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Modified Borohydrides for Reversible Hydrogen Storage (2)

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Abstract

This paper reports the results in the effort to destabilize lithium borohydride for reversible hydrogen storage. A number of metals, metal hydrides, metal chlorides and complex hydrides were selected and evaluated as the destabilization agents for reducing dehydriding temperature and generating dehydriding-rehydriding reversibility. It is found that some additives are effective. The Raman spectroscopic analysis shows the change of B-H binding nature.

Key Word: Lithium Borohydride, Hydrogen, Storage, Reversibility

1. Introduction

The highest gravimetric (18.4wt%) and volumetric (121 kg/m^3) hydrogen content of lithium borohydrides motivate great deal of research activities to make this material as effective hydrogen storage media. The main focus of lithium borohydride research is to reduce dehydrogenation temperature and to make material reversible – rechargeable at the moderate condition. In our previous work, several oxides have been found effective reduce the dehydrogenation temperature of $LiBH_4$ from 673K to 473K. These modified $LiBH_4$ based materials show 8~9wt% reversible hydrogen storage capacity at 873K and 7MPa [1]. Although this is an encouraging step forward, the elevated recharging conditions are still impractical for on-board hydrogen storage application. Further more, the most hydrogen (5-7 wt%) has been librated at above 573 K. It is believed that the oxides may play the role as the decomposition promoters (or catalysts) for releasing hydrogen at lower temperature. The fundamental change of thermodynamic stability of $LiBH_4$ is demanded for reversible hydrogen storage at the moderate conditions.

It is reported that the electrons in ionic compounds such as $LiBH_4$ and $NaBH_4$ are strongly localized, i.e. highly ionic, which gives these materials their stable thermodynamics [2,3]. Partial substitution of the cation (the Li^{+1} in $LiBH_4$) with other cations may change the borohydride bond structure, hopefully producing weakened B-H bond strengths, since such substitution of metal cations with less metallic cations should reduce the ionic character of the M^{+1}(metal)-$[BH4]^{-1}$ system and delocalize its electrons resulting in lower stability. In other words, the thermodynamic stability of the metal borohydrides M^aBH_4 can be reduced by partial substitution of the metal element M^a with the element M^b where M^b is less metallic in nature than M^a. By carefully selecting M^b,

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the B-H bonds could be weakened and the enthalpy (ΔH) of decomposition of the metal borohydride can be reduced, resulting in a lower dehydrogenation temperature.

This concept is expressed by follow dehydrogenation equations:

$$M^aBH_4 \Leftrightarrow MH + B + \frac{3}{2}H_2 \qquad \Delta H_a$$

$$M^a_{1-x}M^b_xBH_4 \Leftrightarrow M^a_{1-x}M^b_xH + B + \frac{3}{2}H_2 \qquad \Delta H_{ab}$$

$$\Delta H_{ab} < \Delta H_a$$

In this work, the research has been focused on weakening the B-H bond in an attempt to further lower dehydriding temperature and ease rehydrogenation conditions while holding high hydrogen storage capacity. The particularly designed formulations and the processes have been developed to exercise the new concept [4]. The experiment data have been presented in this paper.

2. Technical Approach

Several metals, metal hydrides and metal chlorides were added to $LiBH_4$ as the potential destabilization agents. A mechano-thermal diffusion process (MTDP) has been developed to execute the element partial substitution in order to reduce thermodynamic stability of $LiBH_4$. The new materials were then examined for their hydrogen desorption and absorption properties in an attempt to find less stable, reversible, high capacity storage materials.

3. Experimental Details

The $LiBH_4$ powder (99.99% purity) and the destabilization agents (metals, metal hydrides and metal chlorides 99.9-99.99% purity) were purchased from Sigma-Aldrich and used directly without any pre-treatment. Two grams of the appropriate $LiBH_4$ + agents powder mixture was placed in a 25 ml hardened steel grinding bowl with three 11mm diameter tungsten carbide balls in the argon glove box. The sealed grinding bowls were taken out of the glove box and put on Frisch-7 planetary ball mill for 2 hours of 600 rpm milling to mix the powder homogeneously. To promote elements diffusion and substitution, the powder mixtures were transferred to a stainless steel reactor for sintering at 350°C and 100 MPa for 8 hours. To reduce the particle size and improve kinetics, the sintered materials were crushed and ball milled with the catalyst $TiCl_3$ for 10 hours at 600 rpm. The process was named as Mechano-thermal diffusion process (MTDP). Then, new materials were ready for evaluation of hydrogen storage performance. All materials transferring were conducted in the argon glove box.

