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The Stability and Reversibility of Metallic Borohydrides

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Abstract

In effort to develop reversible metallic borohydrides with high hydrogen storage capacity and low dehydriding temperature, several new materials have been synthesized by modifying $LiBH_4$ with various metal halides and hydrides. The investigation shows that the halide modification effectively reduced the dehydriding temperature through ion exchange interaction. The effective halides are $TiCl_3$, TiF_3, ZnF_2 and AlF_3. The material $LiBH_4$+0.1TiF_3 desorbs 3.5wt% and 8.5wt% hydrogen at 150°C and 450°C respectively. It re-absorbed 6wt% hydrogen at 500°C and 70 bar after dehydrogenation. The XRD of the rehydrided samples confirmed the formation of $LiBH_4$. It indicates that the materials are reversible at the conditions given. However, a number of other halides: MgF_2, $MgCl_2$, $CaCl_2$, $SrCl_2$ and $FeCl_3$, did not reduce dehydriding temperature of $LiBH_4$ significantly. TGA-RGA analysis indicated that some halide modified lithium borohydrides such as $LiBH_4$+0.1ZnF_2 evolved diborane during dehydrogenation, but some did not such as $LiBH_4$+0.1$TiCl_3$. The formation of diborane caused unrecoverable capacity loss resulting in irreversibility. It is suggested that the lithium borohydrides modified by the halides containing the metals that can not form metal borides with boron are likely to evolve diborane during dehydriding. It was discovered that halide modification reduces sensitivity of $LiBH_4$. The materials such as $LiBH_4$+0.1$TiCl_3$ and $LiBH_4$+0.5$TiCl_3$ can be handled in open air without visible reaction.

Key words: Borohydride, Hydrogen storage, Reversibility, Stability, Rehydrogenation

1. INTRODUCTION

$LiBH_4$ has high hydrogen content gravimetrically (18.4 wt%) and volumetrically (121 kg/m^3). Unfortunately, releasing the hydrogen from $LiBH_4$ needs the temperature above 400°C and the rehydrogenation requires high temperature (650°C) and pressure (190 bars) [1]. A great interest has been generated to develop borohydride materials for reversible hydrogen storage recently. Most of published papers reported how reduce dehydriding temperature (destabilization) by mixing $LiBH_4$ with additives [2-8]. There are a few reports providing the rehydrogenation data [9-12]. It is largely due to irreversibility of the materials after dehydrogenation. In the early years and recent, several metallic borohydrides with lower dehydriding temperature such as $Zr(BH_4)_2$, $Mn(BH_4)_2$, $Mg(BH_4)_2$ and $Al(BH_4)_3$ have being synthesized and investigated [13-19]. Unfortunately, the materials are irreversible in most case – either decomposes at ambient temperature or release significant amount of diborane during dehydrogenation. From our

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previous investigation on modified $LiBH_4$, it is believed that the reversibility is determined by the stability. In this paper, we will report the results of our study on relationship of stability and reversibility of different metallic borohydrides.

2. EXPERIMENT DETAILS

The $LiBH_4$ (95% purity) and the additives $TiCl_3$, TiF_3, AlF_3, $ZnCl_2$, $FeCl_3$, $MgCl_2$, MgF_2, $SrCl_2$, $CaCl_2$ and TiH_2 (99.9-99.99% purity) were purchased from Sigma-Aldrich and used directly without any pre-treatment. Two grams of the appropriate $LiBH_4$ and additive powder mixture were placed in a 45 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 500 rpm milling. After milling, 0.5 grams of the modified $LiBH_4$ powders were transferred to a Sieverts apparatus, a volumetric device with 5 mbar back pressure for temperature programmed desorption (TPD) measurement. The temperature was ramped up from ambient to 500^{o}C at a rate of 5^{o}C/min. The rehydriding were conducted at 500^{o}C and 70 bar (99.9999% hydrogen) in the same Sieverts apparatus following TPD. The hydrogen absorption and desorption capacities were calculated based on the whole weight of the modified borohydrides including the weight of additives.

Selected modified borohydrides were investigated by X-Ray Diffraction analysis (XRD) in a Panalytical X'Pert Pro X-ray diffractometer to determine the changes of their crystal structure and phase composition in different states – as synthesized, dehydrided and rehydrided. A SRS RGA-300 Residual Gas Analyzer (RGA) coupled with Perkin Elmer's Pyris-1 Thermal Gravimetric Analyzer (TGA) measured the weight loss and simultaneously analyzed the composition of the gas evolved during thermal desorption of the borohydrides. Five milligram of borohydride sample was loaded in the TGA in each measurement. Research grade Argon with a purity of O_2<0.1ppm, H_2<0.1ppm, H_2O<0.5ppm, N_2<0.1ppm, THC<0.1ppm and ($CO+CO_2$) < 0.1 ppm was passed at 60 ml/min from TGA through 1/8" OD PEEK^{TM} tubing to RGA instruments. The target evolving gases monitored by RGA were $H_2O(18)$, $H_2(2)$, $O_2(32)$ and $B_2H_6(26)$ represented by a single mass line in the spectra.

3. RESULTS AND DISCUSSION

3.1 Commercial $LiBH_4$

To establish the baseline for objective comparison, the commercial $LiBH_4$ was ball milled for one hour under argon atmosphere. Then, the ball milled $LiBH_4$ was investigated by TGA-RGA. The results show that it started decomposing from 300^{o}C and lost 12% weight up to 500^{o}C (Fig.1). The RGA shows that the weight loss attributes to hydrogen evolution. The most hydrogen was released at above 400^{o}C. There is no diborane detected from TGA purging gas. A small water vapor detected may come from reaction of hydrogen with oxide components in RGA chamber or hydrated water as one of impurities in commercial lithium borohydride (95% pure).

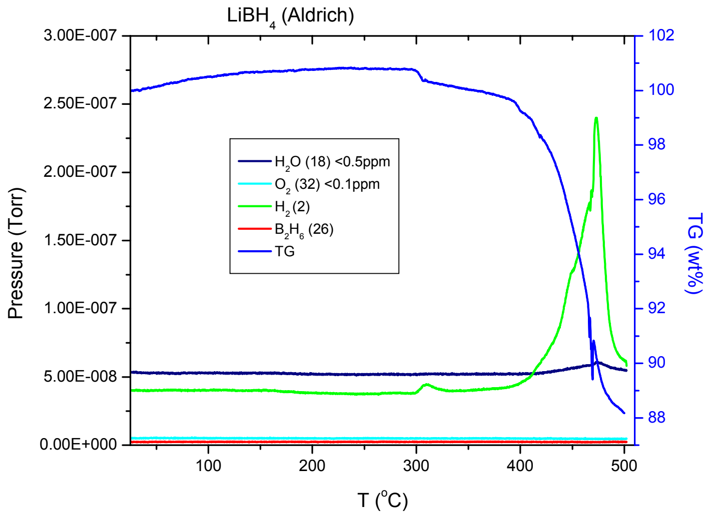

Fig.2 TGA-RGA spectra of the ball milled $LiBH_4$

The dehydriding and rehydriding properties of the ball milled $LiBH_4$ was also investigated by Sieverts apparatus. The results show that it desorbed 12% hydrogen from 300°C to 600°C (Fig.2). After dehyidring, it absorbed 7wt% hydrogen at 600°C and 70 bar (Fig.3).

