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Destabilization of LiBH_4 by SrF_2 for reversible hydrogen storage

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ABSTRACT

The de-/rehydrogenation features of the $6\text{LiBH}_4/\text{SrF}_2$ reactive hydride system have been systematically investigated. It was found that the thermal stability of LiBH_4 can be reduced markedly by combining it with SrF_2 . Dehydrogenation of the $6\text{LiBH}_4/\text{SrF}_2$ system proceeds via the $6\text{LiBH}_4 + \text{SrF}_2 \rightarrow \text{SrB}_6 + 2\text{LiF} + 4\text{LiH} + 10\text{H}_2$ reaction, which involves SrH_2 as the intermediate product. The dehydrogenation enthalpy change was experimentally determined to be 52 kJ/mol H_2 based on the P–C isotherm analysis. For rehydrogenation, LiBH_4 and SrF_2 were regenerated along with LiSrH_3 at 450 °C under ~8 MPa hydrogen pressure; thus, approximately 5.2 wt% of hydrogen can be released during the second dehydrogenation process.

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Introduction

Hydrogen is considered an ideal energy carrier due to its high energy density, clean combustion properties, and possibility of generation from abundant resources. For the effective utilization of hydrogen as an energy carrier, safe hydrogen storage systems with high efficiency are needed. Significant efforts have been devoted to developing solid-state hydrogen storage materials [1–4]. Light metal borohydrides have exceptionally high hydrogen capacity, showing promise for on-board hydrogen storage applications [5–7]. For example, LiBH_4 yields 13.8 wt% of hydrogen through decomposition into LiH and B, with $[\text{B}_{12}\text{H}_{12}]^{2-}$ species acting as the reaction intermediate [8]. However, hydrogen release from LiBH_4 alone starts at temperatures as high as 400 °C and cannot be completed below 600 °C due to the high thermodynamic stability of LiBH_4 [9]. In addition, the reversible rehydrogenation

process requires rigorous conditions at 600 °C under 15 MPa hydrogen pressure due to the chemical inertness of elemental boron [9,10].

Over the last decade, the combination of LiBH_4 with destabilizing additives to form LiBH_4 multicomponent reactive hydride systems has been proved to be an effective approach for improving the dehydrogenation thermodynamics and enhancing the LiBH_4 rehydrogenation process [11–36]. The pioneering work of Vajo et al. [11] found that the combined $2\text{LiBH}_4/\text{MgH}_2$ system could lower the dehydrogenation enthalpy by 25 kJ/mol H_2 with respect to the pristine LiBH_4 , and greatly improve the reversible hydrogenation performance due to the altered de-/rehydrogenation reaction pathways. Following this work, other binary reactive hydride systems (e.g., $6\text{LiBH}_4/\text{CaH}_2$ [12], $6\text{LiBH}_4/\text{SrH}_2$ [13], $2\text{LiBH}_4/\text{AlH}_3$ [14], $4\text{LiBH}_4/\text{YH}_3$ [15], $6\text{LiBH}_4/\text{CeH}_2$ [16], $4\text{LiBH}_4/\text{NdH}_{2+x}$ [17], $4\text{LiBH}_4/5\text{Mg}_2\text{NiH}_4$ [18], $2\text{LiBH}_4/\text{LiAlH}_4$ [19], $\text{LiBH}_4/\text{Li}_3\text{AlH}_6$ [20], $6\text{LiBH}_4/\text{Mg}(\text{AlH}_4)_2$ [21], $\text{LiBH}_4/x\text{LiNH}_2$ [22]) and ternary reactive

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hydride systems (e.g., $\text{LiBH}_4/\text{LiAlH}_4/\text{MgH}_2$ [23], $\text{LiBH}_4/2\text{LiNH}_2/\text{MgH}_2$ [24], $\text{LiBH}_4/\text{NaAlH}_4/\text{MgH}_2$ [25], $\text{Ca}(\text{BH}_4)_2/2\text{LiBH}_4/2\text{MgH}_2$ [26]) were proposed and investigated.

Recently, metal fluorides were investigated as another group of reactive destabilizers for LiBH_4 [27–36]. For example, CaF_2 could react with LiBH_4 to release 9.3 wt% of hydrogen at the peak temperature of approximately 460 °C. More interestingly, their dehydrogenation products of CaB_6 and $\text{LiH}_{2/3}\text{F}_{1/3}$ could be rehydrogenated to $6\text{LiBH}_4 + \text{CaF}_2$ composite at 450 °C under 9.2 MPa hydrogen pressure for 24 h [29]. In our previous work [13], we synthesized SrH_2 powder by reacting metallic Sr scraps with hydrogen, and then succeeded in destabilizing LiBH_4 by the addition of SrH_2 , via the $6\text{LiBH}_4 + \text{SrH}_2 \rightarrow \text{SrB}_6 + 6\text{LiH} + 10\text{H}_2$ reaction. Further considering that SrF_2 can be commercially obtained at a lower price and that F^- may substitute for H^- in LiBH_4 or LiH , which is beneficial to the LiBH_4 de-/hydrogenation processes [27], we investigated the reversible hydrogen storage properties of the $6\text{LiBH}_4/\text{SrF}_2$ system in this work. Moreover, the de-/rehydrogenation reaction mechanisms were discussed in detail based on X-ray diffraction (XRD) and Fourier transform infrared (FTIR) analyses.