A semi-automatic Sieverts apparatus was used for Temperature-Programmed-Desorption (TPD) measurements at 5°C/min, isothermal hydrogen desorption and absorption. Selected destabilized borohydrides were investigated by Raman spectroscopy (Raman) to determine their binding structure change.

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4. Results and Discussion

4.1 TPD Screening of the Modified $LiBH_4$ Based Materials

In this investigation, sixteen modified $LiBH_4$ based materials have been synthesized (Table 1) and evaluated using TPD. Eight of them show the positive effect of the additives such as Mg, Al, $MgCl_3$, MgH_2, CaH_2, $TiCl_3$ and $LiAlH_4$ on destabilization of materials. But, other additives such as NaH, Ni, Ca, In and graphite exhibit the negative influence on reduction of dehydrogenation temperature. Some agents show mix effect on destabilization. The detail results are discussed as below.

Table1. The modified LiBH4 materials

Sample	Composition	Preliminary result	
		Positive	Negative
1	$LiBH_4$+0.2 Mg	x	
2	$LiBH_4$+0.2$MgCl_2$+0.1$TiCl_3$	x	
3	$LiBH_4$+0.5$LiAlH_4$	x	
4	$LiBH_4$+0.076$MgCl_2$+0.047$TiCl_3$	x	
5	$LiBH_4$+0.5MgH_2+2%$TiCl_3$	x	
6	$LiBH_4$+0.5AlH_3	x	
7	$LiBH_4$+0.5NaH		x
8	$LiBH_4$+0.5NaH+0.1TiO_2		x
9	$LiBH_4$+0.2C		x
10	$LiBH_4$+0.2C+0.01$TiCl_3$		x
11	$LiBH_4$+0.04Ni		x
12	$LiBH_4$+0.2 Al	x	
13	0.95$LiBH_4$+0.05Ca		x
14	0.95$LiBH_4$+0.05 In		x
15	$LiBH_4$+0.1Al+0.05TiO_2		x
16	$LiBH_4$+0.5CaH_2	x	

4.1.1. Metal-Modified $LiBH_4$ Based Materials

Commercial $LiBH_4$ decomposes starting at approximately 573 K at a slow rate. At about 450 ^{o}C, the decomposition rate appreciably accelerates, resulting in a final release of 9 wt% hydrogen at 873K. In this investigation, $LiBH_4$ was modified by ball milling with metals Mg, Al, Ca, In and graphite carbon. The TPD results (Fig.1) show that Mg and Al having positive influence on stability reduction, but Ca, In, Ni and carbon graphite are negative additives. Material $LiBH_4$+0.2Mg librated 1 wt% of hydrogen starting from 330 K at a very slow rate. The dehydriding accelerated when temperature increased above 573 K and desorbed 9 wt% of hydrogen upon to 873 K. As an additive, aluminum also shows a positive effect on reducing dehydrogenation temperature. The material $LiBH_4$+0.2Al librated 0.2 wt% of hydrogen at 340K slowly and 7.8 wt% of hydrogen from 573K to 873 K rapidly. It is interested that there are two plateaus at 673 K and 773 K respectively in the TPD curve of this aluminum doped $LiBH_4$. It is the indications of

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the formations of the intermediate compounds, the products of $LiBH_4$ and Al interaction. These compounds may less or more stable than $LiBH_4$. It is our hope to find the less stable intermediate compounds with low desorption temperature and reversibility.

