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Letter

Thermodynamics of the dehydrogenation of the $LiBH_4$–YH_3 composite: Experimental and theoretical studies

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ABSTRACT

Pressure–composition–temperature curves were constructed for the dehydrogenation of the $LiBH_4$–YH_3 composite. The Van't Hoff plot of the plateau pressure values showed that the reaction enthalpy and entropy were 51 kJ/mol H_2 and 101 J/K mol H_2, respectively. Thermodynamic calculations were performed for the reaction in combination with first principles calculation. The calculated reaction enthalpy and entropy are in good agreement with the measured values. The equilibrium temperature for the reaction at 1 bar of hydrogen was estimated to be 232 °C.

1. Introduction

Among complex metal hydrides, lithium borohydride ($LiBH_4$) has received much attention as a promising solid-state hydrogen storage material owing to its high hydrogen capacity, which reaches 13.9 wt% upon dehydrogenation into LiH and B [1]. However, the impractical temperature and pressure for the hydrogen sorption of $LiBH_4$ have been regarded as a major drawback to its use, especially in on-board applications [2]. The equilibrium temperature for the dehydrogenation reaction of $LiBH_4$ into LiH and B reaches approximately 370 °C, and hydrogenation is usually performed at 600 °C and 155 bar of hydrogen [3].

To overcome this drawback, the concept of a reactive hydride composite has been proposed [4–6]. In this concept, $LiBH_4$ reacts with metal hydride, forming LiH and a metal boride instead of B during dehydrogenation. The formation of a thermodynamically stable metal boride is expected to reduce the overall enthalpy change of the dehydrogenation reaction and subsequently the dehydrogenation temperature. A variety of combinations of $LiBH_4$ and metal hydrides, such as $LiBH_4$–MgH_2 [7–9], $LiBH_4$–CaH_2 [10], $LiBH_4$–CeH_2 [11], $LiBH_4$–YH_3 [12], $LiBH_4$–$LiAH_4$ [13] and $LiBH_4$–Li_3AlH_6 [14], have been evaluated to improve the hydrogen sorption properties of $LiBH_4$. In many cases, a decrease in the dehydrogenation temperature and a mitigation of the hydrogenation conditions have been observed. The $4LiBH_4 + YH_3$ composite is a typical example of a reactive hydride composite. We showed that this composite releases approximately 7 wt% hydrogen at 350 °C through the following reaction [12]:

$$4LiBH_4 + YH_3 \leftrightarrow 4LiH + YB_4 + 7.5H_2 \quad (8.5\,\text{wt\%} \quad H_2) \qquad (1)$$

In a previous study [12], we found that the dehydrogenation behavior is dependent on the hydrogen back pressure, and the application of hydrogen back pressure remarkably promotes the formation of YB_4 during dehydrogenation. In addition, the reversibility of the reaction was confirmed under relatively mild rehydrogenation conditions without the need of a catalyst. Approximately 5 wt% of hydrogen was absorbed at 350 °C and 90 bar of hydrogen over a period of 24 h during rehydrogenation. However, the details of the rehydrogenation reaction were not investigated, and little was determined about the thermodynamics of reaction (1) in that study [12], despite the importance of understanding the thermodynamics in determining the optimal hydrogen sorption conditions.

The purpose of this study was to investigate the thermodynamics of the dehydrogenation reaction of the $LiBH_4$–YH_3 composite both experimentally and theoretically. Pressure–composition–temperature (PCT) measurements were carried out during the dehydrogenation of the composite between 375 and 450 °C. In addition, thermodynamic calculations for reaction (1) were conducted in combination with first-principles

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calculations. The Van't Hoff plots and the thermodynamic properties obtained from the PCT measurements and the thermodynamic calculations were compared.

2. Experimental procedures

$LiBH_4$ with 95% purity was purchased from Acros. YH_3 was synthesized via the hydrogenation of yttrium (Acros, 99.9%, −40 mesh powder) at 350 °C and 90 bar of hydrogen (99.9999%) for 2 h. Three grams of the $4LiBH_4 + YH_3$ composite was prepared using a planetary ball mill (Retsch PM200) that was sealed with a lid that included a Viton O-ring at 650 rpm for 12 h. Thirteen 12.7 mm diameter and twenty-four 7.9 mm diameter Cr-steel balls were employed together with a 140 ml hardened steel bowl. The ball-to-powder weight ratio was 50:1. The whole process of sample mixing and loading was carried out inside an argon-filled glovebox (mBraun, UniLab), in which the oxygen and water vapor levels were kept below 1.0 ppm. The PCT curves of the dehydrogenation of the composite were determined using a Sieverts apparatus between 375 and 450 °C. For the measurements, approximately 90 bar of hydrogen (99.9999%) was initially applied, and then the pressure was lowered stepwise until it was less than 10 bar. At each pressure, the amount of desorbed hydrogen was calculated by a volumetric method. XRD analyses of the samples after the PCT measurements and of the as-milled sample were performed using a Bruker D8 Advance X-ray diffractometer with Cu Kα radiation. To prevent air exposure of the samples, borosilicate capillary tubes were used during the measurements.

