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Modified Borohydrides for Reversible Hydrogen Storage

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Abstract

In attempt to develop lithium borohydrides as the reversible hydrogen storage materials with the high capacity, the feasibility to reduce dehydrogenation temperature of the lithium borohydride and moderate rehydrogenation condition has been explored. The commercial available lithium borohydride has been modified by ball milling with metal oxides and metal chlorides as the additives. The modified lithium borohydrides release 9 wt% hydrogen starting from 473K. The dehydrided modified lithium borohydrides absorb 7-9 wt% hydrogen at 873K and 7 MPa. The additive modification reduces dehydriding temperature from 673K to 473K and moderates rehydrogenation conditions to 923K and 15 MPa. XRD and SEM analysis discovered the formation of the intermediate compound TiB_2 that may plays the key role in change the reaction path resulting the lower dehydriding temperature and reversibility. The reversible hydrogen storage capacity of the oxide modified lithium borohydrides decreases gradually during hydriding-dehydriding cycling due to the lost of the boron during dehydrogenation. But, it can be prevented by selecting the suitable additive, forming intermediate boron compounds and changing the reaction path. The additives reduce dehydriding temperature and improve the reversibility, it also reduces the hydrogen storage capacity. The best compromise can be reached by optimization of the additive loading and introducing new process other than ball milling.

Key Words

Borohydride, Lithium, Hydrogen, Storage,

1.   Introduction

Alkali metal borohydrides such as $LiBH_4$ and $NaBH_4$ are lightweight materials contain larger amounts of hydrogen. Their gravimetric and volumetric hydrogen storage capacities (18.5wt%, 121 kg/m^3 and 10.6wt%, 98.7 kg/m^3, respectively) are well above US DOE's bench mark for transportation applications (7.5 wt% and 65 kg/m^3 [1]). The lithium borohydride could be superior over other hydrogen storage options if it is reversible in the moderated conditions, see Table 1. The borohydrides are also relatively inexpensive and can be produced from abundant natural borane deposits [3,4]. Unfortunately, these materials are very stable. Heating above 673 K that is above its melting point is required to release the majority of the hydrogen from $LiBH_4$ [5]. The rehydrogenation conditions

are too harsh for practical application. However, the potential of these materials warrants investigation into possible methods to resolve or alleviate these two major problems.

The majority of borohydride research has focused on "on-demand^{TM}" hydrogen sources, which rely on an irreversible catalyzed hydrolysis reaction. The theoretical hydrogen yield by hydrolysis is only 7.6 wt% and a considerable amount of water will need to be supplied. The novel metal Ru has to be used as the catalyst. Also the safe and cost effective disposal or recycling process for the hydrolysis byproduct such as $NaBO_2$ has not yet been resolved [13]. A reversible borohydride material capable of releasing and reabsorbing hydrogen at moderated conditions similarly to a standard metal hydride would represent a major breakthrough in hydrogen storage technology.

Fig. 1 Solid hydrogen storage materials

Technology	Gravimetric capacity (wt %)	Volumetric density (kg/m^3)	Operating temperature (^{o}C)	Recharging pressure (bar)
LaNi$_5$ [6]	1.7	80	25	10
MgH$_2$ [7]	7.7	102	300	30
Glass microspheres [8]	9.4	8	350	680
NaAlH$_4$ [9]	7.4	69	125	100
LiNH$_2$ [10-12]	6.5	NA	150-250	30
NaBH$_4$ hydrolysis [13]	7.6	75	25	NA
LiBH$_4$ [5]	18.4	121	400	150

Early, Alain Muller reported that 5 gram of LiBH$_4$ decomposed and released 13.8wt% hydrogen at 723K and 10^{-2} mmHg (1.3 Pa) pressure within 24 hours by giving a reaction as LiBH$_4$ à LiH + B + 3/2 H$_2$ – 24.8 Kcal. After dehydrogenation, he was able to put 6.65 liter (11.8wt%) of hydrogen back to the decomposed material at 923K and 15MPa within 48 hours. To improve the dehydrogenation and following rehydrogenation processes, 10wt% aluminum powder was mixed mechanically with LiBH$_4$. It liberated 12.4wt% of hydrogen at 723K and 1 Pa within 24 hours. After then, 15.2 wt% of hydrogen was recharged back to the decomposed material at 923K and 15MPa within 12 hours [14]. Obviously, the dehydriding and rehydriding temperatures are too high and the reactions are too slow. Recently, Zuttle reported that the LiBH$_4$ ball milled with 25% SiO$_2$ librated 9 wt% hydrogen starting from 523K through the reaction LiBH$_4$ à LiH + B + H$_2$. He indicated that the reaction is partially reversible, but with no detail data given in the paper [15]. Orimo studied the Raman spectra of NaBH$_4$, KBH$_4$ and LiBH$_4$ and suggested that the stability of LiBH$_4$ or LiNH$_2$ can be reduced by partial cation substitutions using smaller sized and/or higher valenced-cations with higher electronegativities such as Mg [16]. By adding Mg into LiBH4 at Li/Mg=9:1, the dehydriding temperature was reduced from 850K to 820K [17]. Vajo reported that the LiBH$_4$ was destabilized by adding 0.5 mole of MgH$_2$ and 0.03 mol% TiCl$_3$. The calculation from P-C-T (pressure-composition-temperature) isotherms shows the rehydrogenation enthalpy of LiBH$_4$ was reduced by 25 KJ/mol H$_2$. The kinetics was extreme slow and 100 hours were necessary to reach the equilibrium [18].

Motivated by its high theoretic gravimetric and volumetric capacity, we conducted the systematic investigation to modify the commercial $LiBH_4$ for reversible hydrogen storage. Many potential additives have been screened and several of them show effective in reduction of thermal decomposition temperatures and improvement of the reversibility at relatively moderate conditions. The materials characterizations discovered the interaction of the borohydride with the additives that helps to understand the dehydriding/rehydriding processes. The detail results are reported in this paper.

2. Experimental

The $LiBH_4$ powder (99.99% purity) and the additive powder (99.9-99.99% purity) were purchased from Sigma-Aldrich and used directly without any pre-treatment. Two grams of the appropriate $LiBH_4$ + additive powder mixture was placed in a 25 ml hardened steel grinding bowl with three 11mm diameter tungsten carbide balls. The sealed grinding bowls were taken out of the Argon glove box and put on Frisch-7 planetary ball mill for 600 rpm milling. After milling, the dehydriding temperatures of the new modified borohydrides were first screened on a Perkin-Elmer TG/DTA thermal analyzer. 0.5 grams of selected modified $LiBH_4$ powders were transferred to the Sieverts apparatus, a volumetric device with 500 Pa (5 mbar) back pressure, for Temperature-Programmed-Desorption (TPD) measurements. The temperature was ramped up from ambient to 973K at rate of 5K/min. The rehydrogenations were conducted at 873K and 7MPa (99.9999% hydrogen) in the same Sieverts apparatus. The selected borohydrides that show promising were investigated by X-ray Diffraction (XRD) in a Philips X'Pert Pro X-ray diffractometer to determine their crystal structure and phase composition in different states. The morphology and additive distribution of the new materials were analyzed by Hitachi S3600N Scanning Electron Microscopy (SEM) with an Energy Dispersion Spectrometer (EDS). The composition of the dehydriding gas stream was analyzed by Pfeiffer ThermoStar Mass Spectrometer in the ambient environment.

3. Results and discussion

3.1 Dehydrogenation of the modified $LiBH_4$ materials

Fig. 1 is the comparison of the TPDs of the TiO_2 modified and commercial $LiBH_4$ samples. The commercial $LiBH_4$ decomposes starting from approximately 598 K at low rate. At about 723K, the decomposition rate appreciably accelerates, resulting in a final release of 9.5 wt% hydrogen at 873K. The dehydriding behavior of the 5-hour milled LiBH4 is same as no-milled. It appears that the ball milling alone does neither reduce the dehydriding temperature nor improve dehydriding rates. The modified materials $LiBH_4$ 75%+TiO_2 25% librates same amount of hydrogen, but starting from much low temperature, 473K for 5-10 hour milled samples and 448K for 20 hour milled one. The affect of the TiO_2 in reducing of dehydriding temperature is obvious. It is recognized that that extending milling time does little in reducing dehydriding temperature, but decreases

hydrogen capacity. For example, the 20-hour milled $LiBH_4$ 75%+TiO_2 25% releases 6.9 wt% hydrogen at 873K only. The possible reason will be discussed later in this paper.

In our initial investigation, eight oxides and chlorides have been added into $LiBH_4$ during ball milling. It is found that five additives such as TiO_2, $TiCl_3$, ZrO_2, V_2O_3 and SnO_2 to be effective for increasing the low temperature desorption rate and reducing the onset temperature for more rapid decomposition. In contrast with commercial $LiBH_4$, the materials $LiBH_4$75%+TiO_2 25% and 75%$LiBH_4$+V_2O_3 25% produce ~2-3X the amount of hydrogen at ~200 ^oC, show earlier onset of rapid decomposition, and release 9.2 wt% and 8.5 wt% hydrogen at 600^oC respectively, see Fig.1-2. The onset of noticeable low temperature desorption has also dropped to ~448K. The other three $LiBH_4$ materials modified by $TiCl_3$, ZrO_2 and SnO_2 also show the lower decomposition temperature, faster hydrogen desorption and larger dehydriding capacity at same temperatures than the commercial $LiBH_4$.

