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Evaluation of enthalpy change due to hydrogen desorption for lithium amide/imide system by differential scanning calorimetry

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Abstract

Enthalpy change (ΔH) due to hydrogen desorption (H-desorption) for the lithium amide/imide system was evaluated by differential scanning calorimetry (DSC) measurement. In order to obtain the accurate and precise value of ΔH, we have paid special attention to following two points for correcting raw experimental data. One is to determine a cell constant of DSC equipment, which was evaluated by using the TiO_2-doped MgH_2 compound as a reference because of its quite similar hydrogen desorption properties to that of the lithium amide/imide system. The other is to estimate the sample amount corresponding to the H-desorption reaction from weight loss in the thermogravimetric (TG) analysis. By performing both the corrections, the ΔH value due to the H-desorption reaction from $LiNH_2 + LiH$ to $Li_2NH + H_2$ was evaluated to be 67 kJ/mol H_2.

Keywords: Calorimetry; Thermal analysis; Hydrogen absorbing materials; Gas–solid reactions

1. Introduction

For utilizing hydrogen as one of the secondary energies, it is necessary to establish high-performance hydrogen storage (H-storage) technologies [1]. Until now, three H-storage containers of liquid hydrogen, high-pressure gas hydrogen and absorbed hydrogen in H-storage materials are considered for future practical use as H-storage tanks. Among them, H-storage materials can more densely store hydrogen than high-pressure gas or liquid hydrogen. Therefore, the tank system using the H-storage materials has been considered as the most suitable one for H-storage.

From viewpoint of practical application, there are three important factors to be satisfied as a useful H-storage material. The first is to store high capacity of hydrogen, the second is to possess suitable thermodynamics and the third is to have fast kinetics for H-storage reaction. On consideration of the thermodynamics for (de-)hydrogenating reaction, the enthalpy change (ΔH) due to (de-)hydrogenation is one of the most important factors for evaluating whether the sample has a suitable potential for H-storage material or not. In principle, the value of ΔH for (de-)hydrogenating reaction can be experimentally estimated by van't Hoff plot of equilibrium pressures at different temperatures obtained from pressure-composition-isothermal (PCI) measurement [2] or by direct measurement of differential scanning calorimetry (DSC) [3]. Both methods have been considered to be suitable for conventional metal hydrides. However, it is quite difficult to accurately and precisely evaluate the ΔH value for some complex H-storage materials composed of light elements from the van't Hoff plot [4,5], because it takes too long time to reach an equilibrium condition from the others. Nevertheless, Kojima and Kawai have carefully measured the PCI curve on the lithium amide/imide system at some different temperatures and estimated the value of ΔH from the van't Hoff plot to be -66 kJ/mol H_2 [6]. It is to be noted that this value is much larger than -45 kJ/mol H_2 in magnitude, which was deduced in Chen's report [7]. On the other hand, it is in principle possible to directly observe the ΔH by DSC for any materials, if we can completely control the experimental conditions without an oxidation during hydrogenation or dehydrogenation process.

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Until now, the DSC measurements have been performed on conventional H-storage alloys [8], but the DSC measurements have not been performed for estimating ΔH yet because of lacking for enough fundamental works to control the experimental conditions. In this work, we tried to estimate ΔH on the lithium amide/imide system by the DSC measurement under carefully controlled experimental condition without any exposure of the sample to air at all, and have succeeded in the evaluation of the enthalpy change ΔH for dehydrogenating reaction from the LiH/$LiNH_2$ composite to $Li_2NH + H_2$.

2. Experimental details

Starting samples, MgH_2 (90%, purity), LiH (95%), $LiNH_2$ (95%) and $TiCl_3$ (98%) used in this work were commercially purchased from Sigma–Aldrich, TiO_2 nano-powder (83%) as a catalyst was purchased from Millennium Chemicals. Detailed sample preparation of the mixture of LiH and $LiNH_2$ with 1 mol% $TiCl_3$ was described in our previous paper [9]. All the processes of sample preparation in this work were performed in an Ar glovebox (MDB-2BL, Miwa Mfg. Co. Ltd.) to avoid the sample pollution due to water and oxygen in air.