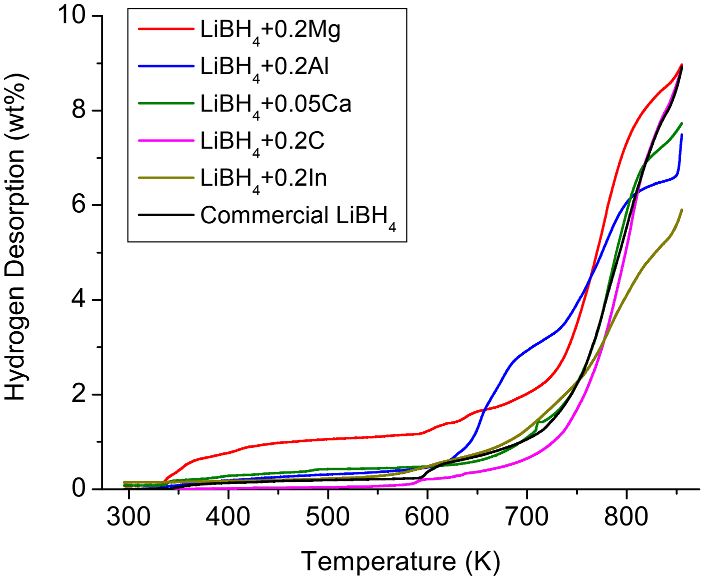

Fig.1 TPD of metal doped $LiBH_4$ based materials

To investigate the benefit of Al doping, the material $LiBH_4$+0.24Al was rehydrided at 10 MPa and 873 K after first desorption at 873 K and 500 Pa. Then the second desorption was carried out. As Fig. 2 shows, the first plateau disappears in the second TPD, desorption starting temperature gone up from 340 K to 623 K and capacity decreased from 8 wt% to 3.5 wt%. It appears that the Al-doping produced more stable and irreversible material.

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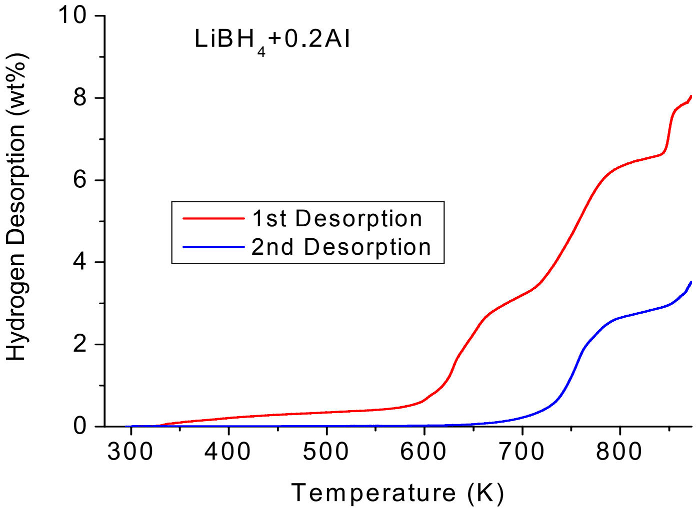

Fig.2 Rapidly dehydriding of LiBH$_4$+0.2Al

The additives, Ca, In and graphite carbon show no or negative influence on reduction of hydrogen desorption temperature. They also did not generate the plateau in TPD curves. It appears that the lithium borohydride has no interaction with the metals Ca, In and carbon.