It is obvious that the additives play a significant role in enabling lower temperature hydrogen desorption. As well the modified borohydrides release more hydrogen than commercial borohydride at same temperature. Fedneva et al [5] investigated $LiBH_4$ by DTA. The thermogram of $LiBH_4$ showed three endothermic effects: at 108-112 ^oC, 268-286 ^oC and 483-492 ^oC. The endothermic effect at 108-112 ^oC is reversible and corresponds to the $LiBH_4$ polymorphic transformation. The second peak at 268-286^oC corresponds to the $LiBH_4$ fusion, accompanied by a slight decomposition, which librates approximately 2% of the hydrogen in the compound. The main evolution of gas starts at 380^oC and librates 80% in the hydrogen in $LiBH_4$. However, the cause of the small effect at 483-492^oC is uncertain, but it coincides with the liberation of 50% theoretic hydrogen content in $LiBH_4$. Zuttle [15] reports that about 50% hydrogen (~ 9 wt %) has been liberated from the SiO_2 catalyzed $LiBH_4$ at 320 ^oC. In our experiments, the same amount of hydrogen (~9 wt%) was released from the $LiBH_4$ materials modified by other oxides, but initiating at much lower temperature (~473K). It is proposed that the possible $LiBH_4$ dehydriding reaction is $2LiBH_4$ à $2LiH + 2B + 3H_2$ because LiH is very stable until 1173K [14,15]. This reaction librates 13.79 wt% of hydrogen from $LiBH_4$. Due to adding 25 wt% TiO_2, the hydrogen released from our modified material $LiBH_4$ 75%+TiO_2 25% will be 10.34 wt% theoretically. Practically, the average dehydriding capacity of our modified $LiBH_4$ materials that has 25wt% additives is about 9 wt%. It is understandable because some hydrogen was lost during ball milling due to the interaction of $LiBH_4$ and TiO_2. It will be discussed in the following XRD analysis section.

It is believed that reducing of the load of the additives will increase hydrogen desorption, but increase dehydriding temperature. Fig. 3 shows the dehydriding comparison of the materials $LiBH_4$ 75%+$TiCl_3$ 25% with $LiBH_4$ 90%+$TiCl_3$ 10%. As expected, the hydrogen desorption increased from 8.2wt% to 9.2wt% at 873K by reducing $TiCl_3$ load from 25% to 10%. However, the rapid dehydriding temperature increased from 373K to 523K. The reaction kinetics also suffers. The similar conclusion was made from the comparison of the materials $LiBH_4$ 75%+TiO_2 25% with $LiBH_4$ 90%+TiO_2 10% as Fig. 4 shown. Obviously, there is the trade off issue existed. More work is planned to seek the reasonable compromise.

The isothermal dehydriding properties of the material $LiBH_4$ 75%+TiO_2 25% is shown in Fig.5. There are two stages: the fast kinetics in the first short period and very slow kinetics afterward. For example, the material desorbed about 8.0wt% hydrogen within the first 100 minutes at 773K. But, the desorption lasts about 10 hours before the reaction completely by adding 0.5wt% hydrogen in total 8.5wt% desorption. It may attribute to the slow motion of boron after most $LiBH_4$ decomposed. The nanostructured materials with some effective promoters are being investigated for increase of the kinetics in the second stage. The material desorbs about 4.5wt% and 1.5wt% hydrogen at 573K and 473K respectively. The desorption is the temperature dependable process. The results of the temperature dependence in both stages are determined and plotted in Fig. 6. The Arrhenius plot shows that the desorption kinetics follow thermally activated behavior illustrated by the equation: $dC/dt = k_o \exp(-Q/RT)$.

3.2 Rehydrogenation of the modified $LiBH_4$ materials

In Muller's work [14], the modified material $LiBH_4$ 90wt% +Al 10wt% desorbs 12.4wt% hydrogen at 723K within 12 hours in the first dehydriding, but the dehydrided material was not able to be recharged in its original capacity. The second dehydriding produced 5wt% hydrogen only. The effect of the second rehydrogenation was almost negligible by gaining 0.6 wt% hydrogen only. To verify the dehydriding-rehydriding cycling stability the modified borohydrides, the material $LiBH_4$ 75%+TiO_2 25% was selected for repeat hydriding and dehydriding tests. After dehydriding at 873K for one hour, the materials $LiBH_4$ 75%+ TiO_2 25% and $LiBH_4$ +V_2O_3 25% were rehydrogenated at 873K and 10MPa. As Fig.7 shows, the dehydrided materials $LiBH_4$+ TiO_2 25% and $LiBH_4$ +V_2O_3 25% absorb 7.8 wt% and 7.9 wt% hydrogen within 45 minutes. The rehydrogenation capacity was above 8 wt% if absorption time was prolonged to one hour. This proves that the new $LiBH_4$ materials are reversible. Obviously, the rehydriding temperature and pressure are still high. However, it is believed that the lower conditions are achievable by optimizing compositions and changing the thermodynamic stability of the modified $LiBH_4$ materials. The Fig. 8 shows the repeated isothermal rehydrogenation of the material $LiBH_4$ 75%+ TiO_2 25% at 873K and 7MPa. It brings our attention that the hydrogen absorption capacity decreases from 8.25wt% to 5.6wt% and 4.2 wt% in the second and the third hydrogenation respectively. To find the possible causes, the XRD and mass spectrum analysis were conducted.

3.3 XRD analysis of the modified and non-modified $LiBH_4$ materials

To identify the phase composition during dehydrogenation and rehydrogenation, the material $LiBH_4$ 75%+TiO_2 25% has been investigated by XRD at three different states: ball-milled, dehydrided, and rehydrided. For reference, the XRD of the raw $LiBH_4$ (as received) and the 5-hour ball milled $LiBH_4$ have been performed as well.

3.31 $LiBH_4$ as received and after ball milling

Fig.9 shows the XRD pattern of as-received commercial $LiBH_4$. After 5 hours ball milling without any additive, there is no significant structure change rather than the slight broaden peaks caused possibly by the mechanical stress and crystal size reduction, see Fig.10.

3.3.2 $LiBH_4$ 75%+TiO_2 25% after ball milling

Fig.11 shows the XRD of the material $LiBH_4$ 75%+TiO_2 25% ball milled for 5 hours. It shows the structure change. The TiO_2 is partially changing its crystal structure from anatase to rutile. Beside the expected $LiBH_4$ and TiO_2, there are traces of TiB_2 and LiB_3O_5 formed through the possible interaction between $LiBH_4$ and TiO_2 during ball milling. The XRD confirmed the partial $LiBH_4$ decomposition and combination of Ti with B. It is important to point out that the intermediate compound TiB_2 dispersed within matrix might facilitate the reversible dehydriding - rehydriding reaction. It may play the role as the "bridge" in B-H bond dissociation and recombination process. However, the additive TiO_2 reduces the hydrogen capacity because of the extra "no-hydrogen" weight loading and the hydrogen release during interaction of $LiBH_4$ and TiO_2. The material $LiBH_4$ 75% + TiO_2 25wt% can be expressed as $LiBH_4$-0.09TiO_2. Based on this molecular ratio, the most $LiBH_4$ is not able to react with TiO_2 during ball milling. In most case of our measurements, the oxide/chloride-modified $LiBH_4$ materials desorb 8~9 wt% hydrogen that equals to half of the theoretic capacity of $LiBH_4$.

After 20 hours of ball milling, the material appears as same as 5 hours milled one that consists of the $LiBH_4$, TiO_2, TiB_2 and trace of LiB_3O_5. The reduced intensity and the peak broadening in XRD spectrum may correspond to an average grain size reduction and increase in the short-range disorder, see Fig.12. To understand the reversible reaction path and the role of the additives, the 20 hours ball milled material $LiBH_4$ 75%+TiO_2 25% is selected for XRD examination in dehydrided and rehydrided states respectively.

3.3.3 $LiBH_4$ 75%+TiO_2 25% after dehydriding

The XRD of the dehydrided material $LiBH_4$ +TiO_2 25% is shown in Fig.13. It appears that the $LiBH_4$ decomposes to LiH, LiOH, TiB_2 and trace of Ti_7B_6 during hydrogen evolution. The additive TiO_2 disappears. The XRD spectrum does not indicate the visible existence of boron as the reaction $2LiBH_4 \grave{a}\ 2LiH + 2B + 3H_2$ suggested [13]. More likely, $LiBH_4$ may have certain interaction with TiO_2 resulting in formation of LiH, LiOH and, more meaningfully, the intermediate compounds such as TiB_2. It is possible that the some boron segregates from $LiBH_4$ as the amorphous clusters without reaction with titanium. The intermediate phases may make the dehydrogenation reversible at relatively moderated conditions. The hypothesis of the reversible reaction is given as $6LiBH_4 + 2TiO_2 \grave{a}\ 2LiH + 4LiOH + 2TiB_2 + 2B + 9H_2$. The additive TiO_2 contribution may attribute to form intermediate boron compounds that promote low temperature dehydriding and the reversibility. It is not our intention to prove the mechanism using the limited data in this paper. We don't have reasonable interpretation on possible existence

of compound Ti_7B_6. But, more material characterizations and particularly designed experiments have been planed. We'll report our results later.