DSC equipment (Q10 PDSC, TA Instruments), thermogravimetry (TG) and thermal gas desorption mass spectrometry (TDMS) equipment (TG: TG8120, Rigaku; TDMS: M-QA200TS, Anelva) were installed in two different gloveboxes (DBO-1.5KP, Miwa Mfg. Co. Ltd. and MDB-1BL, Miwa Mfg. Co. Ltd., respectively) to avoid exposing the sample to air at all in their measurements. In both gloveboxes, gas cycling purification systems were equipped to keep the dew point lower than $-80\,^{\circ}\mathrm{C}$ and the oxygen concentration less than 1 ppm.

In order to evaluate the genuine enthalpy change ΔH due to hydrogen desorption reaction, it is necessary to measure both the DSC and TG-TDMS profiles for the target sample, which detects an apparent endothermic heat due to H-desorption from the sample and the amount of desorbed hydrogen corresponding to the H-desorption reaction, respectively. In this work, both the DSC and TG-TDMS measurements were performed in temperature range from 25 °C to 450 °C at a heating rate of 5 °C/min, respectively, under an argon flow with 300 ml/min and a helium flow with 100 ml/min using aluminum pan as a sample holder. In both the measurements, we have carefully controlled experimental conditions to realize the same H-desorption properties. The peak area corresponding to ΔH was obtained by integrating the DSC signal in the same temperature range as the TG measurement. Under the above conditions, the DSC signal per mole H_2 due to H-desorption was deduced from the amount of H-desorption estimated by TG. In this work, those DSC measurements were performed for at least three times and a good reproducibility was obtained within 1% error. Additionally, it is quite important to confirm that the desorption gas is only hydrogen by the TDMS measurement.

Furthermore, in order to obtain the genuine value of ΔH from the DSC measurement, it is necessary to examine the ratio of the expected DSC signal to the detected one, which is so-called "cell constant". The process to determine the cell constant is an essential issue of the DSC measurement because in fact the DSC sensor cannot completely detect all the heat from the sample. Generally, the cell constant depends on atmospheric conditions in the sample cell, such as temperature, flowing gas speed, gas sort and so on. To determine the cell constant in our DSC measurements, we used magnesium hydride (MgH_2) as a reference sample, because the thermodynamic data of MgH_2 is well known to be $\Delta H = 76.1$ kJ/mol H_2 [10]. Moreover, the hydrogen desorbing properties, e.g. the peak temperature or peak width of H-desorption, can be, in principle, controlled by doping a small amount of some transition metal oxides as catalysts to the MgH_2 system [11]. The catalyzed MgH_2 composite with a small amount of TiO_2 possessing the single H-desorption peak at 220 °C was used in this work as the reference. Because this hydrogen desorption property is almost the same as that of the lithium amide/imide system. Here, the catalyzed MgH_2 composite was prepared by ball-milling the mixture of MgH_2 and 1 mol% TiO_2 under a hydrogen pressure of 1 MPa for 20 h.

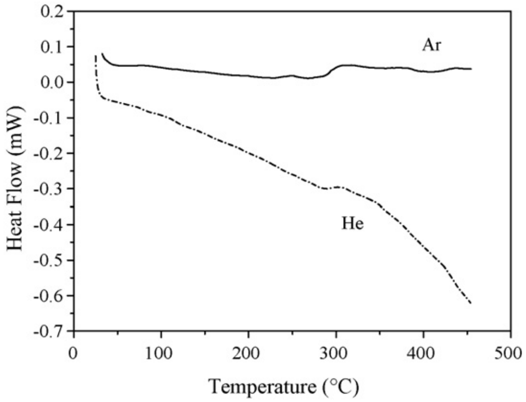

Fig. 1. Baselines for DSC measurements under He and Ar flowing gases with no sample.

3. Results and discussions

First of all, we investigated the carrier gas properties, which give some influence on the estimation of ΔH in the DSC measurement. Both baselines under helium and argon flow from room temperature up to 450 °C are shown in Fig. 1. The result indicates that the baseline under an argon flow condition is much leveler than that under a helium flow. The difference in the behavior should originate in their thermal conductivities, where the thermal conductivity of argon is much smaller than that of helium. Therefore, argon gas was adopted as a suitable carrier gas for the DSC measurements in this work.

