Contract No:

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy.

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REVERSIBILITY ASPECT OF LITHIUM BOROHYDRIDES

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Abstract

Reversibility is key for any hydrogen storage material to be developed. Borohydrides such as $LiBH_4$ have been studied or proposed as candidates for hydrogen storage because of their high hydrogen contents (18.4 wt% for $LiBH_4$). Limited success has been made in reducing the dehydrogenation temperature. However, full rehydrogenation has not been realized. It is found that the dehydrogenation mechanism of metal borohydrides differs signicantly from the well-known metal hydrides such as $LaNi_5H_6$ and MgH_2 that release hydrogen in a single decomposion step. Some of the steps in the multiple step decomposition processes of metal borohydrides are not reversible. Furthermore, the decomposition also produces stable intermediate compounds that can not be rehydrided easily. Although our experiments show the partial reversibility of the doped $LiBH_4$, it was not sustainable during dehydriding-rehydriding cycles because of the accumulation of hydrogen inert species. Doping with additives reduces the stability of $LiBH_4$, but it also makes $LiBH_4$ less reversible. It raises reasonable doubt on the feasibility of making metal borohydrides suitable for reversible hydrogen storage.

Key words: Borohydride, Hydrogen, Storage, Reversibility, Stability, Rehydrogenation, Dehydrogenation

1. INTRODUCTION

Lithium borohydride, $LiBH_4$, has both high gravimetric (18.4 wt%) and volumetric (121 kg/m^3) hydrogen densities making it a potential candidate as a hydrogen storage material. The release of hydrogen from $LiBH_4$ requires temperatures in excess of 300°C and rehydrogenation requires both high temperatures (>650°C) and pressure (>190 bar) [1]. A number of recent papers have reported decreases in dehydriding temperatures (or destabilization) by mixing $LiBH_4$ with additives. Züttel [2] reported that mixing 25wt% $LiBH_4$ with 75wt% of SiO_2 reduced the initial dehydriding temperature from 400°C to 200°C. It was reported that the mixed material was partially reversible, but no experimental details were provided. Orimo added Mg into the $LiBH_4$ through ball milling and reduced the dehydriding temperature from 577°C to 547°C [3]. Pinkerton reported that ball milled $2LiNH_2$+$LiBH_4$ formed a quaternary Li-B-N-H that desorbed 10.2wt% hydrogen from 250°C to 364°C. The dehydrided material, however, did absorb hydrogen at 8MPa (80 bar) [4]. Vajo reported that the ball milled mixture of $LiBH_4$ and LiOH desorbed 10wt% hydrogen from 50°C to 300°C, but the dehydrided mixture was not reversible [5].

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Several reports have also provided evidences for rehydrogenation. Through XRD and Raman spectroscopic analysis, Orimo confirmed the reformation of $LiBH_4$ at 350 bar and 600°C after $LiBH_4$ decomposed at 1MPa (10 bar) and 600°C without quantitative measurement [6]. Vajo reported that the ball milled mixture LiH+0.5 MgB_2 + 0.03 $TiCl_3$ absorbed 9 wt% H_2 at 350°C and 100 bar and desorbed 8wt% H_2 at 450°C [7]. In our previous work, the $LiBH_4$75% + $TiO_2$25% desorbed 9 wt% H_2 from 100°C to 600°C and absorbed 8 wt% H_2 at 600°C and 70 bar [8]. It was also shown that $LiBH_4$ +0.2$MgCl_2$+0.1$TiCl_3$ desorbed 5 wt% H_2 from 60°C to 450°C and absorbed 4.5 wt% H_2 at 600°C and 70 bar [9]. Dehydrogenation heat of the ball-milled mixture of $LiBH_4$ and mesoporous carbon was reduced to 40 kJ/mol H_2 from 67 kJ/mol H_2. The mixture desorbed 7 wt% H_2 up to 600°C and re-absorbed 3 wt% H_2 at 350°C and 30 bar as reported by Zhang et. al. [10]. It was concluded that nano-dispersion and reaction with mesoporous carbon result in destabilization. Yang et al. reported that ball milling $LiBH_4$ with 0.5 moles Al reduced dehydriding temperature from 460°C to 400°C through the reaction $2LiBH_4 + Al \rightarrow AlB_2 + 2LiH + 3H_2$ reversibly at 350°C and 150 bar [11]. Reversible hydrogen absorption of $LiBH_4$+0.5Al+0.04TiF_3 at 400°C/100 bar H_2 after releasing 7.2 wt% H_2 at 450°C starting from vacuum was observed by Kang [11]. Jin reported that ball milled mixture $LiBH_4$-$LiAlH_4$-TiF_3 released 7.2 wt% H_2 at 247°C and reabsorbed 5.1wt% H_2 at 350°C/70 bar [12].