3.3.4 $LiBH_4$ 75%+TiO_2 25% after rehydriding

The XRD of the rehydrided material $LiBH_4$+TiO_2 25% is shown in Fig.14. The intensities of the identifiable peaks are very low that indicates the materials either in short range disorder or in amorphous states. The recombined $LiBH_4$ is not detectable in our XRD experiments although its existence is evidenced by our rehydriding and following dehydriding measurements (Fig. 5, Fig 7-8). It is believed that the recombined LBH_4 is in amorphous state. The visible peaks are identified as the TiB_2, Li_7B_6 and possible Li_3BO_3. The additive TiO_2 is no identifiable in XRD spectrum of the rehydrided material. However, the intermediate compound TiB_2 persists in both states, dehydrided and rehydrided. It is interested to realized that the TiO_2 partially decomposes during the ball milling and completely decomposes and formed TiB_2 during dehydriding. The intermediate compounds derived from oxide and chloride additives, such as TiB_2 in $LiBH_4$ 75%+TiO_2 25%, may play the key role in reducing decomposition temperature and provide reversibility for lithium borohydride materials.

3.4 SEM and EDX mapping of the modified material $LiBH_4$ 75%+TiO_2 25%

To verify the decomposition of the additive TiO_2, SEM and EDX mapping were carried out. The morphology of the material $LiBH_4$ 75%+TiO_2 25% synthesized by 5-hour ball milling is shown in Fig 15. In high magnification, it is estimated that the average particle size is about 2~3 μm with agglomeration. The Ti, B and O element maps indicate that the TiO_2 is mixed with $LiBH_4$ matrix homogenously with no segregation (see Fig.16). After dehydriding at 873K, the material shows its porous feature with coarsen particles size due to re-crystallization, see Fig.17. The maps show that the titanium segregates with oxygen and may combine with boron as XRD data suggested, see Fig. 18. The rehydrogenation at 873K and 7MPa produces layered material (Fig.19). The disassociation of titanium and oxygen through the decomposition of TiO_2 is observed clearly in the Ti, B and O element maps (Fig.20).

3.5 Mass spectrum analysis of the gas stream from decomposition of the material $LiBH_4$ 75%+TiO_2 25%

The mass spectroscope indicates that the gas stream of decomposition of the material $LiBH_4$ 75%+TiO_2 25% consists of the hydrogen mainly with the trace of BH_3 and H_2O, see Fig. 21. The H_2O most likely comes from moisture absorption during sample transfer. But, the BH_3 formation, even trace, causes permanent lose of the boron resulting in graduate decrease of the hydrogen storage capacity during dehydriding-rehydriding cycling. Similar conclusion can be applied to NH_3 formation in $LiNH_2$+LiH system. However, it is believed that the formation of BH_3 can be prevented by change the reaction path using suitable additives.

4. Conclusions

The modified LiBH$_4$ by additives such as metal oxides and chlorides reduces the hydrogen desorption temperature from 673K to 473K. The modified lithium borohydrides desorb about 9 wt% hydrogen and can be recharged to 7-9 wt% hydrogen capacity at 873K and 7 MPa reversibly. Five effective additives have been identified. The materials characterization shows that the additive reacts with lithium borohydride and produces the intermediate compound that facilitates the reversible reaction at relatively moderate conditions. The reversible hydrogen storage capacity of the oxide modified lithium borohydrides decreases gradually during hydriding-dehydriding cycling. One of the possible reasons is the loose of the boron in forming of BH$_3$ within the hydrogen stream during dehydrogenation. It is expected that the boron loose can be prevented by select the suitable additive, form intermediate boron compounds and change the reaction path. While the additives reduce dehydriding temperature and improve the reversibility, it also reduces the hydrogen storage capacity. The best compromise can be reached by optimization of the additive loading. The extended ball milling does little in improve dehydriding performance, but reduce the reversible capacity. It is believed that the additives change the thermal stability of the lithium borohydrides in some degree. It is realized that the other modifiers such metals, metal hydrides, other complex hydrides beside the oxides and chlorides may change the B-H binding energy resulting in the reversible dehydriding and rehydriding at reasonable moderate conditions. The research work on destabilizing lithium borohydrides has been conducting. The detail results will be reported later.

