li^+ cations and $[\text{BH}_4]^-$ complex anions, is one of the promising materials for hydrogen storage due to its high hydrogen densities. The dehydrating temperature of above 673 K, however, is higher than the required temperature for solid state hydrogen storage materials, therefore many approaches have been made to improve the property [1].

We have found that the dehydrating temperature of LiBH_4 can be lowered by combining with another complex hydride Mg_2FeH_6 composed of Mg^{2+} and $[\text{FeH}_4]^{4-}$ complex anions [2]. Fig. 1 shows the thermogravimetry/mass spectroscopy (TG-MS) profiles of $(1-x)\text{LiBH}_4+x\text{Mg}_2\text{FeH}_6$ together with that of pure LiBH_4 . The dehydrating reaction of pure LiBH_4 starts at approximately 650 K by the following reaction: $\text{LiBH}_4 \rightarrow \text{LiH} + \text{B} + 3/2\text{H}_2$. The dehydrating temperature obviously decreases with increasing the amount of Mg_2FeH_6 added. At $x = 0.9$, the hydrogen is released in the temperature range 530–580 K, which is more than 100 K lower as compared to pure LiBH_4 .

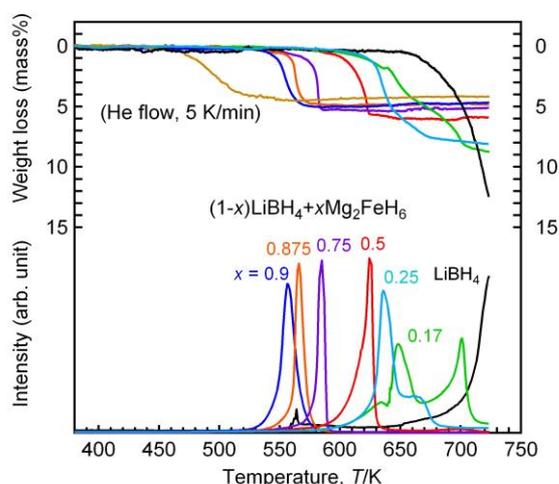


Fig. 1 TG-MS profiles of $(1-x)\text{LiBH}_4+x\text{Mg}_2\text{FeH}_6$.

The *in-situ* high-resolution synchrotron diffraction (SR-XRD) measurements, conducted at the Swiss-Norwegian Beam Line at the European Synchrotron Radiation Facility in Grenoble, suggest the possibility of forming a solid solution between LiBH_4 and Mg_2FeH_6 . As shown in Fig. 2, the lattice expansion of Mg_2FeH_6 in $\text{LiBH}_4+\text{Mg}_2\text{FeH}_6$ ($x = 0.5$) differs from pure Mg_2FeH_6 across the whole temperature range presumably due to the different thermal expansion coefficients. These results imply the possible solid solution formation via the following reaction:

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

Such a complex hydride with mixed non-metal-based and metal-based complex anions has not been reported to date although combinations of metal-based complex anions have been known to exist as the $\text{Mg}_2\text{FeH}_6\text{-Mg}_2\text{CoH}_5$ system [3].

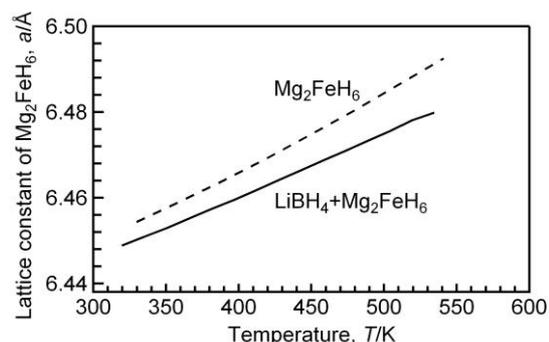


Fig. 2 Lattice expansions of Mg_2FeH_6 in $\text{LiBH}_4+\text{Mg}_2\text{FeH}_6$ ($x = 0.5$) and pure Mg_2FeH_6 obtained from *in-situ* SR-XRD profiles

References

- [1] S. Orimo, Y. Nakamori, J.R. Eliseo, A. Züttel and C.M. Jensen, *Chem. Rev.* 107, 4111 (2007)
- [2] G. Li, M. Matsuo, S. Deledda, R. Sato, B.C. Hauback and S. Orimo, *Mater. Trans.* (in press)
- [3] S. Deledda and B.C. Hauback: *Nanotech.* 20, 204010 (2009)