Several metal borohydrides with lower dehydriding temperature such as $Zr(BH_4)_2$, $Ti(BH_4)_3$, $Mn(BH_4)_2$, $Mg(BH_4)_2$ and $Al(BH_4)_3$ have been synthesized through organic wet chemical reactions [13-18]. Historically, the volatile metal borohydrides such as $Cr(BH_4)_3$, $Zn(BH_4)_2$, and $Sn(BH_4)_2$ [19-21] have been used for generation of diborane, B_2H_6, which is a precursor for boron chemical vapor deposition. Recently, these metal borohydrides have been investigated for possible reversible hydrogen storage. These borohydrides either desorbed hydrogen at high temperature (above 250°C) or evolved significant diborane (B_2H_6) gas. None of these borohydrides appears to be reversible under practical temperatures and pressures. Jeon and Cho synthesized $Zn(BH_4)_2$ and found the material very unstable under ambient conditions [22]. TGA measured 12.1wt % loss between 85-140°C. Concurrently, mass spectroscopy detected both H_2 and B_2H_6. It was concluded that $Zn(BH_4)_2$ is neither reversible nor suitable for hydrogen storage. Diborane emission was observed from unstable $Mg(BH_4)_2$ and $Mn(BH_4)_2$ as well [23,24].

The evolution of B_2H_6 causes loss of boron in the hydrogen gas stream, resulting ultimately in irreversibility. From our previous investigations [8, 9], it is believed that $LiBH_4$ reversibility is determined by its dehydrogenation processes and products. The borohydrides that emit boron-containing volatile gases such as BH_3 and B_2H_6 or form stable compounds (TiB_2, Li_7B_6, LiB_2O_3) and intermediate specie $LiB_{12}H_{12}$ during dehydrogenation are not reversible. The unstable borohydrides capable of liberating H_2 at room temperature are most likely irreversible due to B_2H_6 evolution. In this paper, we report the results of our continued studies on the relationship between stability and reversibility of modified lithium borohydrides.

2. EXPERIMENTAL DETAILS

The $LiBH_4$ (95% purity) and the additives TiO_2, $TiCl_3$, ZrO_2, V_2O_3, SnO_2, $TiCl_3$, TiF_3, $ZnCl_2$, $FeCl_3$, $MgCl_2$, MgF_2, $SrCl_2$ and $CaCl_2$ (99.9-99.99% purity) were purchased from Sigma-Aldrich and used directly without pre-treatment. Two grams of the $LiBH_4$ and additive powders were placed in a 45 mL hardened steel grinding bowl with three 11 mm diameter tungsten carbide balls in an argon atmosphere glove box. The sealed grinding bowls were put on Frisch-7 planetary ball mill for 1 hour milling at 500 rpm. To prevent the temperature from rising excessively, one hour milling was completed through six repetitions of 10 min of milling and 10 min of rest with forced air-cooling. An SRS RGA-300 Residual Gas Analyzer (RGA) coupled with a Perkin Elmer Pyris-1 Thermal Gravimetric Analyzer (TGA) was used to measure the weight loss and analyze the composition of the gases evolved during thermal decomposition, simultaneously. Five mg samples were used in the TGA for 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, total hydrocarbon (THC)<0.1ppm and ($CO+CO_2$) < 0.1 ppm was passed at 60 ml/min from the TGA through a 3.2mm OD PEEK^{TM} tubing to the RGA instrument. The targeted evolving gases monitored by RGA were H_2O(18), H_2(2), O_2(32) and B_2H_6(26). The simultaneous TGA-RGA measurement determined the critical desorption temperature, weight loss and evolved gas composition during thermal decomposition. After TGA-RGA pre-screening, 0.5 g samples were transferred to a 5 mL sample holder connected with the 2 liter desorption chamber of a Sieverts apparatus. The system was evacuated to 5 mbar before temperature programmed desorption (TPD) initiated. An MKS vacuum transducer measured subsequent pressure changes. The temperature was increased from ambient to 500°C at 5°C/min. Rehydriding was conducted isothermally at 500°C and 70 bar utilizing 99.9999% hydrogen. The hydrogen absorption and desorption capacities were calculated based on the total sample mass including the additives. The samples were analyzed by X-Ray Diffraction analysis (XRD) in a Panalytical X'Pert Pro X-ray diffractometer to determine phase compositions in the three states: as synthesized, dehydrided and rehydrided. Solid-state magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectra were measured at the California Institute of Technology using a Bruker Avance 500 MHz spectrometer with a wide bore 11.7 T magnet and employing a boron-free Bruker 4 mm probe.