Acknowledgement

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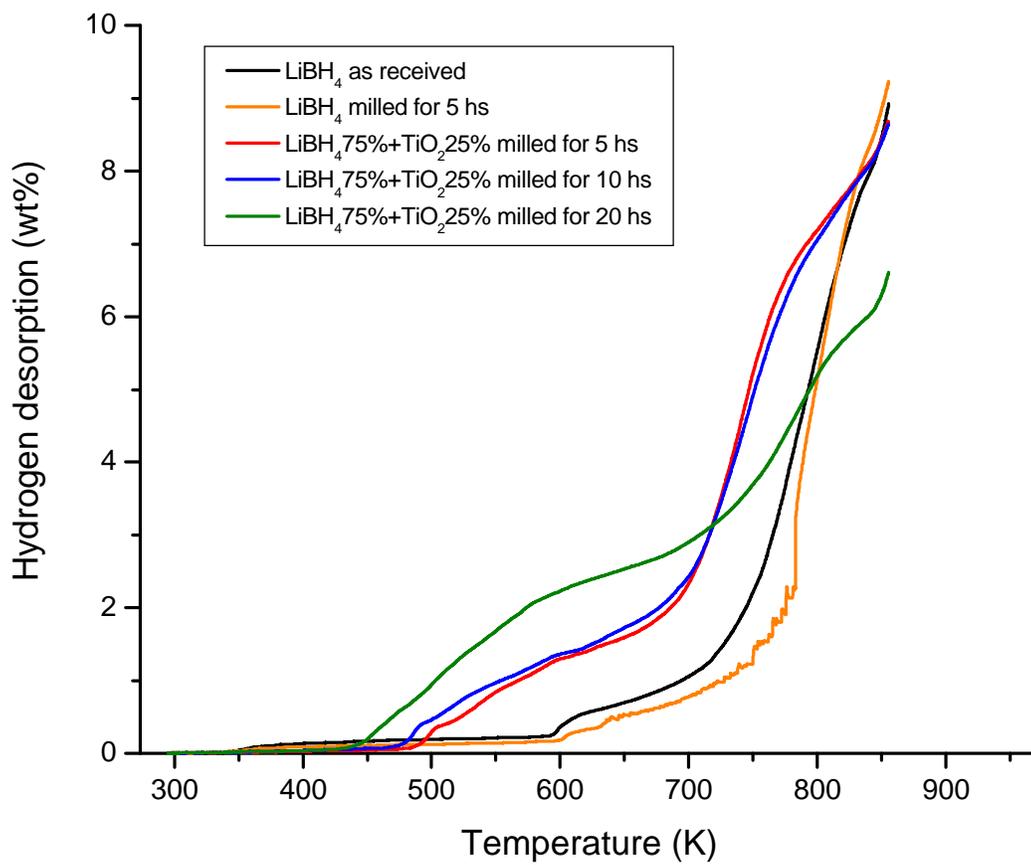
Fig.1. TPD of the commercial LiBH$_4$
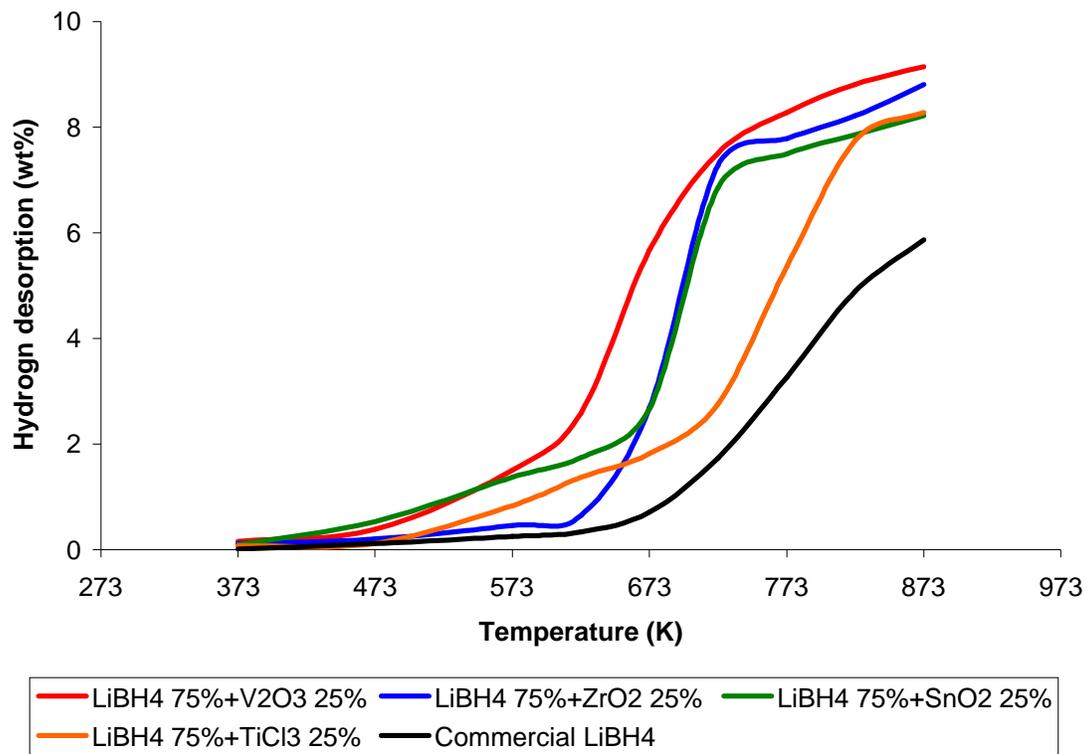
Fig.2　The comparison of other modified LiBH$_4$ materials with the commercial LiBH$_4$
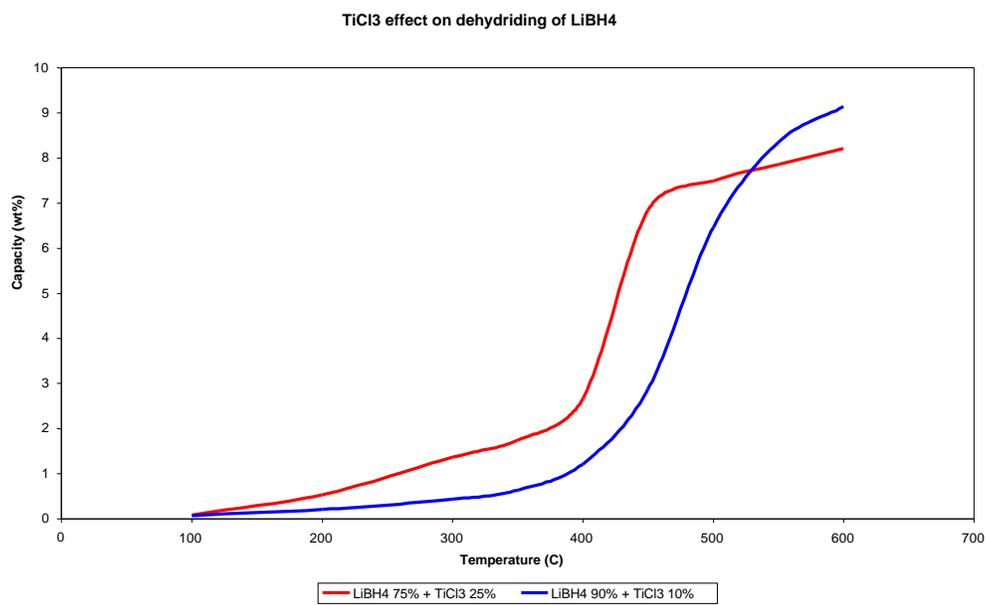
Fig.3 The effect of the additive TiCl$_3$ on dehydrogenation behavior of LiBH$_4$
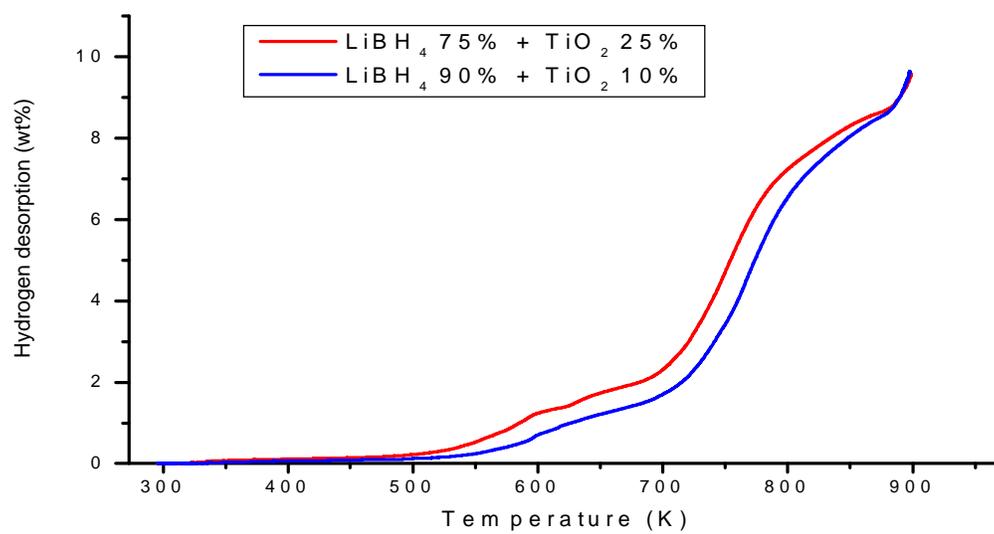
Fig.4 The effect of the additive TiO_2 on dehydrogenation behavior of $LiBH_4$
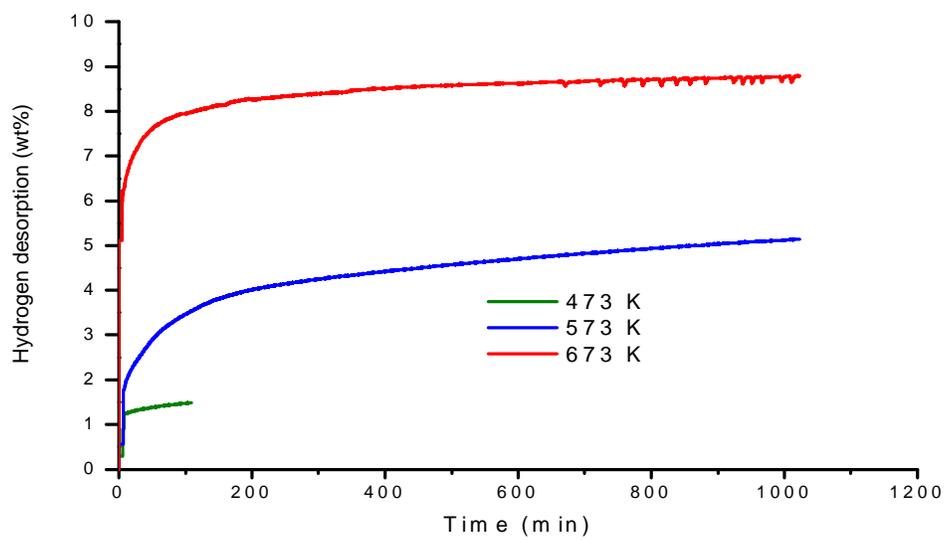
Fig. 5 Dehydrogenation of LiBH$_4$ 75%+TiO2 25% at 473K, 573K and 673K
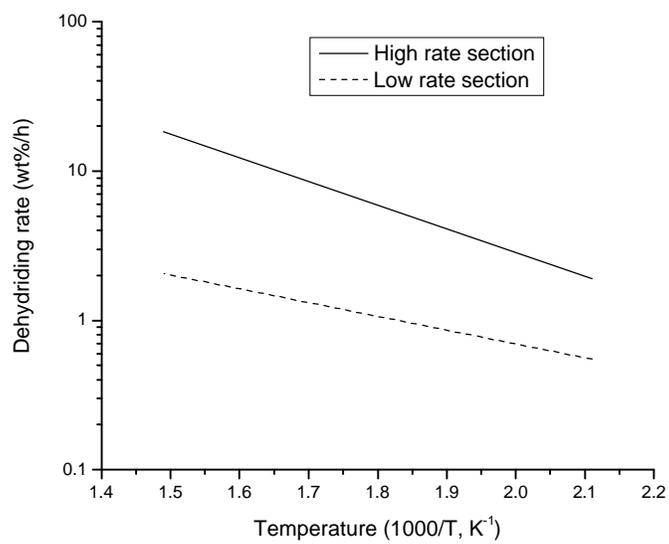
Fig. 6 Arrhenius dehydriding plots of LiBH$_4$ 75%+TiO2 25% for the fast and slow rate
stages.