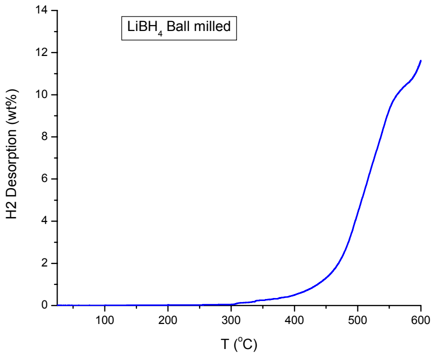

Fig.3 Hydrogen desorption of the ball milled $LiBH_4$

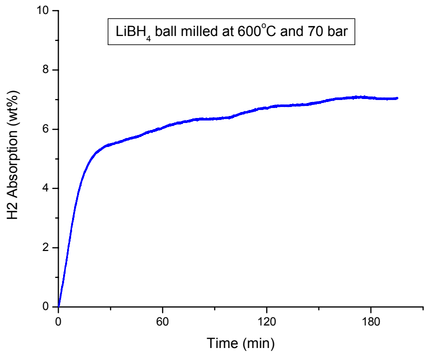

Fig.4 Hydrogen absorption of the ball milled $LiBH_4$

3.2 Materials $LiBH_4$+0.1TiH_2 and $LiBH_4$+0.5TiH_2

To verify if TiH_2 can react with $LiBH_4$ and release hydrogen at lower temperature as a theoretic model of $2LiBH_4+TiH_2 \rightarrow 2LiH+TiB_2+4H_2$ predicted (ΔU_0=22.2 kJ/molH_2) [20], the materials $LiBH_4$+0.1TiH_2 and $LiBH_4$+0.5TiH_2 were synthesized through five hour ball milling. The results showed that TiH_2 did not reduce dehydriding temperature of $LiBH_4$. The TPDs of $LiBH_4$+0.1TiH_2 and $LiBH_4$+0.5TiH_2 are almost same as the commercial $LiBH_4$ (Fig.5). Corresponding to TPD, TGA result shows that 10 wt% of hydrogen was released from 300°C through 500°C. RGA did not detect B_2H_6. (Fig.6) XRD results show that the TiH_2 did not react with $LiBH_4$ after five hour ball milling (Fig.7). The material appears a mechanical mixture. The materials $LiBH_4$+0.1TiH_2 and $LiBH_4$+0.5TiH_2 were partially reversible and absorbed 4.5wt% hydrogen at 500°C and 70 bars after dehydrogenation (Fig.8).

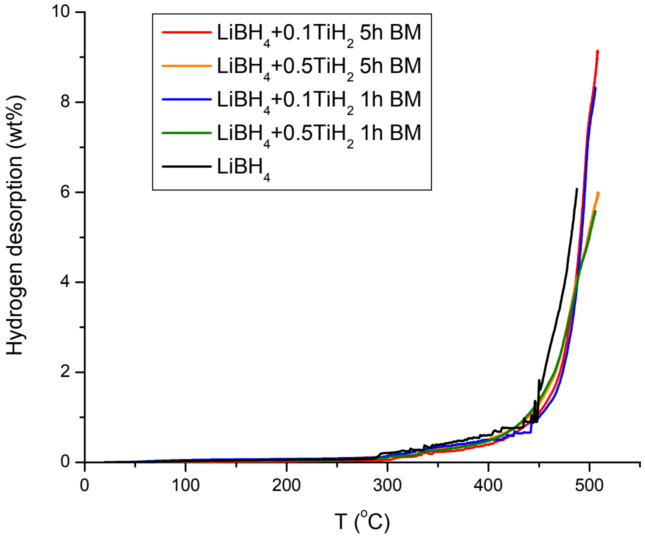

Fig.5 TPD of TiH_2 modified $LiBH_4$

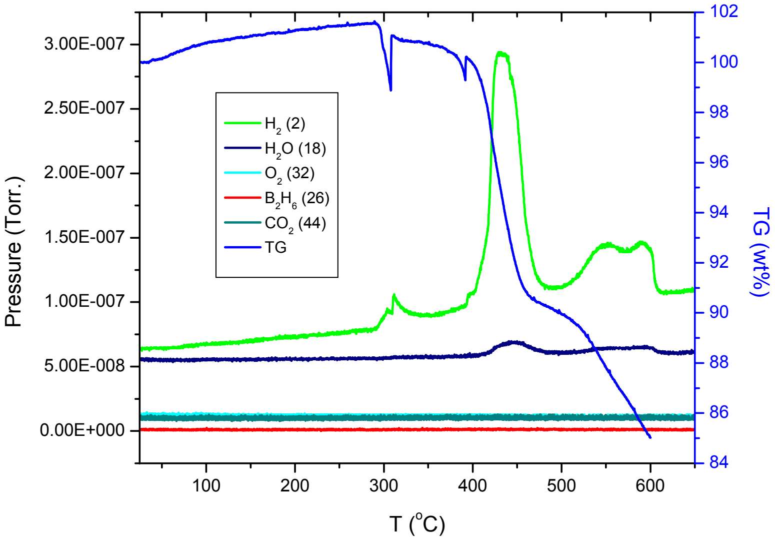

Fig.6 TGA-RGA spectra of materials $LiBH_4$+0.1TiH_2

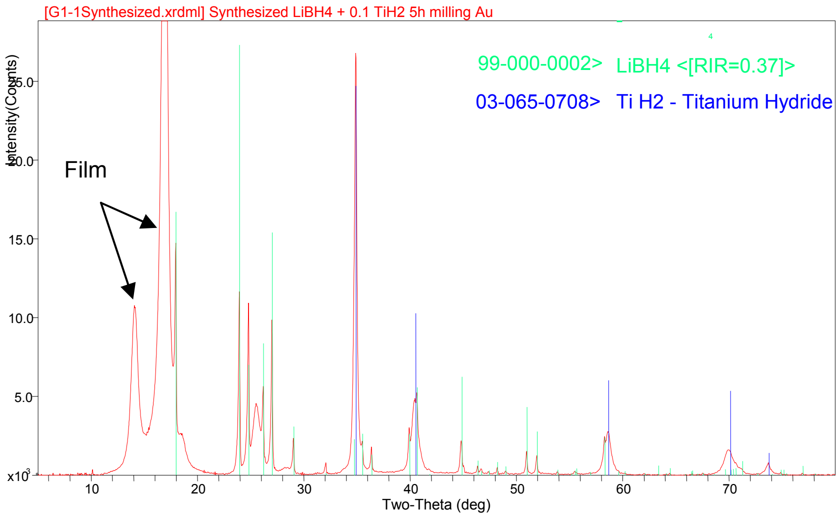

Fig.7 XRD spectrum of $LiBH_4$+$0.5TiH_2$ after 5 hour ball milling

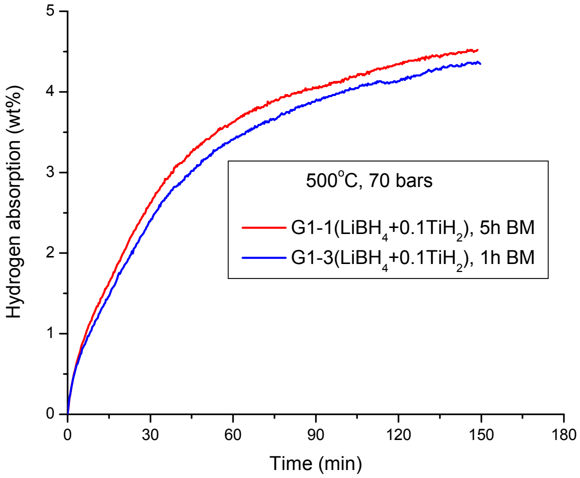

Fig.8 Hydrogen absorption of the material $LiBH_4$+$0.1TiH_2$

It seems the conclusion of theoretic simulation far from reality due to the simplification of the models and complicity of real world materials.