4.1.2. Metal Chloride-Modified LiBH$_4$ Based Materials

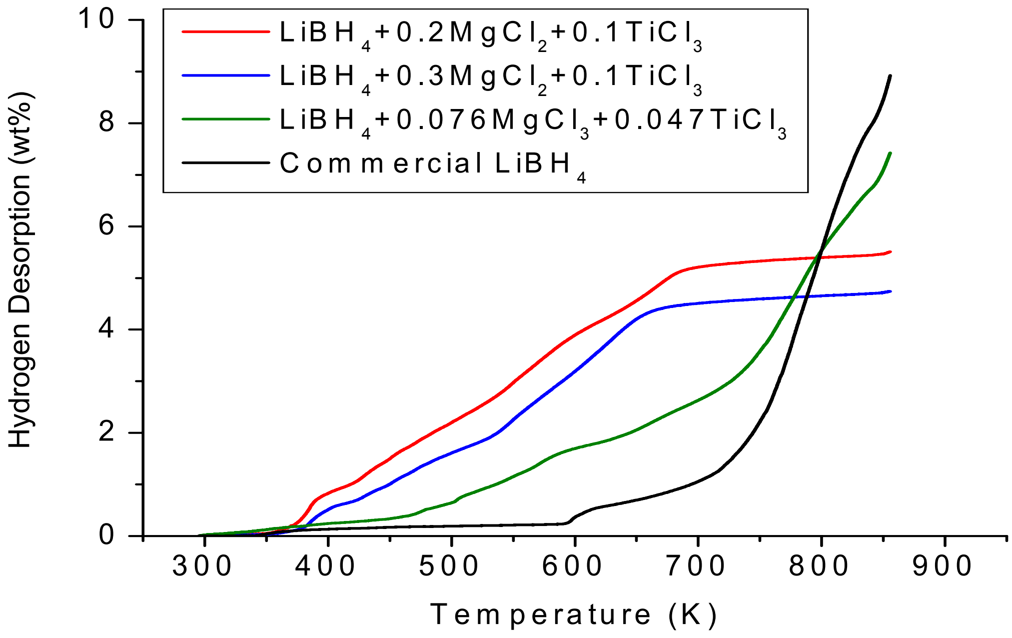

Fig.3 TPD of LiBH$_4$ based materials modified by MgCl$_2$ and TiCl$_3$

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In this investigation, three $LiBH_4$ based materials modified by $MgCl_2$ and $TiCl_3$ at different molar ratios have been synthesized using MTDP process. Their TPD results are shown in Fig.3. Material $LiBH_4$+0.2 $MgCl_2$+0.1$TiCl_3$ released 5.5wt% hydrogen starting from 330K. Unlike metal oxide-modified $LiBH_4$ that have the typical slow dehydrogenation rate below 623K [1], the material $LiBH_4$+0.2 $MgCl_2$+0.1$TiCl_3$ desorbed 5.2 wt% hydrogen linearly at high rate from 330K to 673K. The additives ($MgCl_2$ and $TiCl_3$) also changed the TPD curve shapes by comparing with oxide modified $LiBH_4$ and commercial $LiBH_4$. This may imply that some less stable intermediate compounds with less thermodynamic stability form during processes. Identifying and generating more this kind of intermediate compounds might result in more hydrogen being released at lower temperature. As material $LiBH_4$+0.3$MgCl_3$+0.2$TiCl_3$ shows, increasing additives loading did little in reducing dehydrogenation temperature further, but decreased hydrogen storage capacity about 0.9 wt%. As material $LiBH_4$+0.076Cl_3+0.047$TiCl_3$ shows in Fig.3, decreasing additive loading resulted in capacity increase, lower dehydrogenation temperature, slow reaction and shape change of the curve.
It is encouraging that the most reaction of dehydrogenation was completed below 673 K although the capacity is low. It is believed that the additives $MgCl_3$ and $TiCl_3$ may reduce the thermodynamic stability of $LiBH_4$ through interaction or possible formation of intermediate compounds. The comprehensive material characterization will provide the clues. The overall low capacity of $MgCl_2$ and $TiCl_3$ doped $LiBH_4$ is attributed to heavy additive loading (67.4wt%). Obviously, the optimization of the additive loading will increase the dehydriding capacity while retain lower dehydriding temperature. The material $LiBH_4$+0.3$MgCl_3$+0.2$TiCl_3$ was selected for evaluation of the isothermal desorption and absorption. The results will be discussed later.

4.1.2. Metal Hydride-Modified $LiBH_4$ Based Materials

In an attempt to form less-stable intermediate compound, several metal hydrides such as MgH_2, AlH_3, $LiAlH_4$ were added into $LiBH_4$ using MTDP process.

The material $LiBH_4$+0.5MgH_2+2%$TiCl_3$ desorbed 8.5wt% hydrogen at 873 K. There are two stages in desorption curve. The first desorption released about 2.8wt% hydrogen slowly from 373 K to 673 K and the second one librated 5.8wt% from 673 K to 873 K with relatively fast desorption rate. The first stage may attribute to MgH_2 dehydriding and the second one may correspond to $LiBH_4$ dehydriding. The possible interaction of $LiBH_4$ and MgH_2 may take place during ball milling and following dehydriding at certain temperature. The result agrees with Vajo's claim. He believes that the intermediate compound MgB_2 plays a role in making reaction reversible [5].

The material $LiBH_4$+0.5AlH_3 desorbed 8.5wt% hydrogen in two steps. It released hydrogen slowly from 373 K. Above 453 K, the dehydrogenation rate picks up and the material delivered 2.5wt% hydrogen at 493 K. This step may be dominated by decomposition of AlH_3. There is no significant hydrogen desorption between 493 K and 673 K. Above 673 K, the material desorbed about 5.8wt% hydrogen until 873 K. The second step attributes mainly to decomposition of $LiBH_4$. It is unlikely that the Al element substitutes some of the B as expected.