Rehydriding of LiBH$_4$ at 873K and 10 MPa
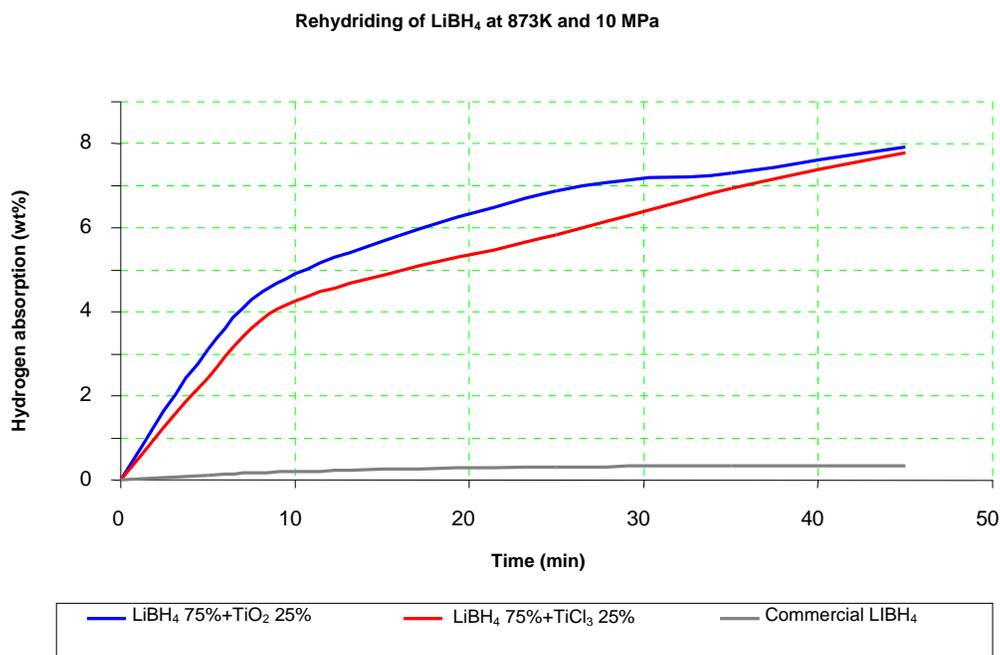
Fig. 7 Hydrogen absorption of the dehydrided materials LiBH$_4$ 75%+ TiO$_2$25% and LiBH$_4$75%+V$_2$O$_3$25%
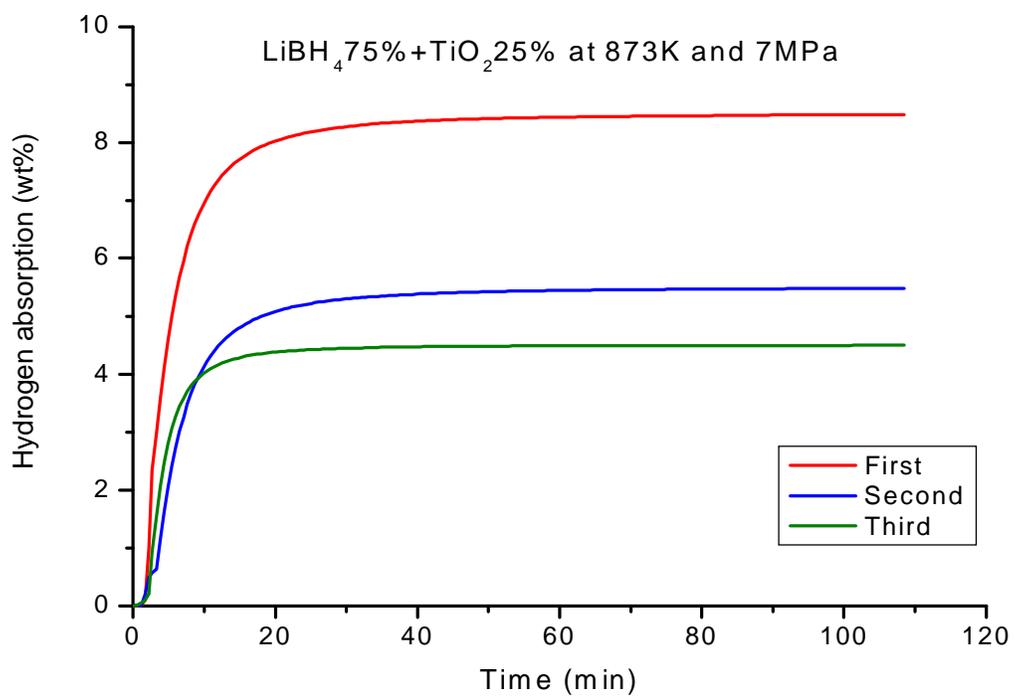
Fig.8 The isothermal hydrogen absorption of the material $LiBH_4$ 75%+TiO_2 25%
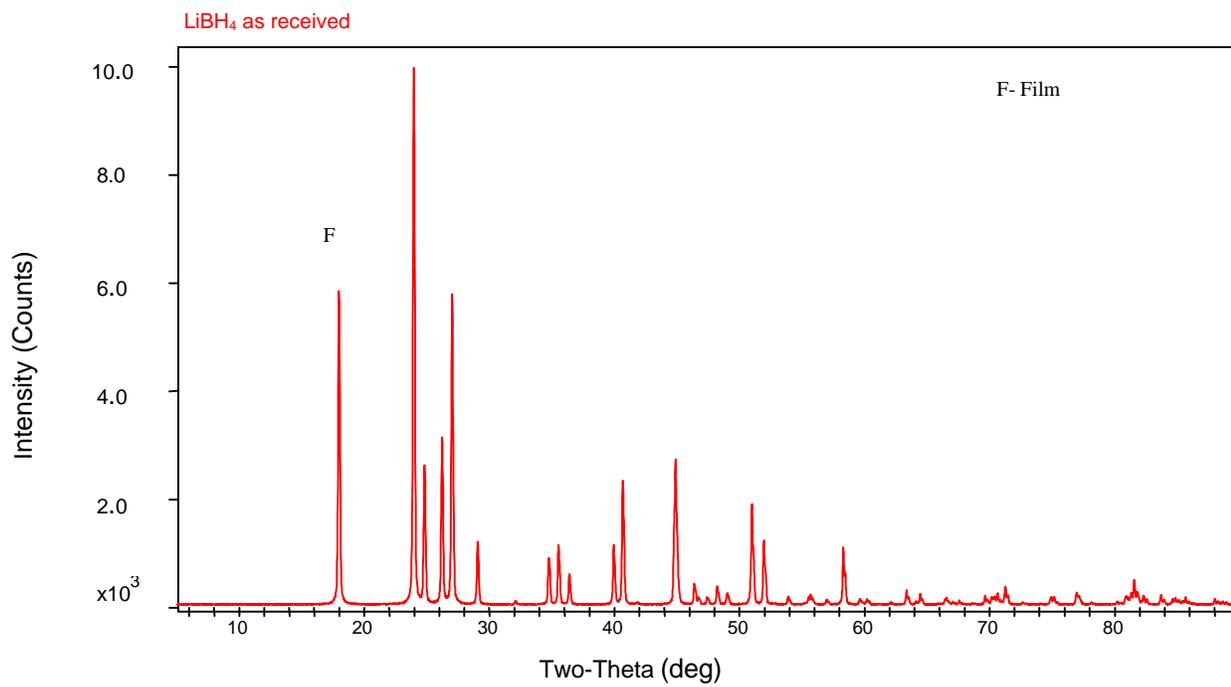
Fig. 9 The XRD of the borohydride LiBH$_4$ as received
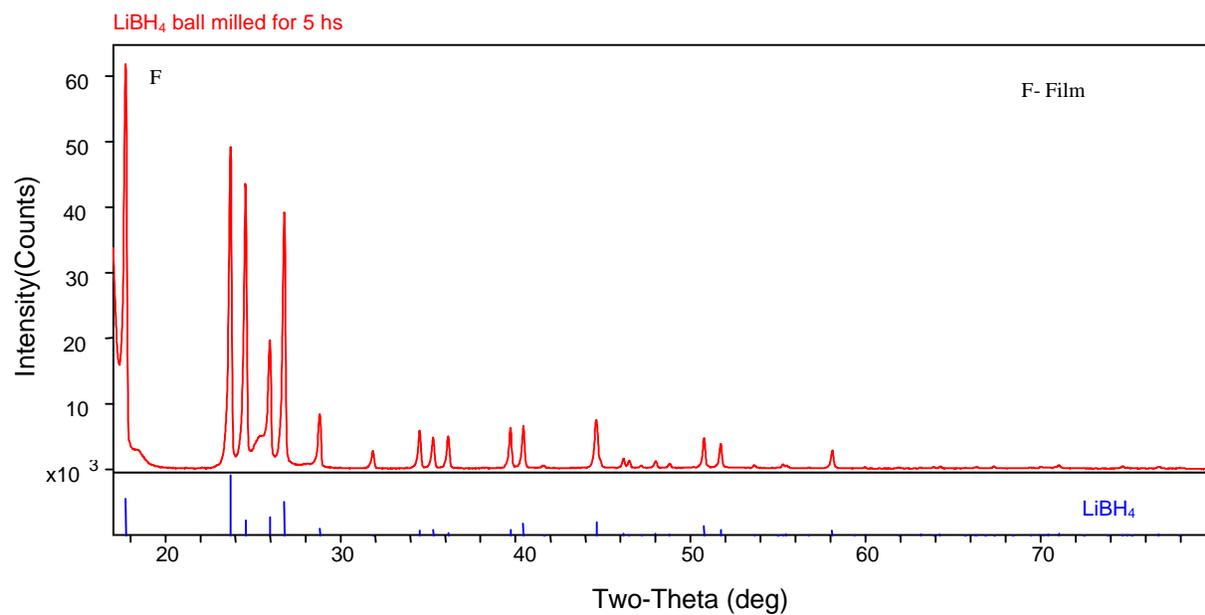
Fig.10 The XRD of commercial LiBH$_4$ ball milled for 5 hours
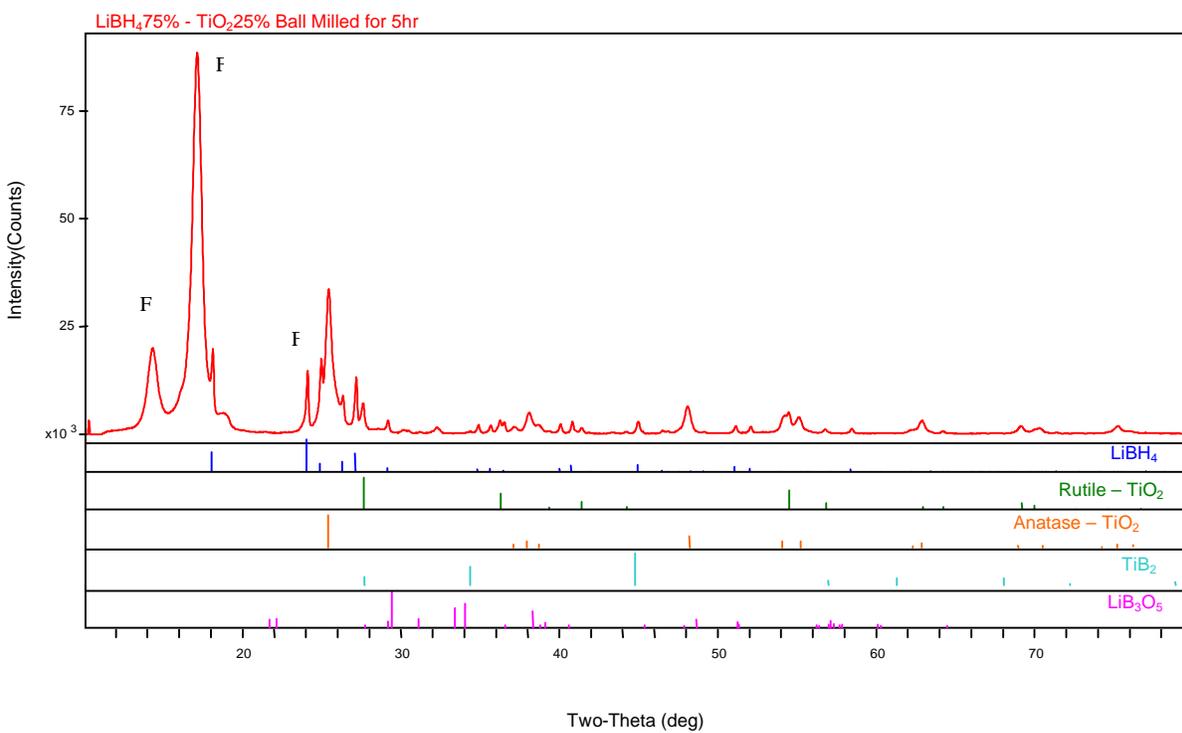
Fig. 11 The XRD of $LiBH_4$ 75%+TiO_2 25% ball milled for 5 hours
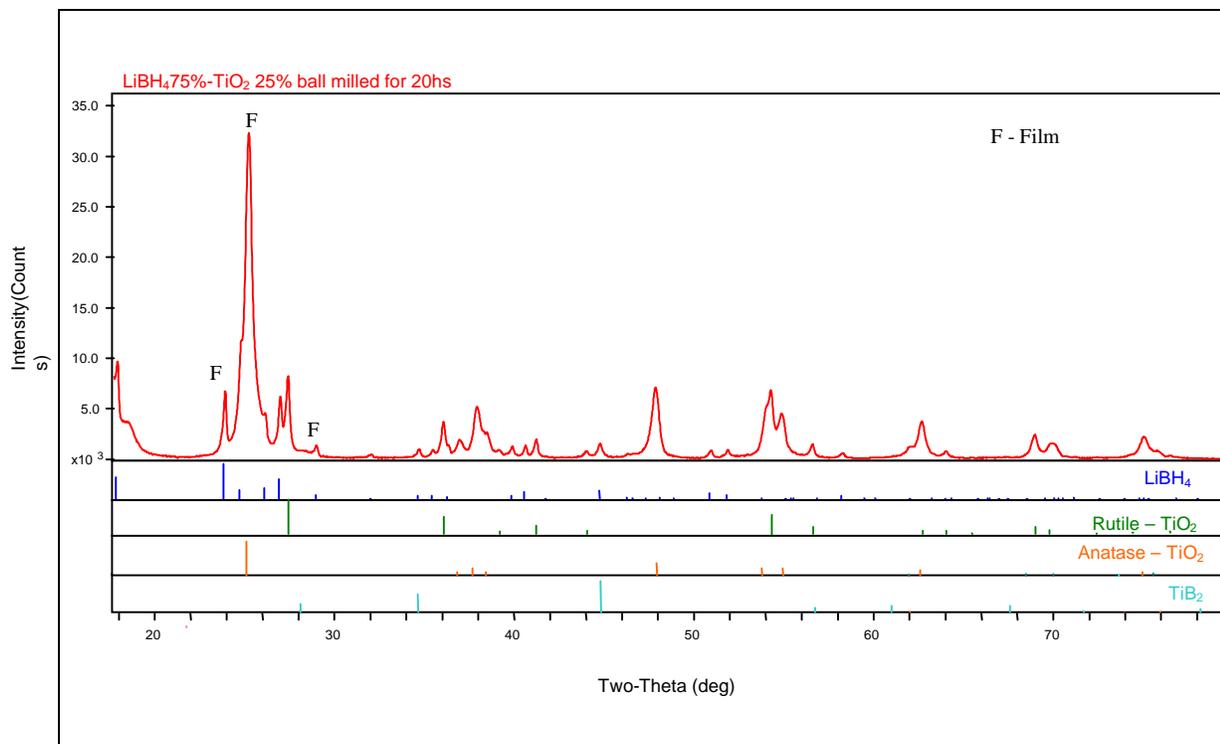
Fig. 12 The XRD of LiBH$_4$ 75%+TiO$_2$ 25% ball milled for 20 hours