3. Thermodynamic calculation

Thermodynamic calculations for reaction (1) were performed based on Gibbs free energy models. The Gibbs free energy parameters of the phases involved in the reaction were the input data for the thermodynamic calculation. Although the parameters for $LiBH_4$, LiH and H_2 are included in the SGTE substance database that is incorporated into the Thermo-Calc program [15], the parameters for YH_3, YH_2 and YB_4 are not available in this database or in the literature. Therefore, the Gibbs free energy functions of YH_3, YH_2 and YB_4 were parameterized based on first-principles calculations as follows: the total energies and vibrational frequencies were calculated from first-principles using the Quantum-ESPRESSO package [16]. The calculations were performed within the generalized gradient approximation by Perdew and Wang [17]. For the solid-state compounds, the Helmholtz free energy is used instead of the Gibbs free energy, ignoring the small PV term. The Helmholtz free energy was estimated with the harmonic approximation. Hydrogen gas was assumed to be an ideal gas. Detailed methods and computational and structural parameters have been published elsewhere [12,18]. Parametrization for $^{\circ}G_X$ was performed by fitting the calculated free energy to a typical Gibbs free energy function form, $A0 + A1 \cdot T + A2 \cdot T\ln(\mathrm{T}) + A3 \cdot T^2 + A4 \cdot T^3 + A5/T$, in the range of 100–1100 K.

The thermodynamic calculations were carried out using the Thermo-Calc program [15] to construct the Van't Hoff plot for reaction (1) as follows. First, we determined chemical compositions corresponding to the reaction. Then, the equilibrium temperature was calculated under the Gibbs free energy minimization condition after fixing the pressure of hydrogen gas. This process was repeated, varying the pressure from 0.1 to 100 bar.

4. Results and discussion

The PCT curves for the dehydrogenation of the $LiBH_4$–YH_3 composite measured at four different temperatures between 375 and 450 °C are presented in Fig. 1. Each curve exhibits a clear plateau. A single plateau implies that the dehydrogenation reaction takes place in a single step during the measurement, which agrees with our in situ synchrotron XRD analysis presented in our previous study [12]. As expected, the plateau pressure increases with increasing temperature. Comparison with the PCT curves of pure $LiBH_4$ determined by Mauron et al. [3] between 413 and 517 °C revealed that the plateau pressure of the composite was much higher than that of $LiBH_4$. For example, the plateau pressure of the composite was approximately 30 bar at 425 °C, whereas that of $LiBH_4$ was less than 3 bar at 424 °C. The significant increase in the plateau pressure of the composite compared with that of $LiBH_4$ proves that the composite is highly effective in lowering the dehydrogenation temperature in a thermodynamic sense. The amount of hydrogen desorbed during the PCT measurements was less than 6 wt%, which is lower than the theoretical capacity (8.5 wt%). This result might be attributed to partial oxidation of the composite during sample handling, particularly the PCT measurements, as shown in Fig. 2. In addition, small leaks at high temperature and pressures were likely to contribute to the unusually small dehydrogenation capacity (~3.5 wt%) at 450 °C.

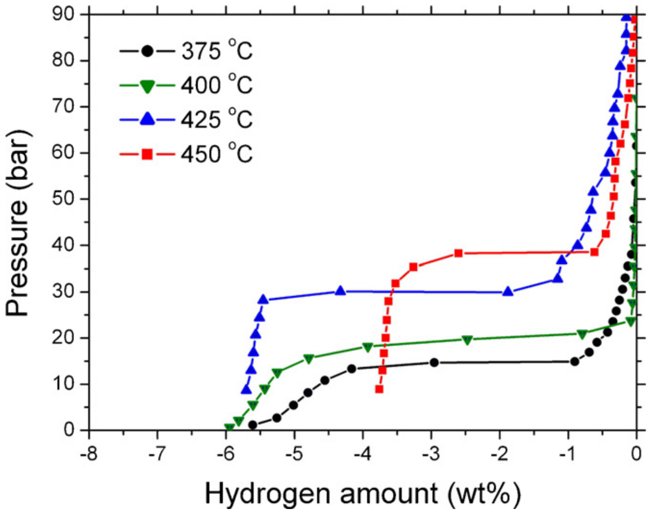

Fig. 1. PCT curves of the dehydrogenation reaction of the $4LiBH_4 + YH_3$ composite at 375, 400, 425 and 450 °C.