The material $LiBH_4$+0.5$LiAlH_4$ desorbed hydrogen starting from 453 K in two stages. The material desorbed about 3wt% hydrogen in the low temperature stage (below 553 K) and 6.2wt% in high temperature stage (above 673 K). It is known that $LiAlH_4$ decomposes at 448 K and liberates about 7.5wt% hydrogen. The two stages of dehydrogenation may reflect the some mixed behavior of $LiAlH_4$ and $LiBH_4$. But, most hydrogen comes from $LiBH_4$ based on the molar ratio. The possible interaction of $LiAlH_4$ and $LiBH_4$ is warranted for investigation to produce less stable materials.

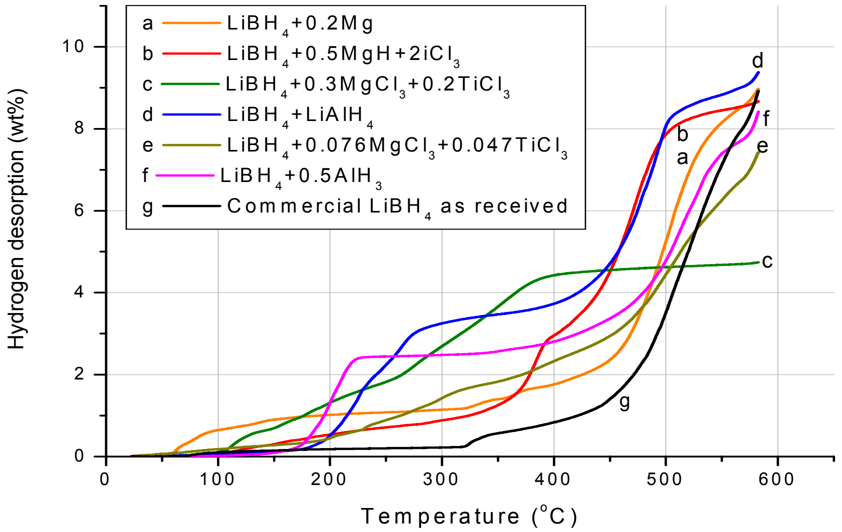

Fig.3. Hydrogen desorption of the modified $LiBH_4$ materials with positive effect

Although the positive influence of the additives on dehydrogenation of $LiBH_4$ is discussed in above, it is realized that some additives have negative effect on dehydrogenation of $LiBH_4$ as Fig.2 shows. We don't have sufficient material characterization data to interpreter the negative effect yet. One possible reason is that the Na substitutes Li to form more stable $NaBH_4$ in the $LiBH_4$+0.5 NaH and $LiBH_4$+0.5 NaH+0.1TiO_2. The sample 11 ($LiBH_4$+0.04Ni) and 14 ($LiBH_4$+0.05In) also show negative results, but not is listed in the chart.

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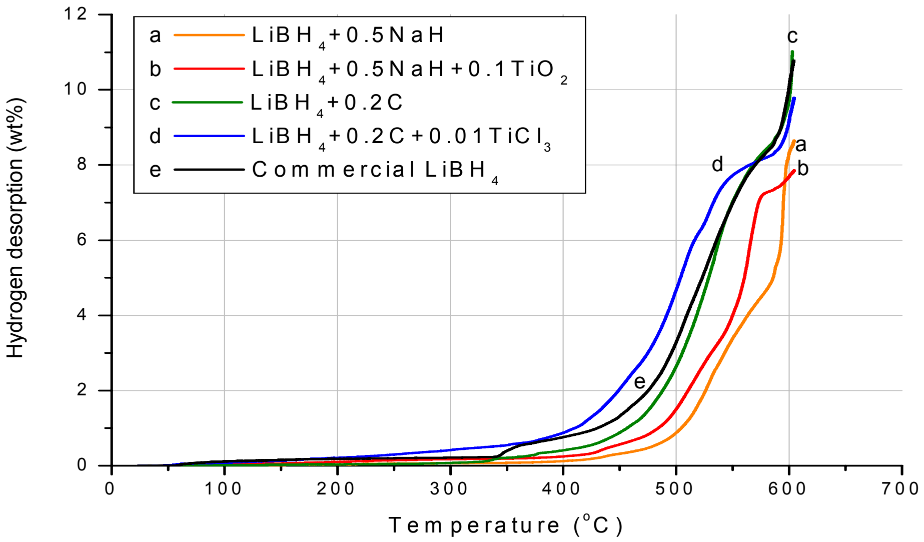

Fig.4. Hydrogen desorption of the modified $LiBH_4$ materials with negative effect