Experimental details

Sample preparation

Commercial LiBH_4 (95%, Alfa Aesar) and SrF_2 (99%, Alfa Aesar) powders were used as-received without further purification. The combined $6\text{LiBH}_4/\text{SrF}_2$ system was prepared by ball-milling the $6\text{LiBH}_4 + \text{SrF}_2$ mixture under 0.5 MPa hydrogen pressure at the rotation speed of 400 rpm for 2 h using a QM-3SP2 planetary mill. Stainless steel vials (250 mL in volume) and balls (10 mm in diameter) were used. The ball to sample weight ratio was 20:1. To avoid air exposure, all sample handling was carried out in an Ar-filled glove box equipped with a purification system maintaining the typical $\text{O}_2/\text{H}_2\text{O}$ levels below 1 ppm.

Sample characterization

De-/rehydrogenation properties of the samples were examined based on the volumetric method by using a carefully calibrated Sieverts-type apparatus (Suzuki Shokan Co., Ltd., Japan). The temperature dependence of dehydrogenation was determined by heating the sample from ambient temperature to 600 °C at the heating rate of 2 °C/min. The hydrogen back-pressure for the study of dehydrogenation was below 0.1 MPa. Pressure–composition (P–C) isotherms for dehydrogenation were measured at 400, 450 and 500 °C to investigate the thermodynamic properties of the $6\text{LiBH}_4/\text{SrF}_2$ system. The rehydrogenation P–C isotherm was recorded at 450 °C with the maximum hydrogen pressure of 8 MPa.

To elucidate the phase components of the as-received, ball-milled, dehydrogenated and rehydrogenated samples, XRD measurements were performed using a Rigaku D/Max 2500VL/PC diffractometer with Cu K α radiation at 50 kV and 150 mA. The XRD samples were loaded and sealed in a special holder that can keep the sample under argon atmosphere. In

addition, the XRD pattern of the dehydrogenated product was analyzed using the Rietveld refinement program RIETAN-2000 [37]. FTIR spectra of the samples (KBr dispersion) were collected at ambient conditions using a Nicolet 6700 FTIR spectrometer.

Results and discussion

Dehydrogenation characteristics

Thermal dehydrogenation property

Fig. 1 shows the temperature-programmed dehydrogenation curve of the $6\text{LiBH}_4/\text{SrF}_2$ system at a heating rate of 2 °C/min. For comparison, the hydrogen desorption curve of the previously studied $6\text{LiBH}_4/\text{SrH}_2$ system [13] is also included in Fig. 1. It can be seen that the $6\text{LiBH}_4/\text{SrF}_2$ system started to release hydrogen at approximately 140 °C, which is 80 °C lower than the $6\text{LiBH}_4/\text{SrH}_2$ system. Further increasing the dehydrogenation temperature to 400 °C, the amount of the hydrogen desorbed from the $6\text{LiBH}_4/\text{SrF}_2$ system reaches approximately 2.4 wt%, while only approximately 1.1 wt% was released from the $6\text{LiBH}_4/\text{SrH}_2$ system. Thermal dehydrogenation of the $6\text{LiBH}_4/\text{SrF}_2$ system was accomplished at approximately 500 °C, with approximately 7.6 wt% of hydrogen totally desorbed. From the above results, two important conclusion can be obtained as follows: (i) SrF_2 exhibits a somewhat stronger destabilization effect on LiBH_4 than SrH_2 , especially in the temperature range of 140–400 °C, and thus, (ii) the dehydrogenation reaction mechanism for the $6\text{LiBH}_4/\text{SrF}_2$ system may be different from that of the $6\text{LiBH}_4/\text{SrH}_2$ system, as discussed below.

Thermal dehydrogenation process

To elucidate the dehydrogenation reaction mechanisms of the $6\text{LiBH}_4/\text{SrF}_2$ system, the as-received LiBH_4 as well as the solid residues after ball milling and dehydrogenation at different temperatures followed by cooling were analyzed by XRD and FTIR. As seen from Fig. 2a, the as-received LiBH_4 exists in a low-temperature polymorph (i.e., o- LiBH_4). After ball milling

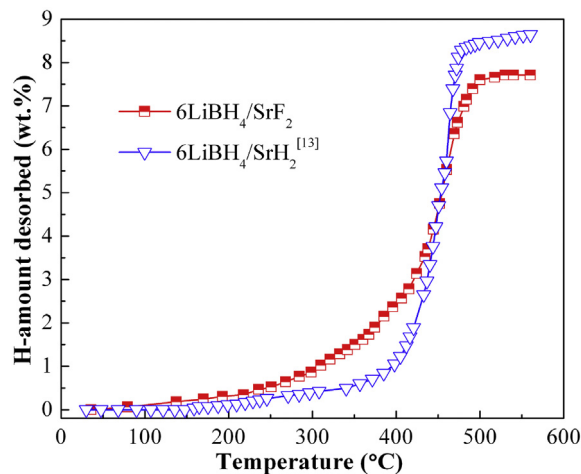


Fig. 1 – Temperature-programmed dehydrogenation curves of the $6\text{LiBH}_4/\text{SrF}_2$ and $6\text{LiBH}_4/\text{SrH}_2$ systems.

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