The next step is to determine the cell constant around 220 °C. For that, both the TG-TDMS and DSC measurements were performed for the MgH_2 sample catalyzed with TiO_2, the result of which is shown in Fig. 2. From the TDMS profile, a sharp peak due to H-desorption is located at about 220 °C. We also confirmed that only the hydrogen gas was desorbed from the catalyzed MgH_2 sample within our experimental accuracy. Therefore, from these results, it was estimated that the amount of the TiO_2-catalyzed MgH_2 corresponding to H-desorption is 89.2 mass% in all samples as listed in Table 1. As is shown in

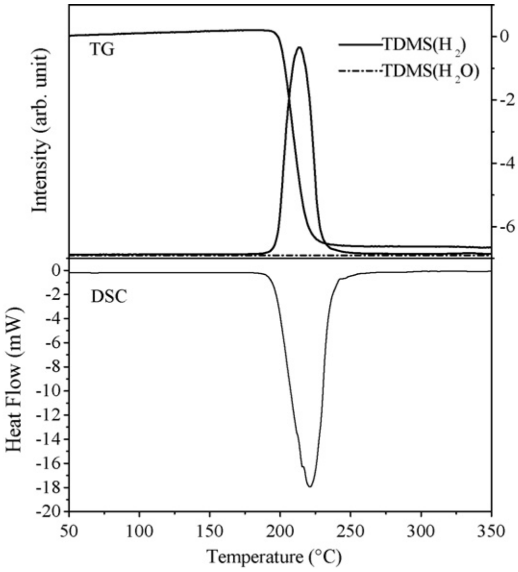

Fig. 2. Thermal desorption mass spectrometry (TDMS), thermogravimetry (TG) and differential scanning calorimetry (DSC) profiles for TiO_2-doped MgH_2 product as a reference sample.

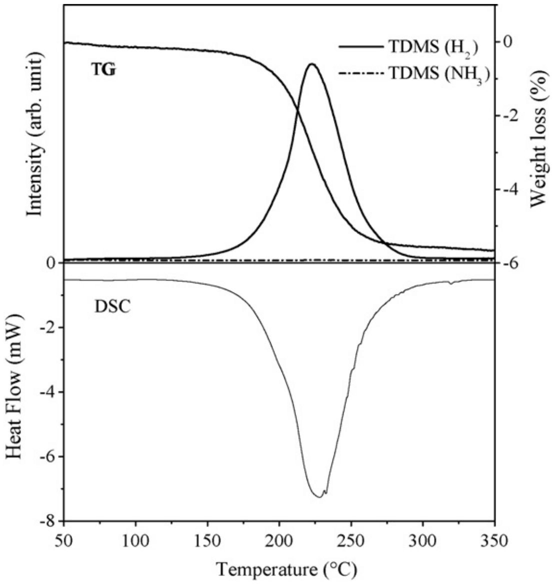

Fig. 3. Thermal desorption mass spectrometry (TDMS), thermogravimetry (TG) and differential scanning calorimetry (DSC) profiles for the ball-milled mixture of LiH and $LiNH_2$ catalyzed with 1 mol% $TiCl_3$.

the lower part of Fig. 2, we notice that the DSC profile is quite similar to the TDMS one. Here, we have to take into account the thermal contribution to DSC with respect to a reduction of TiO_2, which should be an exothermic reaction. From our recent results of the XAFS measurement for the Ti K-edge, we confirmed that the valence state of Ti in the catalyzed MgH_2 did not change before and after the thermal analyses up to 350 °C [10]. Furthermore, even if TiO_2 was remained after the catalyzing treatment, the amount of TiO_2 should be much less than 1 mol%. Therefore, the thermal contribution from the reduction should be negligible. Even after considering the amount of reference sample by TG-TDMS profile analysis, the detected value of ΔH is 58.5 kJ/mol H_2 as an average of three time measurements. This value is expected to be equal to 76.1 kJ/mol H_2, which is well known as the standard enthalpy change at standard ambient temperature (25 °C) and pressure by H-desorption for MgH_2. Therefore, the cell constant was estimated to be 1.30 (=76.1/58.5 [without any units]) around 220 °C. On the other hand, it should be noted that the cell constant in the case of no H-desorption reaction was determined to be 1.08 around 160 °C from the melting reaction of indium metal itself. Surely, this value is smaller than that in the case of H-desorption reaction, indicating that the DSC sensor detects less completely heat loss from sample with gas desorption than without gas release.