3. RESULTS

3.1 Metal oxide doped $LiBH_4$

3.1.1 Metal oxide doping reduced dehydriding temperature of $LiBH_4$

Temperature Programmable Desorption (TPD) was conducted in Sieverts apparatus at heating rate of 5°C/min. It is found that five metal oxides, TiO_2, ZrO_2, V_2O_3 and SnO_2, effectively reduced the decomposition temperature (Fig.1). The samples $LiBH_4$75%+TiO_2 25%, $LiBH_4$ 75%+V_2O_3 25%, $LiBH_4$ 75%+ZrO_2 25% and $LiBH_4$ 75%+SnO_2 25% desorbed 8-9wt% hydrogen starting from 200°C respectively, while the commercial $LiBH_4$ desorbed 6wt% H_2 starting from 350°C. The dehydriding temperature

was reduced 150°C by metal oxide doping. The dehydriding kinetics was also improved in contrast with commercial $LiBH_4$.

3.1.2 Metal oxide modified $LiBH_4$ are partially reversible

The isothermal desorption of selected sample $LiBH_4$75%+TiO_2 25% was conducted at 5 mbar. The sample released 1.7wt%, 5wt% and 8.7wt% H_2 at 200°C, 300°C and 400°C respectively (Fig.2). After dehydriding, the sample absorbed hydrogen at 600°C and 70 bar (Fig.3). However, the absorption capacity decreased gradually from 8.5wt% in the first rehydriding to 4.5wt% in the third rehydriding. The partial reversibility demonstrated seems unsustainable. We will discuss it in the special section below.

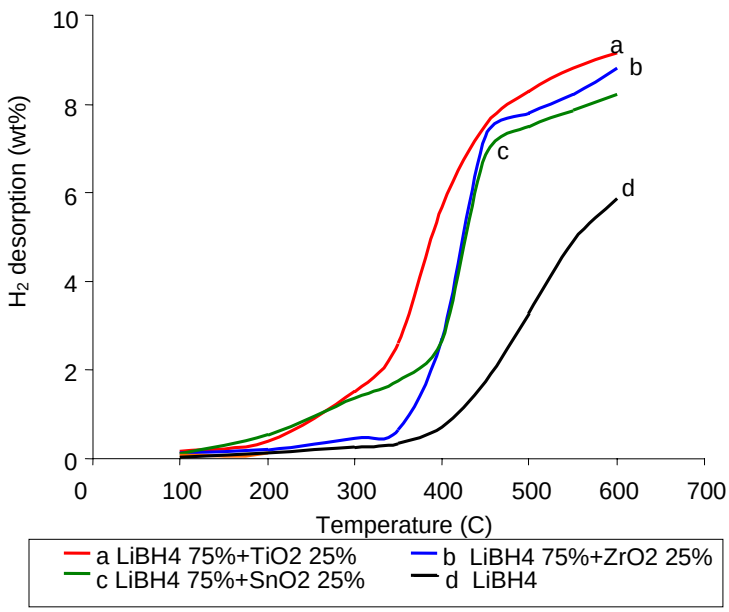

Fig.1 The comparison of the modified $LiBH_4$ materials with the commercial $LiBH_4$