Fig. 2 shows the XRD patterns after the PCT measurements at 375 and 450 °C together with the pattern of the as-milled composite. $LiBH_4$ and YH_3 were present together with a small amount of YH_2 after ball milling without any indication of reactions between $LiBH_4$ and the yttrium hydrides. The XRD patterns after the PCT measurements at 375 and 450 °C exhibited the same dehydrogenation products of LiH and YB_4 and similar peak intensities, implying that the dehydrogenation of the composite proceeded via the same pathway during the PCT measurements between 375 and 400 °C.

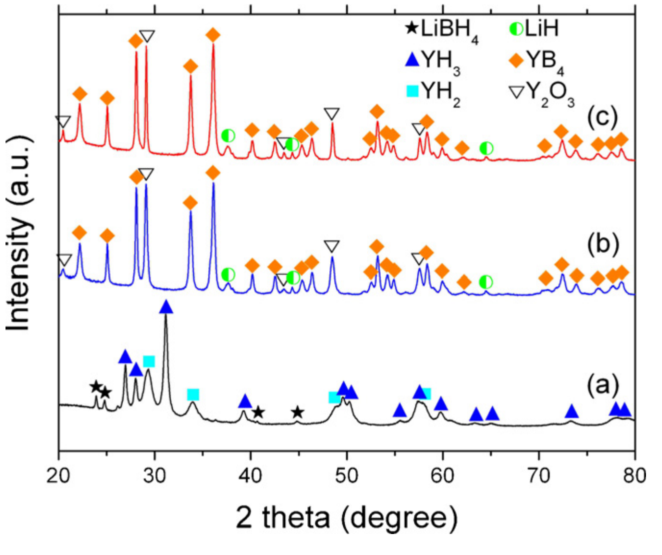

Fig. 2. XRD patterns of the (a) as-milled and dehydrogenated samples after the PCT measurements at (b) 375 and (c) 450 °C.

Table 1
Parameterized standard Gibbs free energies of YH_3, YH_2 and YB_4 as a function of temperature.

Phase	Gibbs free energy functions (J/mol)
YH_3	${}^{\circ}G_{YH_3} = {}^{\circ}G_Y + 3/2\,{}^{\circ}G_{H_2} - 232\,650 - 229.34T + 71.323T\ \ln(T) - 0.092449T^2 + 1.6187 \times 10^{-5}T^3 - 21\,487/T$
YH_2	${}^{\circ}G_{YH_2} = {}^{\circ}G_Y + {}^{\circ}G_{H_2} - 200\,200 - 210.82T + 57.729T\ \ln(T) - 0.073075T^2 + 1.3033 \times 10^{-5}T^3 - 68\,271/T$
YB_4	${}^{\circ}G_{YB_4} = {}^{\circ}G_Y + 4{}^{\circ}G_B - 297\,900 + 75.591T - 11.178T\ \ln(T) + 0.011225T^2 - 2.0923 \times 10^{-6}T^3 + 71\,634/T$

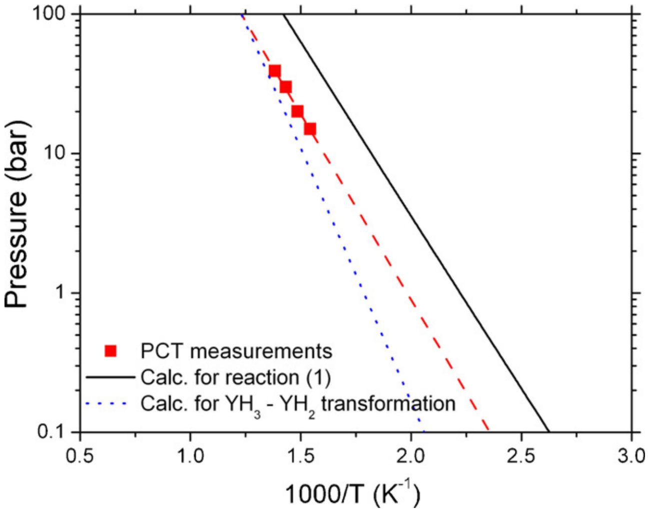

Fig. 3. Calculated Van't Hoff plot for reaction (1) together with the measured plateau pressures. The dotted line represents the equilibrium pressure for the YH_3–YH_2 transformation.