Fig.13 The XRD of the dehydrided $LiBH_4$ 75%+TiO_2 25%
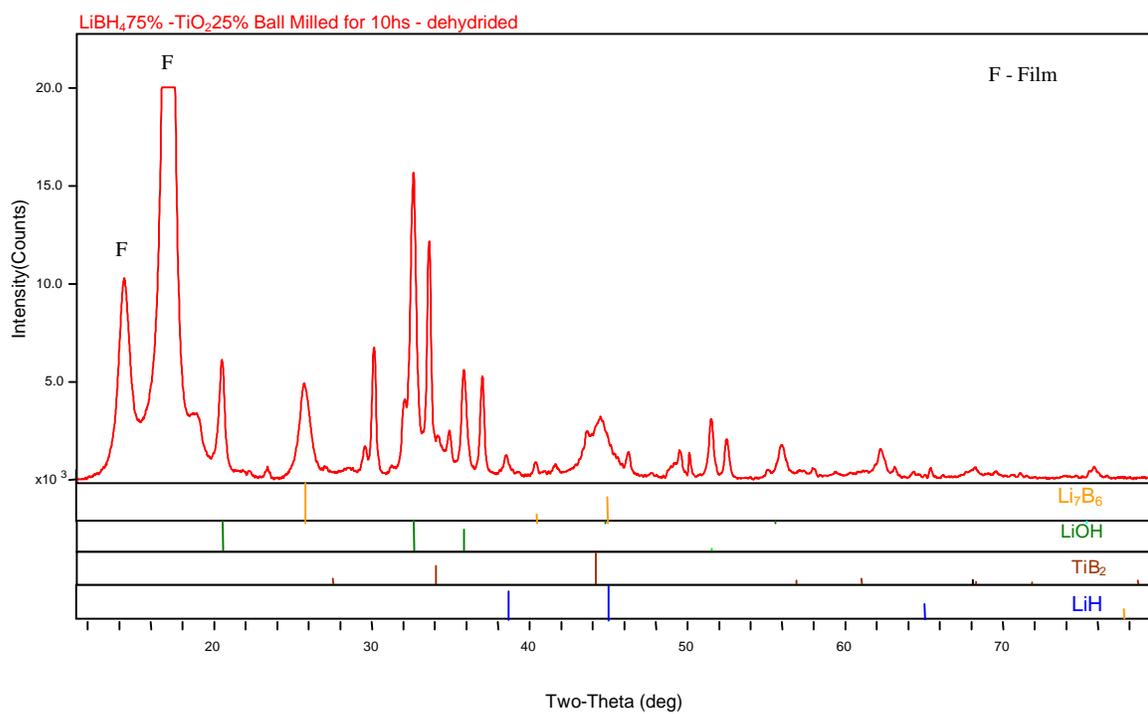
Fig.14 The XRD of the rehydrided LiBH$_4$ 75%+TiO$_2$ 25%
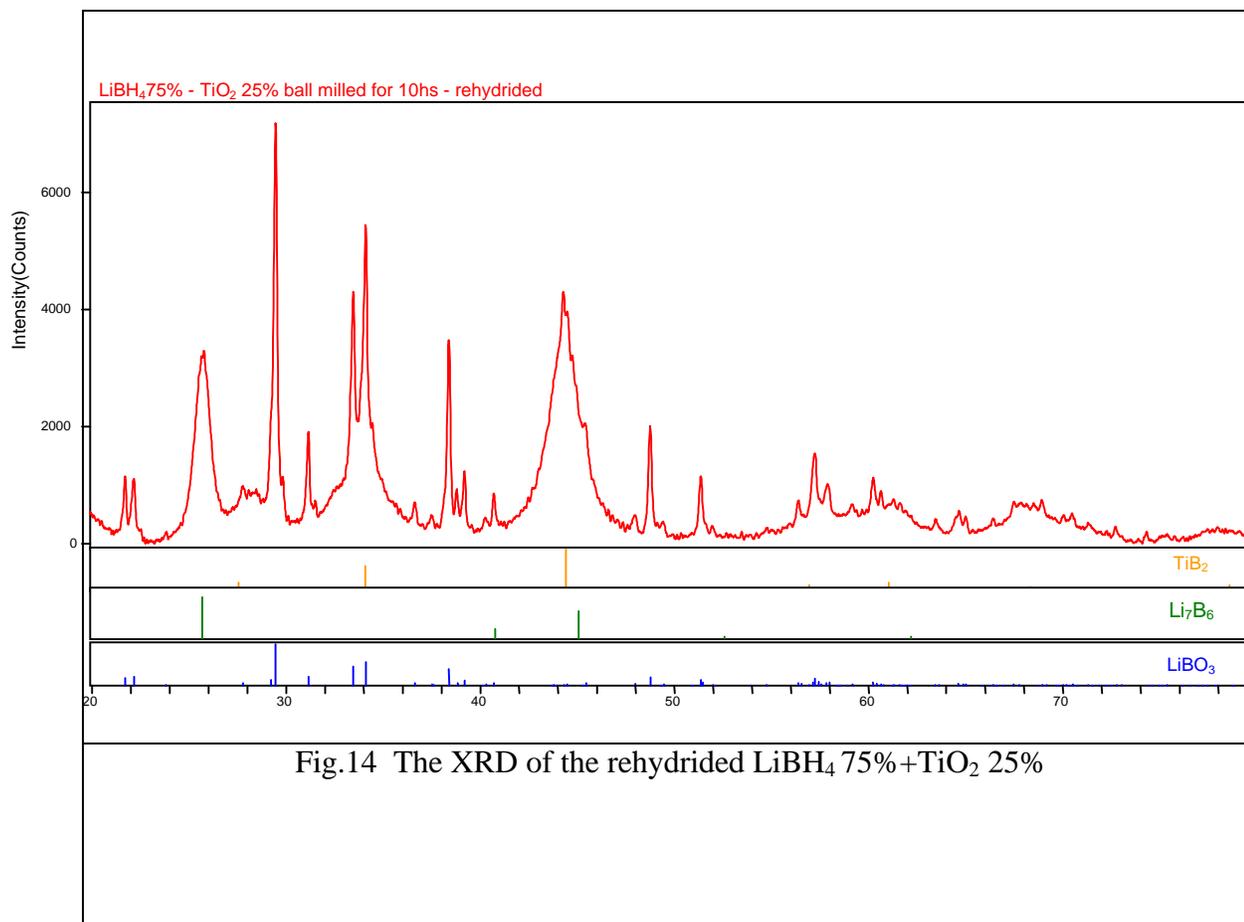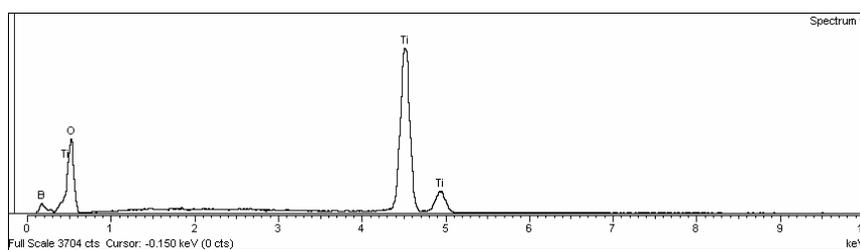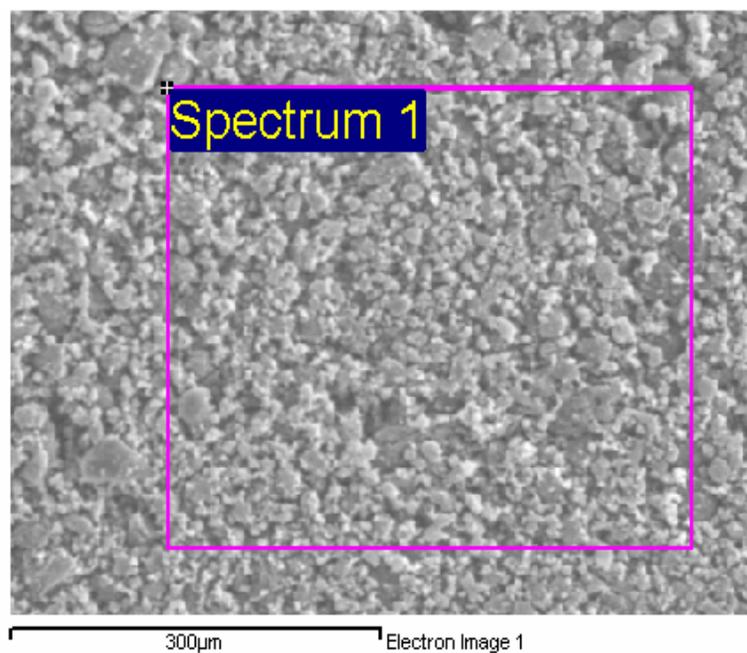
| Element	Weight%	Atomic%
B K	26.76	42.31
O K	44.35	47.38
Ti K	28.89	10.31
Totals	100.00	