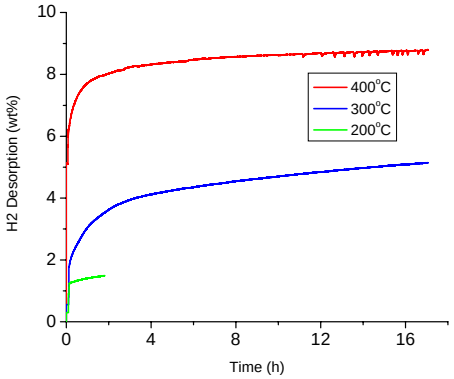

Fig.2 Dehydriding of $LiBH_4$ 75% + TiO_2 25%

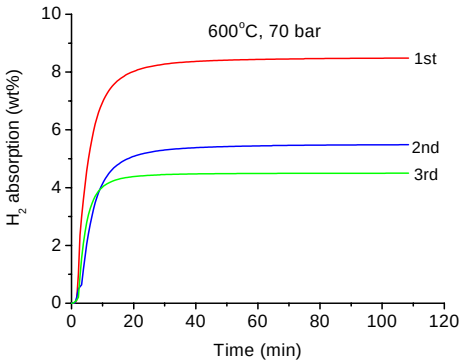

Fig.3 Rehydriding of $LiBH_4$ 75% + TiO_2 25%

3.2 Metal halide doped $LiBH_4$

3.2.1 Metal halide doping reduced dehydriding temperature of $LiBH_4$ significantly

Five $LiBH_4$ samples doped by metal halides $TiCl_3$, TiF_3, AlF_3 and ZnF_2 were investigated by TPD. It was found that the additives $TiCl_3$, TiF_3 ZnF_2 and AlF_3 reduced dehydriding temperatures significantly (Fig.4). The samples of $LiBH_4$+0.1TiF_3, $LiBH_4$+0.1ZnF_2 $LiBH_4$+0.1$TiCl_3$ and $LiBH_4$+0.5$TiCl_3$ desorbed H_2 at as low as 60°C. It means that the stability of these samples was reduced a great deal. TGA measured large weight losses (11- 12 wt%). However, RGA detected diborane (B_2H_6) gas in addition to hydrogen during decomposition of the less stable borohydrides such as $LiBH_4$+0.1TiF_3 and $LiBH_4$+0.1ZnF_2 (Fig.5-6). The discharge of B_2H_6 will reduce the boron content in the decomposed solid resulting in "boron" loss. We will discuss its impact on reversibility later.

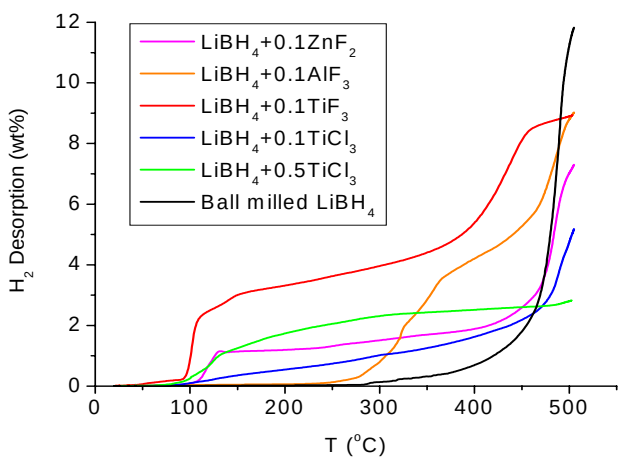

Fig.4 TPD of $LiBH_4$+0.1$TiCl_3$, $LiBH_4$+0.5$TiCl_3$, $LiBH_4$+0.1TiF_3, $LiBH_4$+0.5TiF_2, $LiBH_4$+0.1ZnF_2, $LiBH_4$+0.1AlF_3 and ball milled $LiBH_4$