The peaks of Y_2O_3 indicate partial oxidation of the yttrium hydrides during the period in which the measurements were taken.

Table 1 presents the standard Gibbs free energy functions of YH_3, YH_2 and YB_4 parameterized in this study. The reference states for the pure elements Y, H and B are hexagonal close packed (hcp), diatomic gas and rhombohedral, respectively.

The calculated Van't Hoff plot for reaction (1) is presented in Fig. 3 together with the plateau pressures obtained by the PCT measurements. In addition, the calculation for the YH_3–YH_2 transformation was included to confirm if the transformation took place before the dehydrogenation and $LiBH_4$ reacted with YH_2 rather than YH_3 because YH_3 tends to transform into YH_2 at high temperatures [12]. The measured pressures exhibit a good linear correlation (dashed line), although the measured values are slightly lower than the calculated values for reaction (1). The likelihood that the measured data reflect the reaction between $LiBH_4$ and YH_2 is low because the calculated pressure, at which the transformation takes place, is lower than the measured pressure below 500 °C, as shown in Fig. 3.

Table 2 shows the changes in enthalpy and entropy and the equilibrium temperature at 1 bar of hydrogen for reaction (1), which were derived from the measured and calculated plots (Fig. 3). The measured reaction enthalpy (51 kJ/mol H_2) is in very good agreement with the calculated value (48 kJ/mol H_2). In addition, the agreement between the measured and calculated reaction entropies is reasonable. The equilibrium temperature at 1 bar of hydrogen derived from the measured plot is 232 °C, which is higher than the calculated value by approximately 50 °C. Compared with pure $LiBH_4$ (~370 °C) [3], the $4LiBH_4 + YH_3$ composite is proven to reduce the equilibrium temperature significantly. This equilibrium temperature is comparable with that of $2LiBH_4 + MgH_2$ (~225 °C) [7], which has the lowest equilibrium temperature among $LiBH_4$-based reactive hydride composites investigated to date.

Table 2
Changes in the enthalpy and entropy and the equilibrium temperature at 1 bar of hydrogen for reaction (1) derived from the measured and calculated Van't Hoff plots.

	ΔH (kJ/mol H_2)	ΔS (J/K mol H_2)	$T_{eq,1\ bar}$ (°C)
Meas.	51	101	232
Calc.	48	106	180

To obtain more precise thermodynamic values of the composite, the investigation of PCT data for the rehydrogenation is necessary. However, the rehydrogenation rate of the composite does not seem to be sufficient for PCT measurements, although the reversibility has been confirmed [12]. Therefore, a method to improve rehydrogenation kinetics, such as the addition of catalytic additives, needs to be developed for the more precise measurement of the thermodynamic properties.

In terms of the theoretical hydrogen capacity and the equilibrium temperature, the $4LiBH_4 + YH_3$ composite exhibits slightly more favorable dehydrogenation properties than MgH_2, which is a representative intermediate-temperature hydrogen storage material. Further studies are needed to improve the hydrogenation and dehydrogenation kinetics of $4LiBH_4 + YH_3$ to make it more practical for intermediate-temperature hydrogen storage applications.

5. Conclusions

The thermodynamic properties of the dehydrogenation reaction of the $4LiBH_4 + YH_3$ composite were investigated both experimentally and theoretically. PCT measurements were conducted for the composite between 375 and 450 °C. At four different temperatures, the measured plateau pressures exhibited a good linear correlation in the Van't Hoff plot. The reaction enthalpy and entropy derived from the plot were 51 kJ/mol H_2 and 101 J/K mol H_2, respectively. Based on the plot, the equilibrium temperature for the reaction at 1 bar of hydrogen was estimated to be 232 °C, which is significantly lower than that of $LiBH_4$. Thermodynamic calculations were carried out based on the Gibbs free energy functions of the individual phases involved in the reaction, which were taken from the SGTE substance thermodynamic database, except those of YH_3, YH_2 and YB_4, for which the Gibbs free energy functions were parameterized using first-principles calculations. The calculated reaction enthalpy and entropy were 48 kJ/mol H_2 and 106 J/K mol H_2, respectively, which are in good agreement with the measured values.

Acknowledgments

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