Several other metals and metal hydrides such as Al, Ca and CaH_2 were also added into $LiBH_4$ as the destabilization agents. The results are given in Fig.5. It is found that the Al and CaH_2 reduced the decomposition temperature to less than 323 K in the samples 11(81.7wt%$LiBH_4$+18.3wt% Al) and 15 (75wt%$LiBH_4$+10wt% Al+15wt%TiO_2). The sample 11 desorbed 3wt% of hydrogen at 673 K and 8wt% of hydrogen at 873 K. However, it desorbed 3.5wt% of hydrogen at 873 K only in the second dehydriding after rehydriding at 873 K and 10 MPa, see Fig. 6. It is doubt if the material is reversible, the more work is needed.

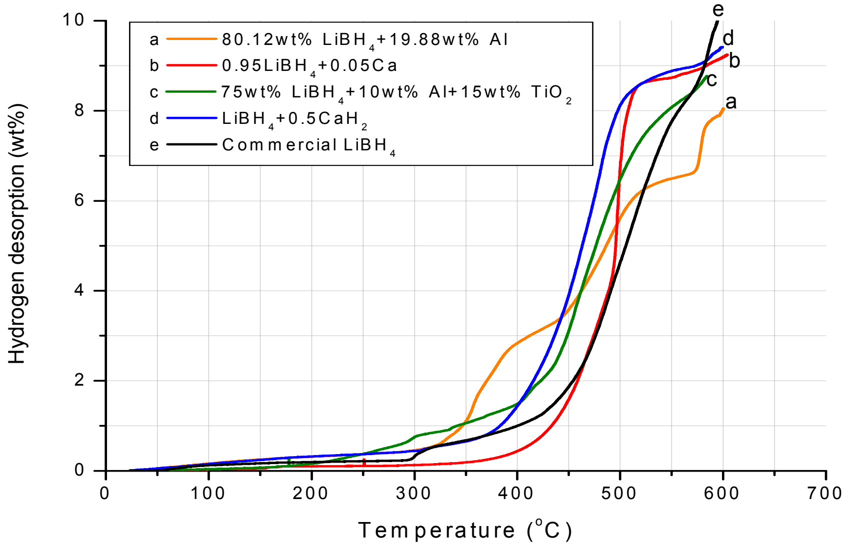

Fig.5 Hydrogen desorption of the modified $LiBH_4$ materials with mix effect

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The material $0.95LiBH_4+0.05Ca$ shows the negative effect of adding Ca metal. But, the material $LiBH_4+0.5CaH_2$ shows the positive role of CaH_2 in the reducing of the decomposition temperature. It is believed that the Ca metal is covered by the CaO layer preventing Ca from interaction with $LiBH_4$. Differently, CaH_2 can provide the fresh metallic Ca during thermal decomposition and ball milling.

In summary, the additives Mg, $MgCl_3$ and $TiCl_3$ reduced dehydriding temperature from 593 K to 373 K or less (samples 1, 2 and 4). The dehydrogenations were completed in a single stage. The positive effect of these additives implies that the thermodynamic stability of the $LiBH_4$ was reduced due to possible partial substitution of Li by Mg, but more supporting evidences have to be generated such as P-T-C isotherms and advanced spectrum analysis. The additives $LiAlH_4$, AlH_3 and MgH_2 also reduced dehydriding temperature and produced more hydrogen at lower temperature (samples 3, 5 and 6). The dehydrogenations were completed in two stages, low temperature and high temperature. Somehow, the two stages may be dominated by the decomposition of the hydrides additives and the $LiBH_4$ in the lower and higher temperature ranges respectively. But, the interaction of additives with $LiBH_4$ have to be considered. MTD process may promote the interaction and produce the interesting intermediate compounds that play the important role as the bridge to facilitate the reversible reaction at moderate condition.