3.3 $LiBH_4$ based materials modified by $TiCl_3$, TiF_3 and ZnF_2

After preliminary screening, it is fund that the additives $TiCl_3$, TiF_3 and ZnF_2 reduced dehydriding temperature remarkably in the first dehydrogenation as Fig.9 shown. The details of investigation are reported in the below.

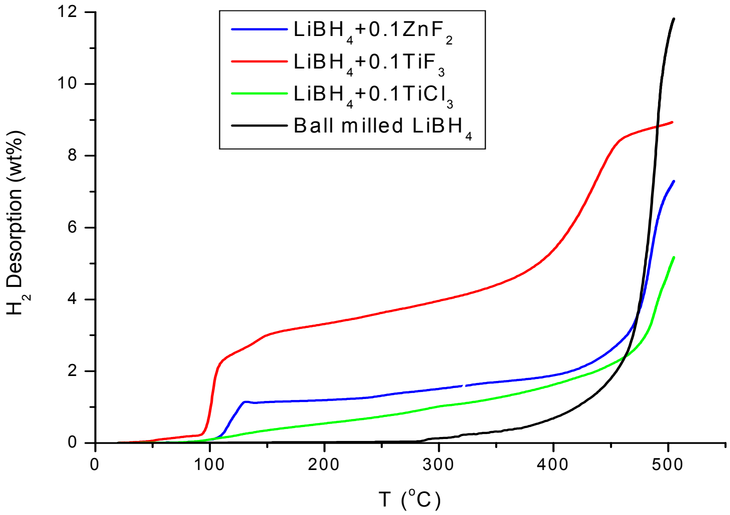

Fig.9 TPD of materials $LiBH_4$+0.1$TiCl_3$, $LiBH_4$+0.1TiF_3, $LiBH_4$+0.1ZnF_2 and ball milled $LiBH_4$

3.3.1 Materials $LiBH_4$+0.1$TiCl_3$ and $LiBH_4$+0.5$TiCl_3$

TGA-RGA spectra show that the materials $LiBH_4$+0.1$TiCl_3$ desorbed hydrogen slowly from 100°C to 350°C. The most hydrogen was released rapidly from 350°C to 450°C. Above 450°C, the dehydriding slowed down. Upon 500°C, about 6wt% hydrogen was librated from materials. There is no diborane detected by RGA (Fig.10). The RGA result consists with other published data on 3$LiBH_4$+$TiCl_3$ [5]. The weight loss of TGA corresponds to hydrogen desorption of TPD (Fig.9).

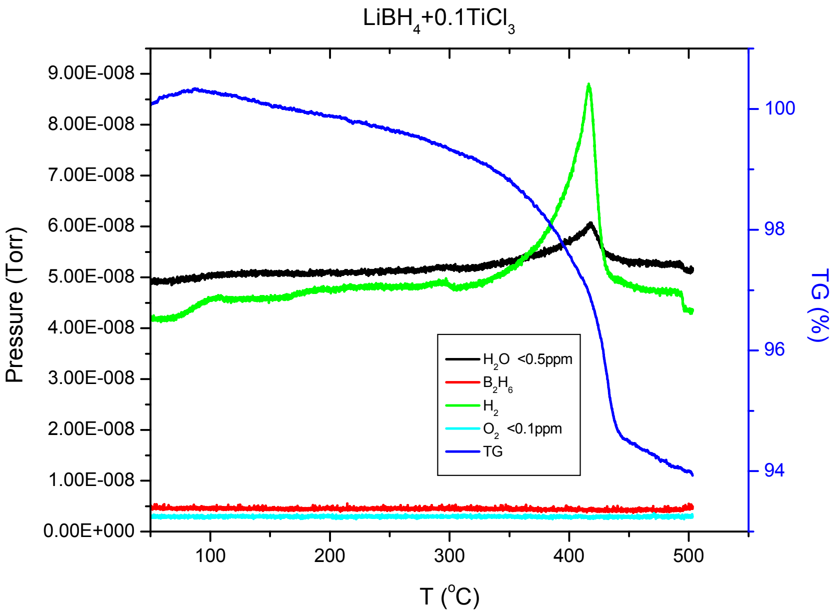

Fig.10 TGA-RGA spectra of materials $LiBH_4$+0.1$TiCl_3$

The XRD of the synthesized $LiBH_4+0.1TiCl_3$ detected $LiBH_4$ and LiCl. $TiCl_3$ disappeared from XRD spectrum (Fig.11). It means that $TiCl_3$ reacted with $LiBH_4$ through the ion exchange reaction $3LiBH_4+TiCl_3 \rightarrow 3LiCl + Ti(BH_4)_3$ during ball milling. However, XRD analysis did not detect $Ti(BH_4)_3$ because it is unstable at room temperature [15]. It decomposed and released hydrogen through the possible decomposition $Ti(BH_4)_3 \rightarrow TiH_2+3B+5H_2$. The hydrogen emission was evidenced by internal pressure building up in the sealed grinding jar after ball milling. According to the reaction, 0.1 mole $TiCl_3$ reacts with 0.3 mole of $LiBH_4$ leaving 0.7 mole of $LiBH_4$ non-reacted. Therefore, the most hydrogen was librated around 400^oC.

The XRD of the dehydrided $LiBH_4+0.1TiCl_3$ detected LiH and LiCl only (Fig.12). Boron could be in amorphous state and undetectable as other researchers speculated. The dominated reaction is suggested as $2LiBH_4 \rightarrow 2LiH+2B+3H_2$ (releasing 13.8% H_2 above 400^oC). The side reaction could be $3LiBH_4+TiCl_3 \rightarrow 3LiCl +TiH_2+3B+5H_2$ (releasing 4.56wt% H_2 at 100^oC). Combining both reactions above, the overall decomposition reaction can be expressed as $LiBH_4+0.1TiCl_3 \rightarrow 0.7LiH+0.3LiCl+0.1TiH_2+B+1.55H_2$ that give 8.3wt% theoretic dehydriding capacity. Practically, the dehydriding capacity will be less because of hydrogen emission during ball milling and slow desorption in limited time of the experiment. As Fig.9 and Fig.10 show, the dehydriding has not completed at cut-off temperature of 500^oC. The total desorption capacity could be higher than 5% if the increasing temperature or extending soak time.

The XRD spectrum of the rehydrided $LiBH_4+0.1TiCl_3$ shows $LiBH_4$, LiH and LiCl (Fig.13). It indicates that the material is partially reversible. The LiCl did not take part of dehydriding and rehydriding reactions as neutral specie.