Strictly speaking, since the DSC measurements in the above examination were performed under an inert gas flow, we should take account of the contribution of "work ($p\Delta V$)" by hydrogen gas evolution to atmosphere in the standard condition on H-desorption reaction. However, this contribution was roughly estimated to be 100 [kPa] × 0.0224 [m^3] ∼2 [kJ/mol H_2] on the standard condition, which corresponds to increase in a few percentage of the standard enthalpy change of 76.1 kJ/mol H_2. Therefore, we ignored this small contribution in this examination. Therefore, our evaluation has at least 5% error as accuracy.

In the same way, the evaluation of ΔH was performed on the lithium amide/imide target system. Fig. 3 shows the results of the TDMS-TG and DSC measurements for the ball-milled mixture of LiH and $LiNH_2$ catalyzed with 1 mol% $TiCl_3$. As is evident from the upper part of Fig. 3, the TDMS profile shows that the target sample desorbs only hydrogen gas without any ammonia emission in our experimental accuracy. Therefore, the TG value was available for the determination of the amount of sample taking place of the H-desorption reaction. As is shown in Table 1, the amount of target sample corresponding to H-desorption was evaluated to be 88.1 mass% in the whole composite. From the peak area of the DSC profile in Fig. 3, the enthalpy change was detected to be 51.2 kJ/mol H_2 as an average. In this case, since the peak temperature of H-desorption was almost 220 °C as well as

Table 1
Purity of the sample, which is the amount of the sample corresponding to the H-desorption reaction, estimated by thermogravimetry (TG) measurement, the raw and averaged data of enthalpy change ΔH due to H-desorption reaction for TiO_2-doped MgH_2 sample and the ball-milled mixture of LiH + $LiNH_2$ catalyzed with a small amount of $TiCl_3$

	MgH_2 catalyzed with 1 mol% TiO_2			LiH + $LiNH_2$ catalyzed with 1 mol% $TiCl_3$		
Sample purity corresponding to H-desorption [mass%]			89.2			88.1
ΔH (experimental) [kJ/mol H_2]	58.0	58.7	58.7	50.5	52.0	51.1
ΔH (average) [kJ/mol H_2]			58.5			51.2
ΔH (genuine) [kJ/mol H_2]			76.1			66.7

that of the reference (TiO_2-catalyzed MgH_2), we used the value of 1.30 as the cell constant for the evaluation of most probable ΔH for the H-desorption. Consequently, the genuine ΔH for the H-desorption from $LiNH_2 + LiH$ to $Li_2NH + H_2$ was evaluated to be 67 kJ/mol H_2, where the sample amount corresponding to H-desorption and the cell constant used for evaluation of ΔH were listed in Table 1 as well. Here, it is to be noted that the estimated value of ΔH by the DSC measurement is in good agreement with the ΔH value evaluated from the van't Hoff plot [6]. In this work, we regarded the obtained ΔH of $LiH + LiNH_2 \rightarrow Li_2NH + H_2$ as ΔH of $LiH + LiNH_2 \rightarrow Li_2NH + H_2$ with the stoichiometry, although recent study shows that non-stoichiometry is rife in this system and that ionic migration is the key to hydrogen desorption [13]. However, the results of the TG measurements indicated the reaction could proceed with the complete stoichiometry in this work.

In the above estimation, we ignored the thermal contribution of the ammonia emission on the evaluation of the enthalpy change due to H-desorption. So far, we have really claimed that the ammonia emission should be essential for the proceeding of the H-desorption reaction in the metal–N–H system under a closed system [12]. Since the result indicated that the amount of the ammonia emission was less than 0.1 mol% of the total amount of desorbed hydrogen, the thermal contribution of the ammonia emission to the total enthalpy change was deduced to be less than 0.1%. Therefore, we conclude that the evaluated value of ΔH is within an experimental accuracy in at least 5% error.

4. Conclusion

In this work, we evaluated the ΔH for H-desorption on the lithium amide/imide system by the direct measurement of DSC. For evaluating the genuine ΔH value, we paid attention to the following two points. One is to carefully determine the cell constant by using the well-known MgH_2 sample catalyzed with TiO_2, which has quite similar H-desorption properties to the target system. The other is to evaluate the sample amount corresponding to H-desorption reaction, which was estimated by the TG measurement. From both the estimations of the cell constant and the sample purity, we were able to accurately determine the genuine enthalpy change ΔH to be 67 kJ/mol H_2 for the H-desorption reaction from $LiH + LiNH_2$ to $Li_2NH + H_2$.

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