4.2 Isothermal dehydrogenation of the selected modified borohydrides

Although the TPD show a whole picture of the dehydrogenation process in a broad temperature range, the isothermal dehydrogenation study are normally used to judge material performance characteristics such as storage capacity and kinetics at desired temperature. The Fig. 6 shows the isothermal dehydrogenation performance of the sample 2 ($LiBH_4 +0.3MgCl_2+0.2TiO_2$). At 673 K, the material desorbed 2.5 wt% of hydrogen rapidly in the first 15 min. Following two incubation periods, the material desorbed 4.9 wt% of hydrogen in 18 hours. The second desorption at 773 K is almost same with 4.9wt% of hydrogen released in 18 hours. In the third dehydriding, the materials desorbed 4.25wt% hydrogen in 22 hours. It is interested that there is no incubation in the third dehydriding. It may imply the settle down of certain material interaction. The repeatedly dehydriding and rehydriding shows the reversibility of the material, at least in the preliminary expression. Obviously, the desorption kinetics is too slow for practical application. But, there are number of the ways to improve the kinetics such as reduce the particle size to nanoscale, disperse the materials on the nonporous subtract, synthesize thin film and add catalysts to change the reaction path and so on. We believe that the reducing thermodynamic stability while maintain high capacity is the focused points of the development of reversible borohydride materials.

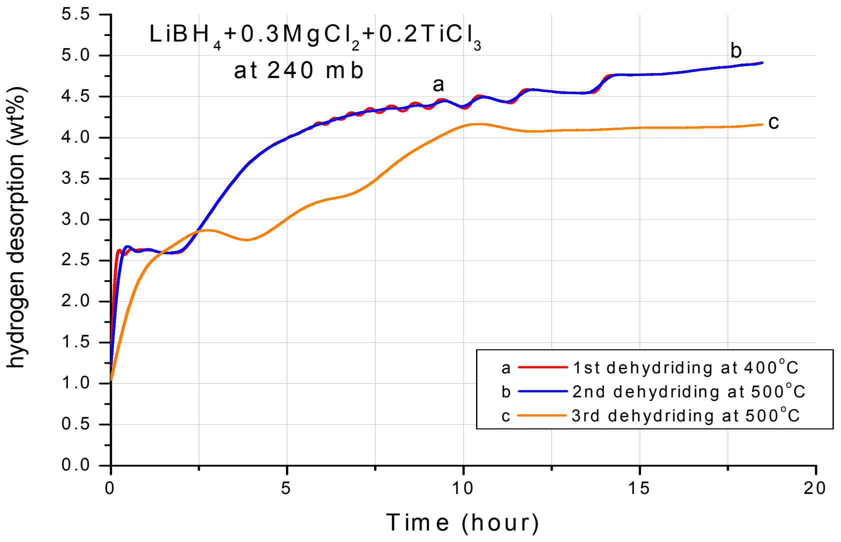

Fig. 6 The isothermal hydrogen desorption of the material $LiBH_4$+0.3$MgCl_2$+0.2$TiCl_3$

4.3 Isothermal rehydriding of the selected borohydrides

After dehydriding at 873 K for one hour, the sample 3 ($LiBH_4$ +0.3$MgCl_2$+0.3TiO_2) was selected for rehydrogenation at 873 K and 70 bars. As Fig.7 shows, the material absorbs 2.8 wt% of hydrogen in 17 hours, but it absorbed more hydrogen (4.4wt%) in the second rehydrogenation. It is not clear that if more dehydriding-rehydriding cycling will result to higher capacity or fast kinetics. But, it demonstrates that the material is the reversible in the limited cycles. In other side, the rehydrogenation kinetics of the destabilized $LiBH_4$ is much slower comparing with catalyzed $LiBH_4$ reported in the previous paper 1]. Also, the rehydriding temperature and pressure are still too high for immediately application. More work has to be done.

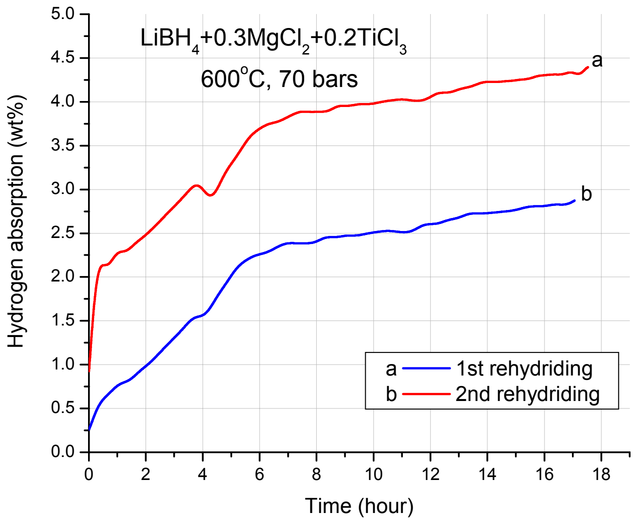

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Fig. 7 Hydrogen absorption of the material $LiBH_4$+0.3$MgCl_2$+0.2$TiCl_3$