Fig. 15 The SEM morphology and Ti-B-O mapping of LiBH$_4$ 75%+TiO$_2$ 25% as synthesized by 5-hour ball milling (X 200)
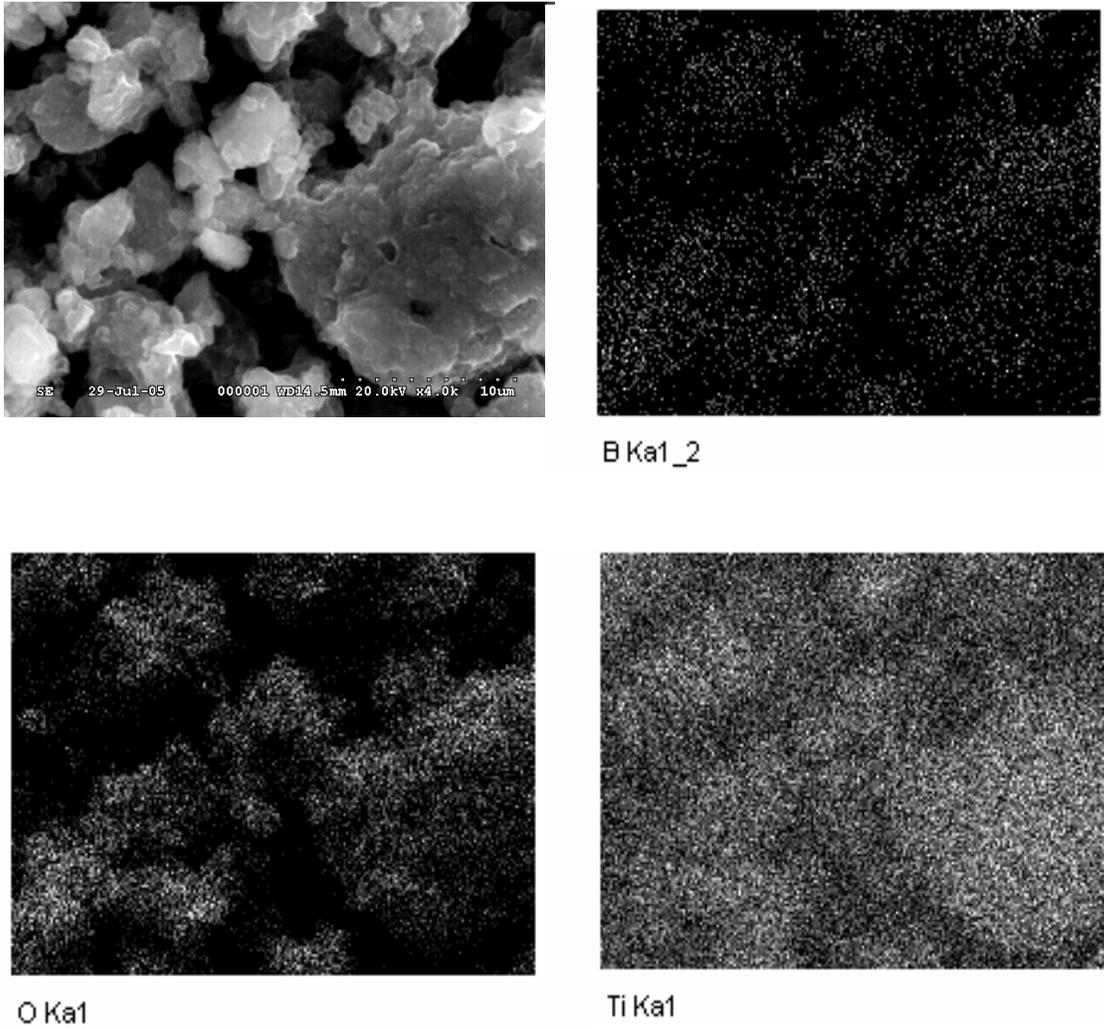
Fig. 16 The SEM morphology and Ti-B-O mapping of LiBH$_4$ 75%+TiO$_2$ 25% as synthesized by 5-hour ball milling (X 4000)
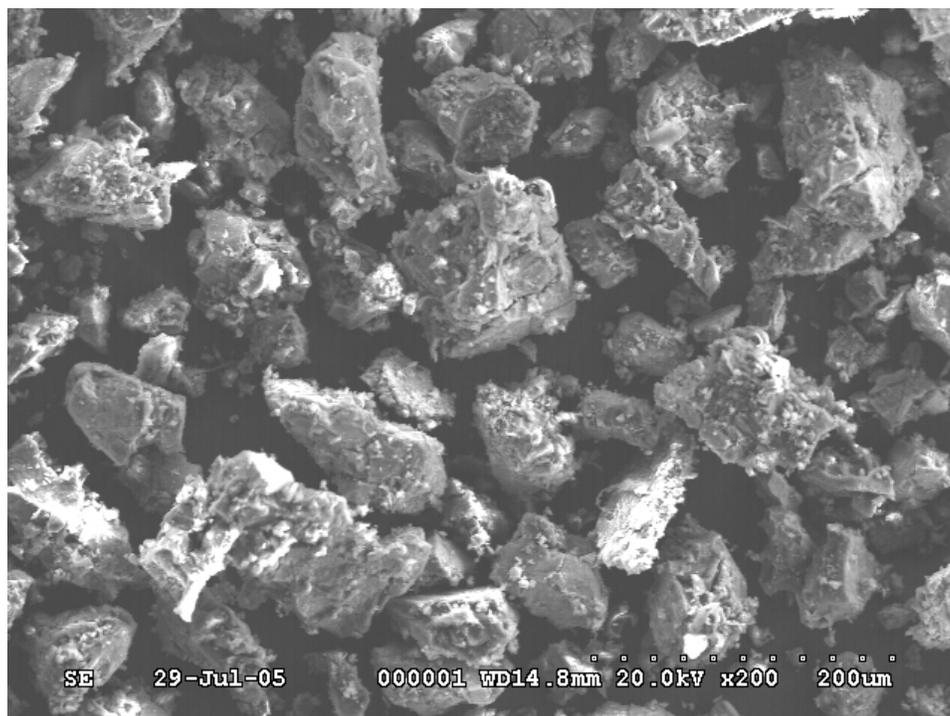
Fig. 17 The SEM morphology of the dehydrided LiBH$_4$ 75%+TiO$_2$ 25% (X200)
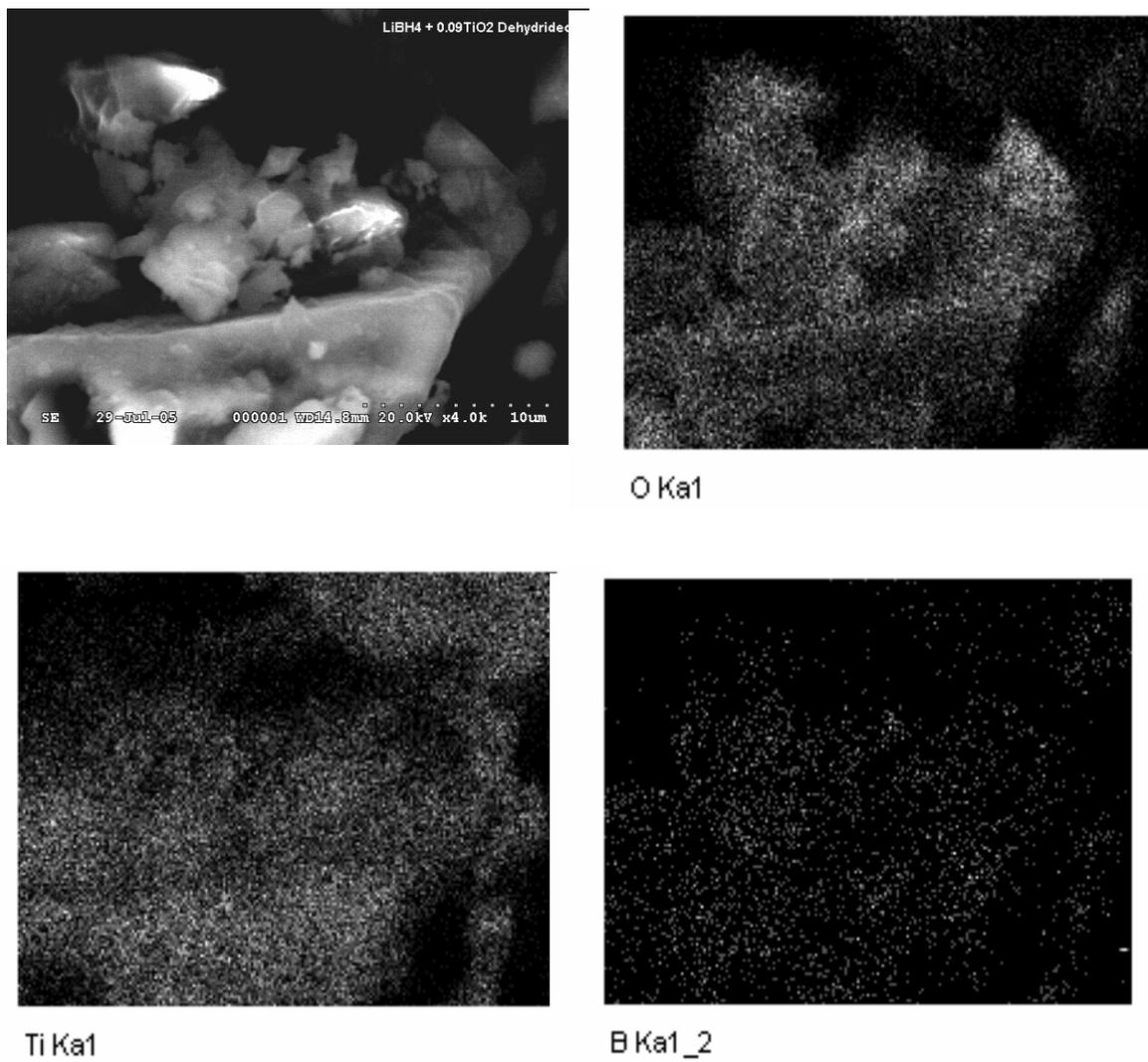
Fig. 18 The SEM morphology and Ti-B-O mapping of the dehydrided LiBH$_4$ 75%+TiO$_2$ 25% (X 4000)