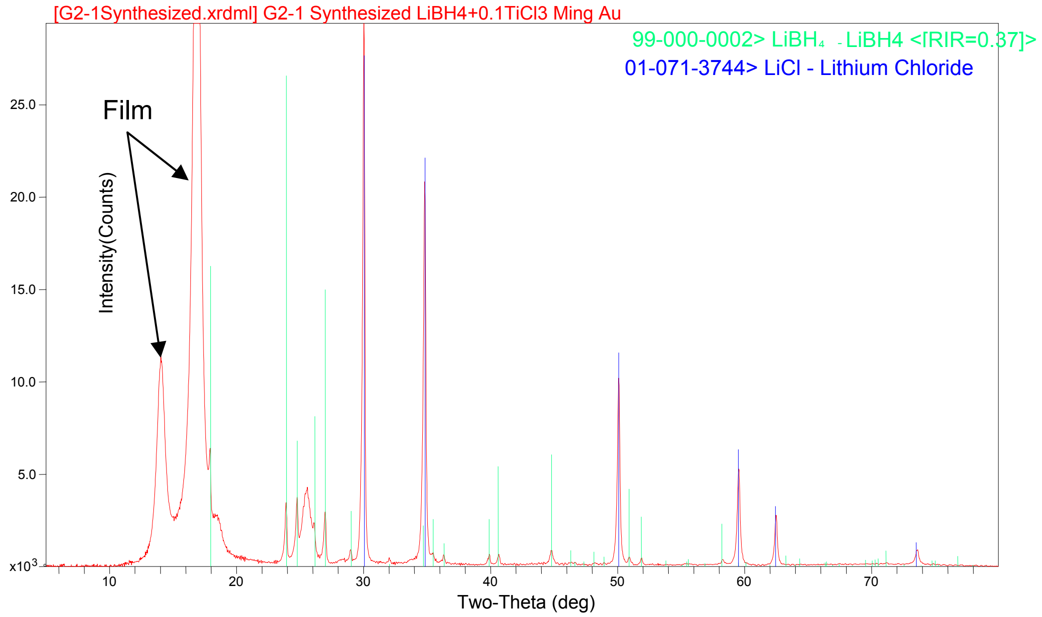

Fig. 11 XRD of material $LiBH_4+0.1TiCl_3$ as synthesized

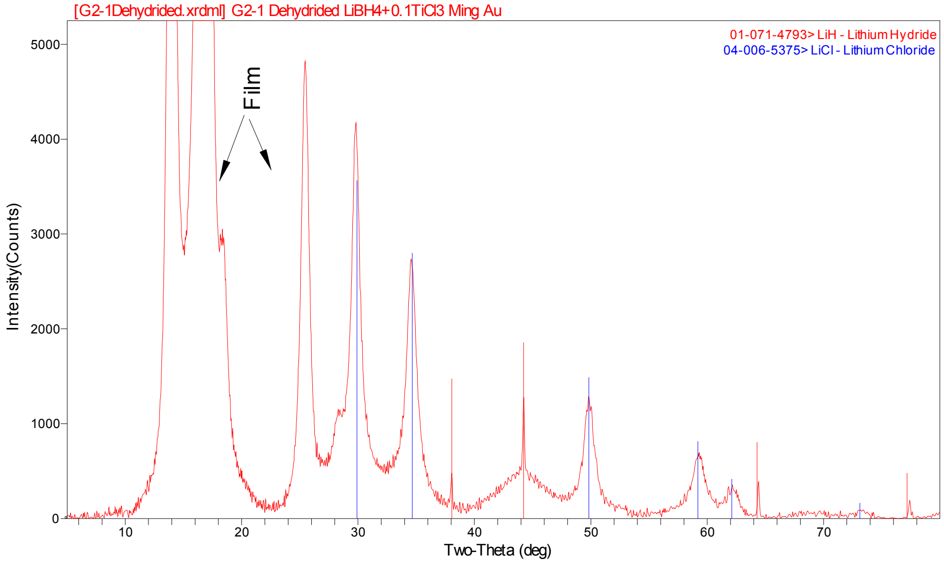

Fig. 12 XRD of material $LiBH_4$+0.1$TiCl_3$ as dehydrided

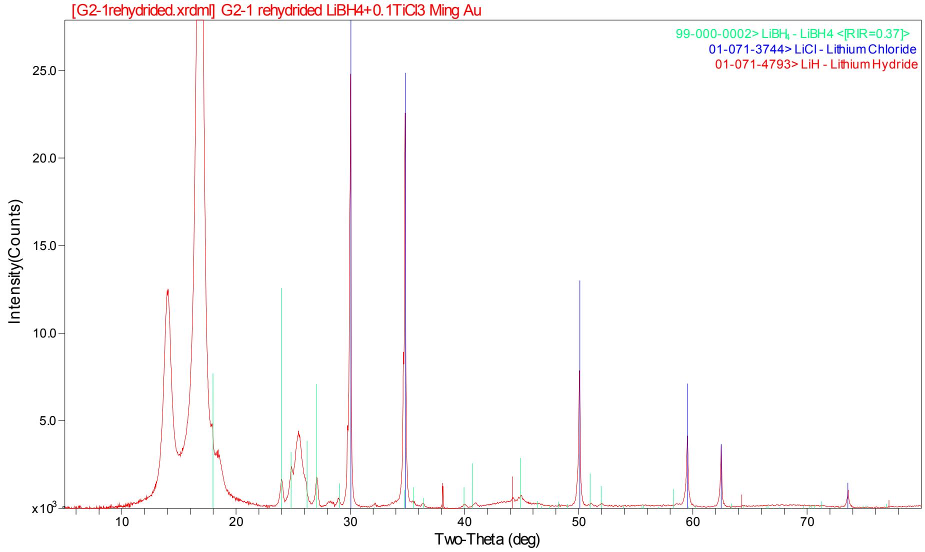

Fig. 13 XRD of material $LiBH_4$+0.1$TiCl_3$ as rehydrided

After desorbing 6wt% hydrogen at 500°C, the material $LiBH_4$+0.1$TiCl_3$ absorbed 3.4wt% hydrogen at 500°C and 70 bar (Fig.14) corresponding to partial recombination of $LiBH_4$. This conclusion is supported by the XRD data (Fig.13).

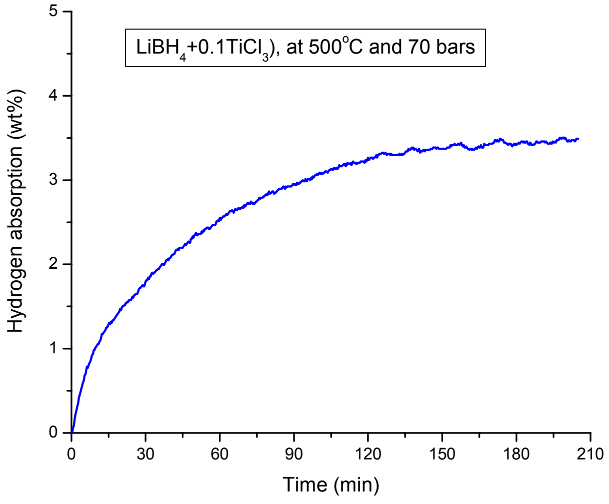

Fig.14 Rehydrogenation of material $LiBH_4$+0.1$TiCl_3$

The TGA spectrum shows that the material $LiBH_4$+0.5$TiCl_3$ lost 37% weight at 100°C (Fig.15). Obviously, such large weight loss can not be attributed to hydrogen evolution alone. Other gases must have emitted from material. RGA detected B_2H_6 qualitatively. It is noted that TGA registered the weight loss even before started heating. Repeated TGA-RGA measurement provided same results. To verify if gas BCl_3 formed, we run RGA again and fund none (Fig.16). It is possible, but unlikely B_2H_6 may react with PEEK tubing before entering RGA. It is important to point out that adding more reactive halides such as $TiCl_3$ makes material more unstable and volatile. The new materials will be less reversible if volatile gases evolved during dehydrogenation.