4.4 Raman scattering analysis of the destabilized $LiBH_4$

At room temperature, two Raman active internal BH_4^{-1} vibrations ν_4 and ν'_4 occur at 1253 and 1287 cm^{-1} respectively, and two overtones $2\nu_4$ and $2\nu_4'$ at 2240 and 2274 cm^{-1}, respectively as blue spectrum shows in the Fig.8. However, the ν_4, ν'_4, and $2\nu_4$ stretching disappear from the spectrum after adding agents in the material $LiBH_4$+0.5$LiAlH_4$. The $2\nu_4'$ stretching is weakened and shifted to 2300 cm^{-1} as the red spectrum shows in the Fig.8. It is implied that the B-H binding strength is changed by partial Li^{+1} substitution. The weakened bond results in lower dehydriding temperature. Similar result was obtained from material $LiBH_4$+0.3$MgCl_2$+0.2$TiCl_3$, see Fig.9.

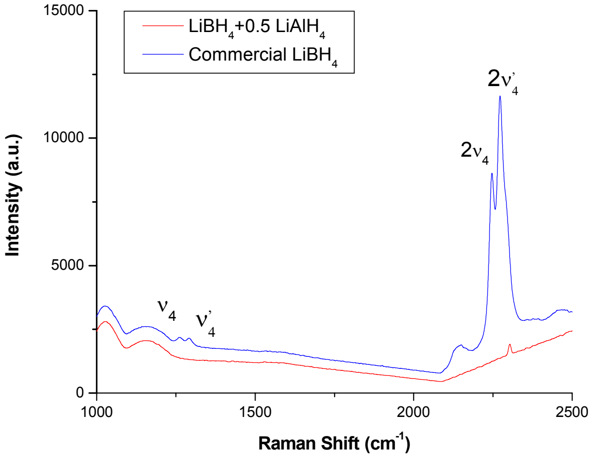

Fig. 8 Raman spectra of $LiBH_4$+0.5 $LiAlH_4$

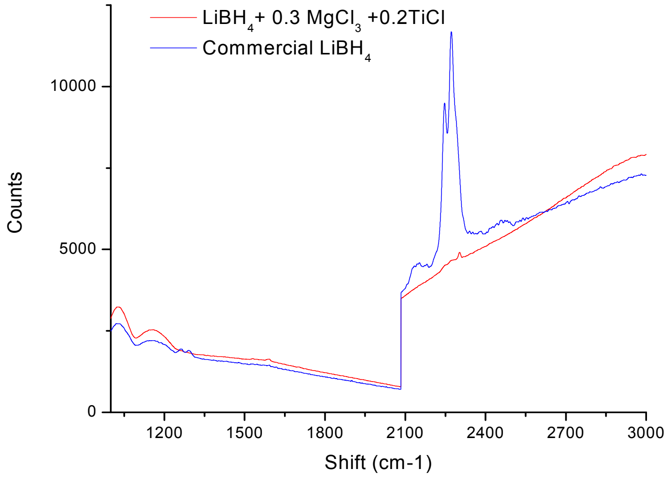

Fig.9 Raman spectra of $LiBH_4$+0.3$MgCl_3$+0.2$TiCl_3$

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5. Conclusions

In attempt of destabilizing lithium borohydride, a number of metals, metal hydrides, metal chlorides and metal complex hydrides have been selected and evaluated as the destabilization agents. The experimental results show that additives, such as Mg, Al, MgH2, AlH3, CaH2, MgCl3, TiCl3 and LiAlH4, are effective in reducing dehydriding temperature, but some are negative such as Ni, C, In, Ca and NaH. The destabilized lithium borohydrides are reversible in the limited dehydriding-rehydriding cycles with slow reaction kinetics. The required rehydriding temperature and pressure are still elevated. Raman spectroscopic analysis shows H-B stretch change after adding of destabilization agents. The material $LiBH_4$+0.3$MgCl_3$+0.2$TiCl_3$ desorbed 5 wt% of hydrogen from 333 K and desorbed 4.5wt% of hydrogen at 873 K and 7 MPa during rapidly dehydriding-rehydriding cycles. This investigation indicates that the thermodynamic stability of lithium borohydride can be reduced by the additives. More comprehensive work could lead to possible breakthrough in developing new lithium borohydride based materials for reversible hydrogen storage with practical operating conditions.

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