LiBH $_4$ Pyrolysis Mass Spectra
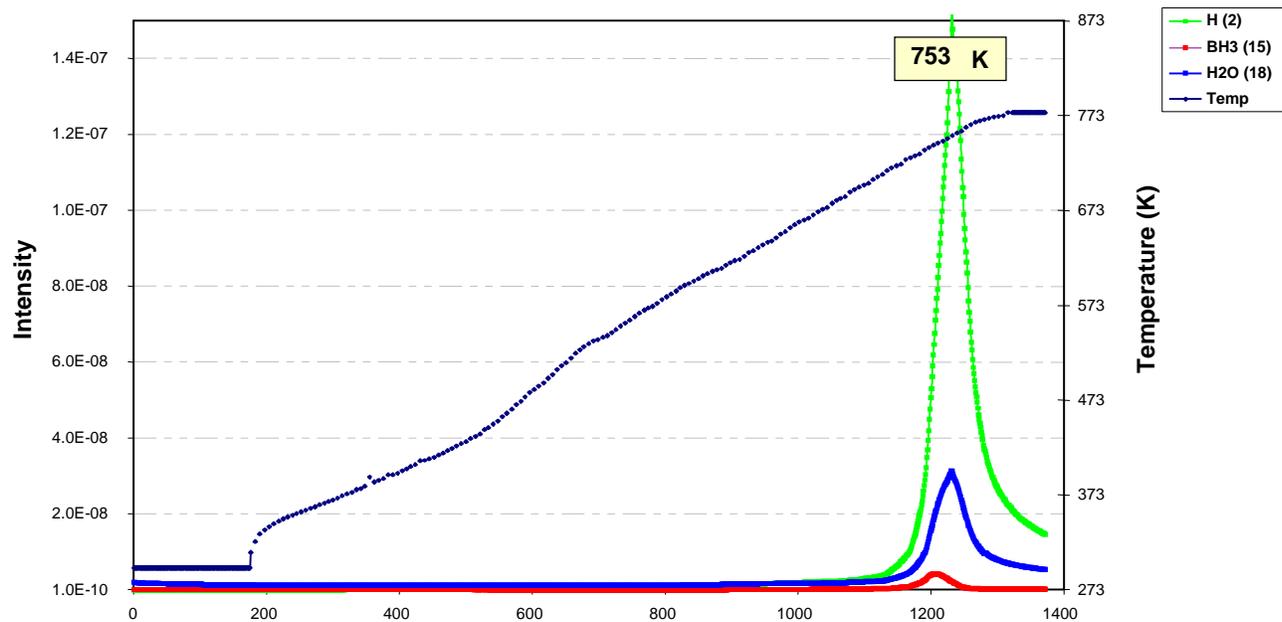
Fig. 21 The mass spectra of thermal decomposition of the material LiBH$_4$ 75%+TiO$_2$ 25%