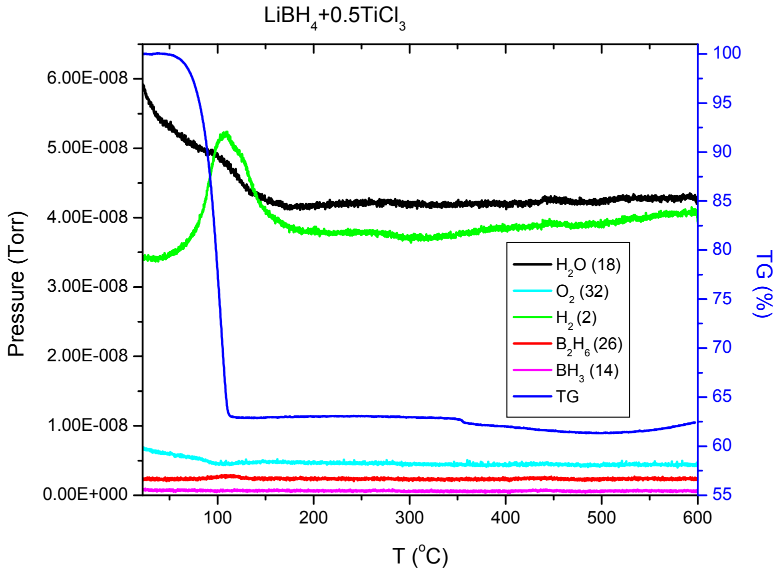

Fig.15 TGA-RGA spectra of materials $LiBH_4$+0.5$TiCl_3$

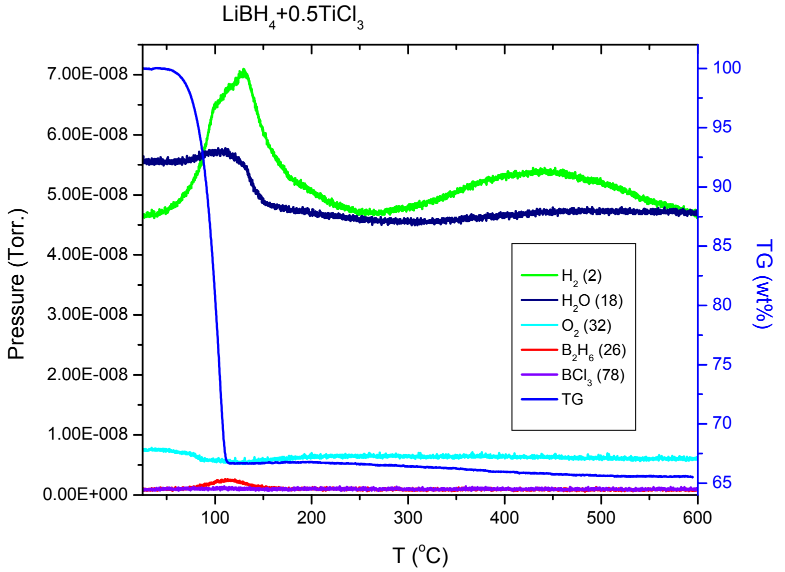

Fig.16 RGA spectra of materials $LiBH_4$+0.5$TiCl_3$ from repeated experiment

The Sieverts measurement shows that the material $LiBH_4$+0.5$TiCl_3$ desorbed 3wt% hydrogen up to 500°C (Fig.17). The 3wt% of desorption is much lower than 37wt% of weight loss measured by TGA because of dehydrogenation during evacuation of Sieverts. In each of our TPD measurements, the reactor of Sieverts was evacuated to <5mbar before TPD started. Due to volatility and instability of the material $LiBH_4$+0.5$TiCl_3$, most hydrogen was librated during evacuation at ambient temperature. After dehydriding, the material did not absorb hydrogen at 500°C and 70 bar (Fig.18). It is believed that the boron loss caused by evolution of diborane is the major reason of irreversibility of this material.

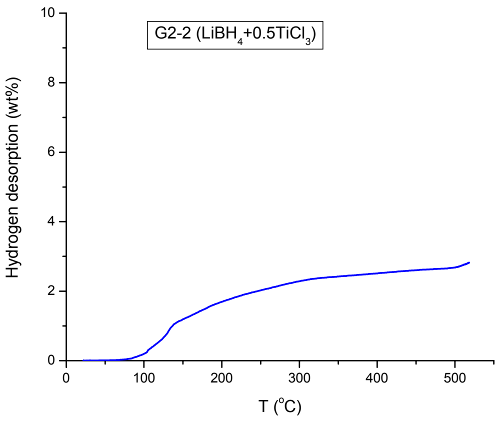

Fig.17 TPD of material $LiBH_4$+0.5$TiCl_3$

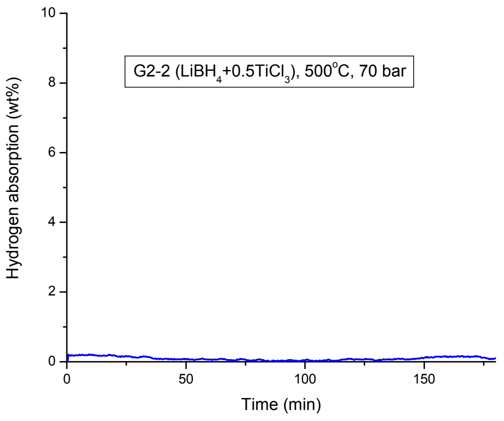

Fig. 18 Rehydriding of material $LiBH_4$+0.5$TiCl_3$

3.3.2 Materials $LiBH_4$+0.1TiF_3 and $LiBH_4$+0.5TiF_3

TGA-RGA spectra show that the materials $LiBH_4$+0.1TiF_3 desorbed hydrogen in two stages. At 100°C, the material lost 5wt% of weight that most attributed to hydrogen evolution with a trace of diborane emitted. At 400°C, the materials lost another 5wt% of weight with no diborane detected (Fig.19). Upon to 500°C, the material desorbed 12 wt% hydrogen. This implies that there are two compounds with different thermal stabilities in the materials. One was less stable and released hydrogen and trace of diborane at low temperature (100°C). The other is stable and released hydrogen only at higher temperature (400°C). It is noted that TPD measured 3wt% of hydrogen desorption at 100°C only because some hydrogen was emitted from material due to initial evacuation before TPD heating began (Fig.9).

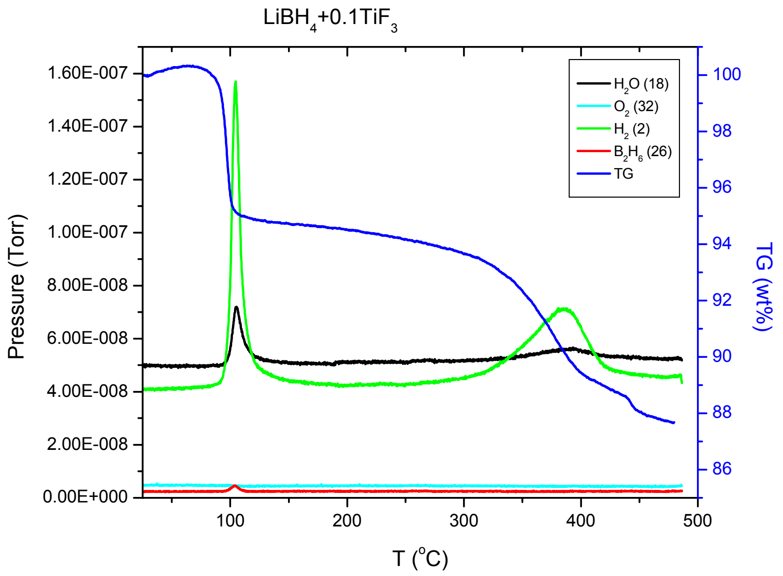

Fig.19 TGA-RGA spectra of the materials $LiBH_4$+0.1TiF_3

The XRD spectrum identified $LiBH_4$, LiF and TiF_3 in the synthesized material $LiBH_4$+0.1TiF_3 as (Fig.20). This differs from the material $LiBH_4$+0.1$TiCl_3$, in which $TiCl_3$ disappeared after ball milling. A considerable amount of TiF_3 did not react with $LiBH_4$ after ball milling under same milling scheme. It is beneficial using less active TiF_3 rather than $TiCl_3$ to avoid hydrogen loss during ball milling.

The XRD of dehydrided $LiBH_4$+0.1TiF_3 show the presence of LiF, LiH and possible TiB_2 (Fig.21). There were small broad peaks un-identified that may represent B and TiH_2 in the mixed state of the short range order and the amorphous structure. The possible dehydriding reaction at 100°C is proposed as $0.3LiBH_4+0.1TiF_3 \rightarrow 0.3LiF+0.1TiH_2+0.25B+0.025B_2H_6+0.2H_2$ (Reaction1) that will lead to 6.17wt% of weight loss caused by evolution of H_2 and B_2H_6. The theoretic calculation closes to 5wt% weight loss measured by TGA. There was not significant hydrogen evolution between 100°C and

300°C. It is understandable that the interaction of $LiBH_4$ and TiF_3 was completed and decomposition of $LiBH_4$ not yet started. In the second stage of dehydriding, the remaining $LiBH_4$ decomposed from 300°C to 500°C and liberated 7.5wt% hydrogen through the reaction $LiBH_4 \rightarrow LiH+B+1.5H_2$ (Reaction 2). Assume 0.1 TiF_3 reacts with $0.3LiBH_4$ completely at 100°C and the remaining $0.7LiBH_4$ decomposes at 300°C, the overall reaction can be expressed as $LiBH_4+0.1TiF_3 \rightarrow 0.7LiH+0.9B+0.05B_2H_6+0.3LiF+0.1TiH_2+1.3H_2$ by combining the reaction1 and the reaction 2. The theoretical weight loss will be 12.1wt% (8.07wt% from H_2 evolution and 4.03% from B_2H_6) that seems in agree with the data TGA measured (Fig.19). The two compounds dehydriding at low and high temperatures are assumed as the intermediate $Ti(BH_4)_3$ and $LiBH_4$ respectively.

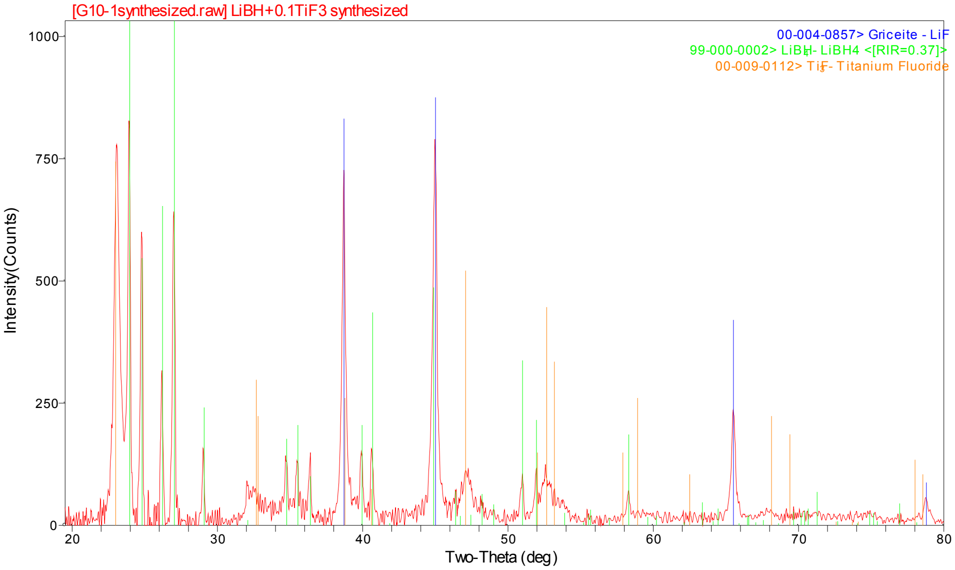

Fig. 20 XRD of the material $LiBH_4+0.1TiF_3$ as synthesized

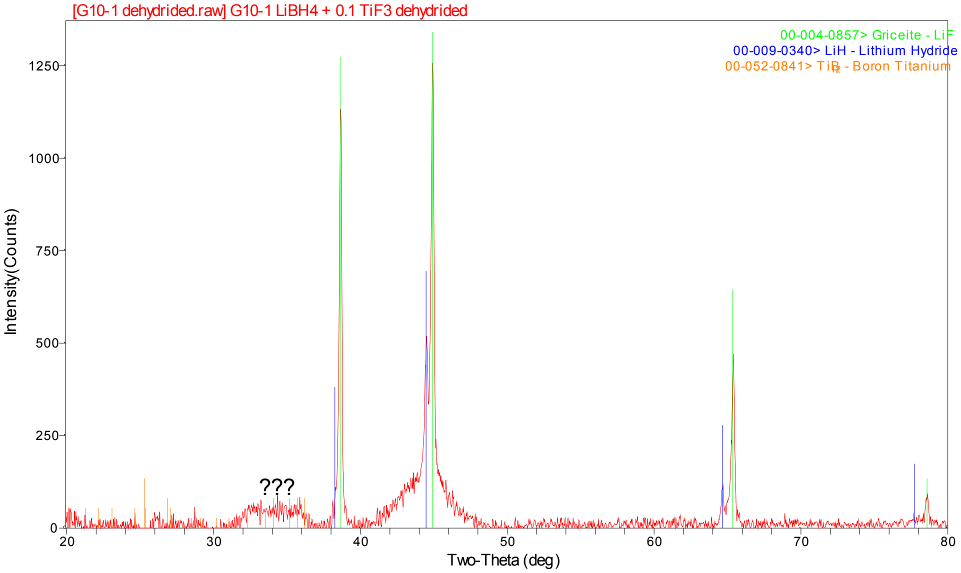

Fig. 21 XRD of the material $LiBH_4$+0.1TiF_3 as dehydrided

Sieverts measurement shows that the material $LiBH_4$+0.1TiF_3 absorbed 6wt% of hydrogen at 500°C and 70 bars after dehydrided 9wt% hydrogen (Fig.22). The XRD of rehydrided $LiBH_4$+0.1TiF_3 shows the presence of $LiBH_4$, LiF and LiH. There was a small peak un-identified (Fig.23). It is indicated that the material is partially reversible.

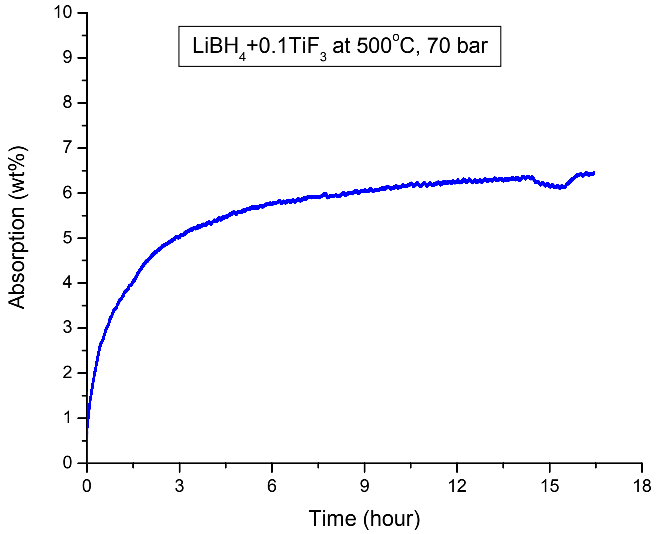

Fig. 22 Rehydrogenation of the material $LiBH_4$+0.1TiF_3

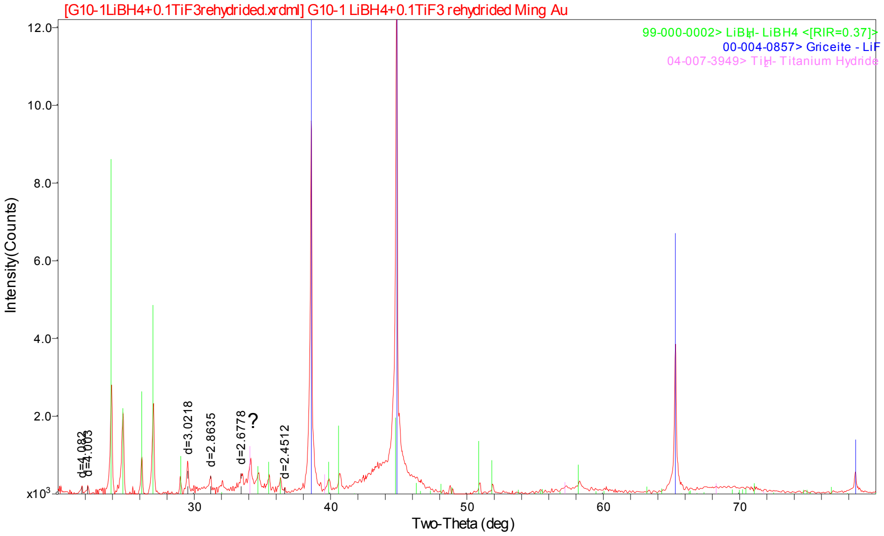

Fig. 23 XRD of material $LiBH_4$+0.1TiF_3 as rehydrided

TGA-RGA spectra show that the materials $LiBH_4$+0.5TiF_3 lost 7wt% of weight by releasing hydrogen and trace of B_2H_6 at 100°C (Fig.24). There was no weight loss from 150°C to 300°C. From 300°C to 500°C, it lost another 7wt% of weight. Upon to 500°C, it totally lost 14 wt% of weight, most from hydrogen desorption with trace of diborane. It is noted that TGA did not measured the unexpected large weight loss (37wt%) as the material $LiBH_4$+0.5$TiCl_3$ shown. It implies that the material $LiBH_4$+0.5TiF_3 is less volatile than $LiBH_4$+0.5$TiCl_3$. The reaction mechanism should be same as $LiBH_4$+0.1TiF_3, but more hydrogen was released from ion exchange reaction at low temperature (100°C) than $LiBH_4$+0.1TiF_3.

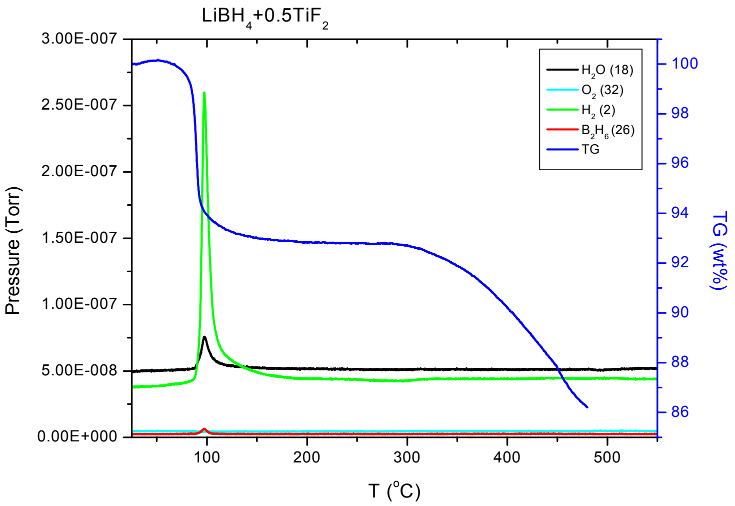

Fig.24 TGA-RGA spectra of materials $LiBH_4$+0.5TiF_3

3.3.3 Materials $LiBH_4$+$0.1ZnF_2$ and $LiBH_4$+$0.5ZnF_2$

TGA measured 4wt% weight loss and RGA detected the evolution of hydrogen and diborane at 120°C (Fig.25). From 350°C to 500°C, the sample lost 6wt% of weight that comes from hydrogen evolution only. Between150°C and 350°C, sample desorbed hydrogen 1wt% slowly. The first and the second stages of decomposition can be attributed to reaction of $LiBH_4$ and ZnF_2 and the thermal decomposition of $LiBH_4$ respectively. It is noted that Sieverts TPD measured about 1wt% of hydrogen desorption at 120°C only (Fig.9) because some hydrogen was released during initial evacuation before TPD started. In other hand, it is also noted that the different principles of measurements of TGA and Sieverts lead to difference of the results. The molecular weight of diborane is 13 time heavier (26) than hydrogen (2). Although the weight loss measured by TGA attributes to evolution of diborane and hydrogen both, diborane evolution causes weight loss 13 times higher than hydrogen if same moles of diborane and hydrogen emitted. TGA is more sensitive to diborane emission. The volumetric measurement, TPD, conducted with Sieverts apparatus registers the volume of gases evolved from materials and converts it to weight percentage of out-gassing. In this case, the diborane and hydrogen contribute to our-gassing weight percentage equally. For these reasons, the weight loss measured by TGA usually higher than TPD measured.

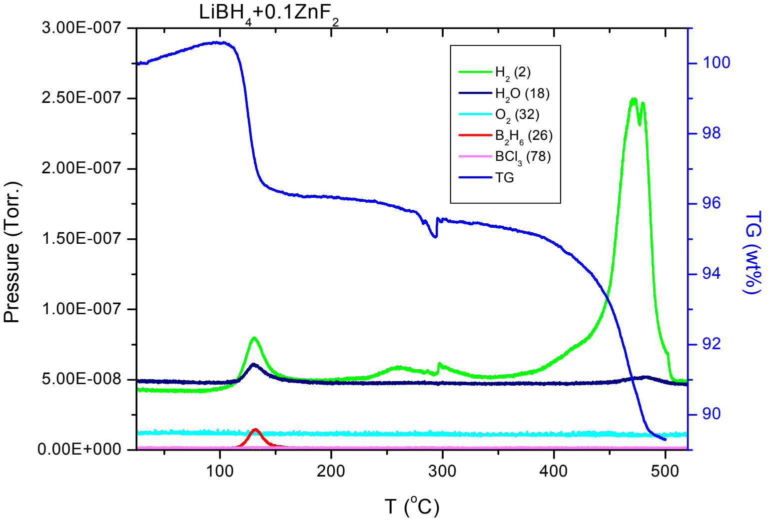

Fig.25 TGA-RGA spectra of materials $LiBH_4$+$0.1ZnF_2$

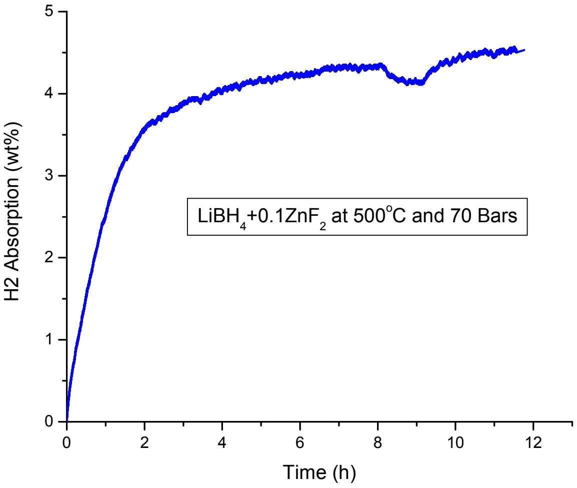

Fig. 26 Rehydriding of material $LiBH_4$+0.1ZnF_2

The material $LiBH_4$+0.1ZnF_3 is partially reversible and absorbed 4.5wt% hydrogen at 500°C and 70 bars after dehydrided 7wt% hydrogen. With more TiF_3 added, the material tends to be more unstable and volatile. The TGA spectrum of $LiBH_4$+0.5ZnF_2 shows that the material lost 15wt% weight at 130°C (Fig.27). Significant amounts of diborane and water vapor were detected with hydrogen evolution. The exceed water vapor could come from zinc hydroxide or hydrated water in precursor of the commercial ZnF_2 (99% pure). For similar reason as the material $LiBH_4$+0.5TiF_2, we do not expect the $LiBH_4$+0.5ZnF_2 will be reversible.

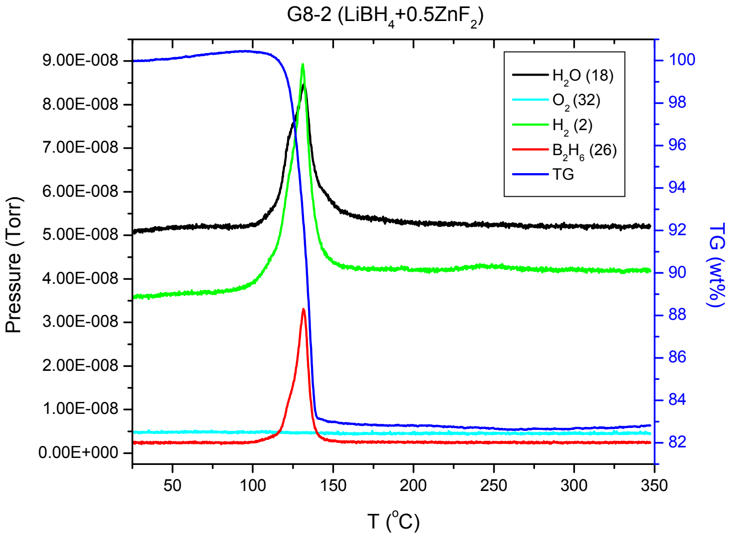

Fig.27 TGA-RGA spectra of materials $LiBH_4$+0.5ZnF_2

4. Observation of air sensitivity of the modified lithium borohydrides

It was found that the additives $TiCl_3$ and TiF_3 reduce the air sensitivity of $LiBH_4$. The synthesized, dehydrided and rehydrided materials $LiBH_4$+0.1$TiCl_3$ and $LiBH_4$+0.1TiF_2 were stable in open air with no visible reaction (Fig.28). The pure $LiBH_4$ melted first at 275°C and then desorbed hydrogen at above 300°C from liquid state. The gas-liquid dehydriding reaction causes material evaporation and deposition. After dehydriding, the material deposited on the wall of the sample holder and absorbed moisture, generating bubbles (Fig.29 left). $LiBH_4$+0.1$TiCl_3$ did not lead to evaporation during dehydriding (Fig.29 right). Adding $TiCl_3$ or TiF_3 apparently changes the dehydriding process from a gas-liquid to a gas-solid reaction. The material was sintered as a cylindral chunk after dehydriding and rehydriding (Fig.28-29) which implies that the addition of $TiCl_3$ and TiF_3 increased the melting point of the materials. It is believed that changing the dehydriding-rehydriding reactions from gas-liquid to gas-solid may increase reaction kinetics and improve reversibility.

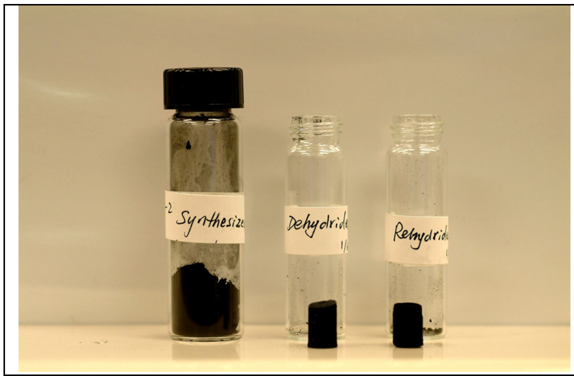

Fig.28 $LiBH_4$+0.1$TiCl_3$ samples as synthesized, dehydrided and rehydrided

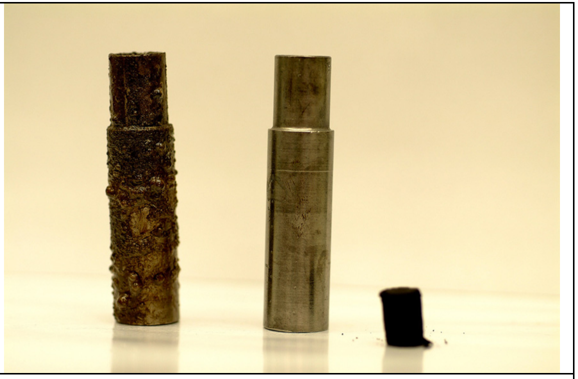

Fig.29 $LiBH_4$+0.1TiF_2 (right) and $LiBH_4$+0.1$SrCl_3$ (left) samples after dehydriding.

5. Conclusion

To reduce dehydriding temperature and make materials reversible, the metal hydride and halides have been added into $LiBH_4$ for possible elemental substitution and reversible interaction of additive. It was found that the metal hydride, TiH_2, did not substitute for Li in $LiBH_4$ or react with $LiBH_4$. The halides TiF_3, $TiCl_3$ and $ZnFl_2$ effectively reduced the dehydriding temperature from 300°C to less than 100°C through the interaction with $LiBH_4$. After dehydriding 6-9wt% hydrogen, the materials reversibly absorbed 3-6wt% hydrogen at 500°C and 70 bars.

Some halide modified $LiBH_4$, such as $LiBH_4$+0.1ZnF_2, emitted diborane gas during dehydrogenation, while others such as $LiBH_4$+0.1$TiCl_3$ did not. The formation of diborane will lead to unrecoverable capacity loss and irreversibility. It is suggested that lithium borohydride modified with halides containing metals that can not form metal borides with boron are likely to evolve diborane during dehydriding. The halide modification reduces the material sensitivity. The materials $LiBH_4$+0.1$TiCl_3$ and

$LiBH_4$+0.1TiF_3 can be placed in open air without visible reaction. It would be significant progress in concerning of the safety of complex hydrides.

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