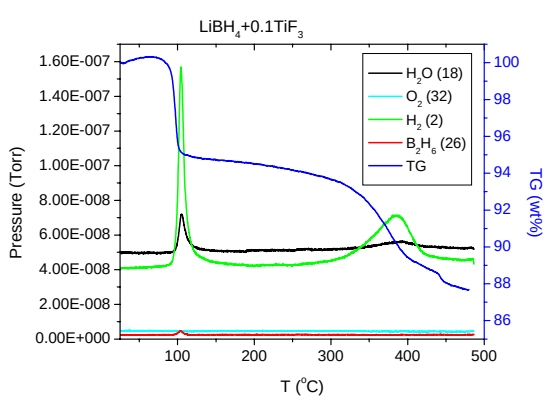

Fig.5 TGA-RGA spectra of $LiBH_4$+0.1TiF_3

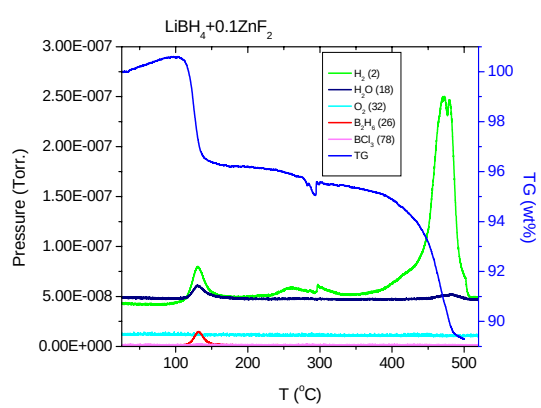

Fig.6 TGA-RGA spectra of $LiBH_4$+0.1ZnF_2

3.2.2 Metal halide modified $LiBH_4$ is not reversible

The dehydrided halide modified samples were rehydrided at 500°C and 70 bar (Fig.7). They absorbed less hydrogen than oxide modified $LiBH_4$ (3wt% - 5.6wt%). Particularly, two samples with higher content of dopants such as $LiBH_4$+0.5TZnF_3 and $LiBH_4$+0.5TiF_3 absorbed less than 1wt% H_2. Although the high dose of additives reduced their stability to a great deal by showing low decomposition temperature and larger weight loss in TGA measurements, their reversibility is negligible.

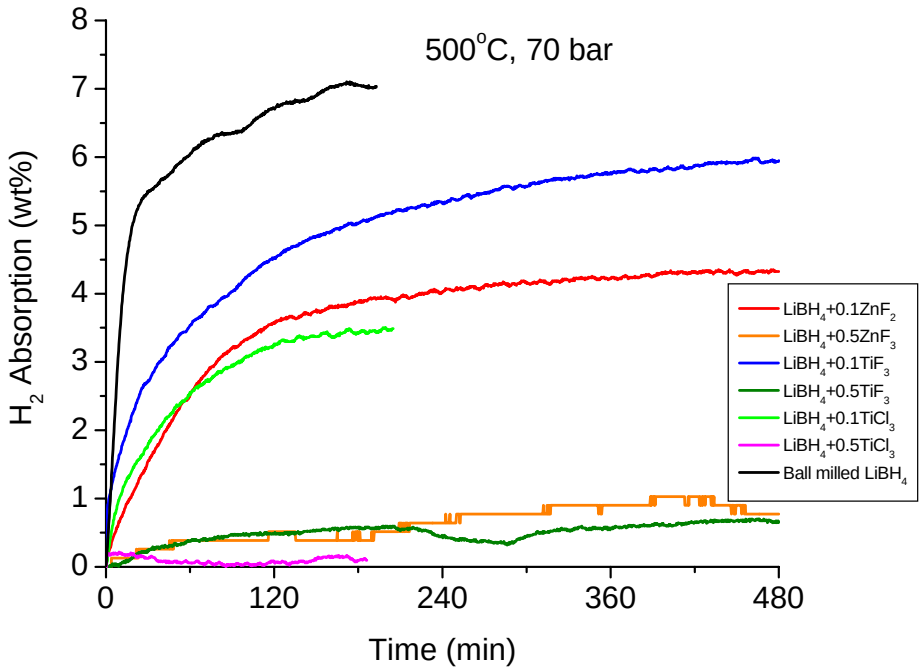

Fig.7 Hydrogen absorption of the $LiBH_4$+0.1$TiCl_3$, $LiBH_4$+0.5$TiCl_3$, $LiBH_4$+0.1TiF_3, $LiBH_4$+0.5TiF_3, $LiBH_4$+0.1ZnF_2, $LiBH_4$+0.5ZnF_2 and ball milled $LiBH_4$

4. DISCUSSION

In order to be viable hydrogen storage materials, metal borohydrides must have two physical properties. They must be fully reversible, and they must be capable of operating under acceptable conditions (low temperature and moderate pressure). In spite of enormous efforts and resource invested, there is no breakthrough. Most published reports only describe how to reduce the dehydriding temperature or stability; there is still much difficulty in rehydriding the decomposed borohydrides. Based on our investigation of the reversibility of metal borohydrides in the past five years, we would like to share our vision in this section.

4.1 Commercial $LiBH_4$

<u>$LiBH_4$ is partially reversible in limited dehydriding-rehydriding cycles</u>
Our previous experiments show that commercial $LiBH_4$ decomposes at 300°C and loses 12% weight hydrogen up to 500°C [25]. In addition to H_2, trace amounts of B_2H_6 (~15 ppm) evolve in thermal decomposition [8]. This raises the question of whether $LiBH_4$ is fundamentally reversible.

The dehydrided sample absorbed 7 wt% H_2 at 500°C and 70 bar [25]. After rehydrogenation, XRD confirmed reformation of $LiBH_4$, but the residual dehydriding products LiH and B were still present [25]. NMR identified amorphous boron and an intermediate specie $M[B_{12}H_{12}]^{-2}$ in dehydrided $LiBH_4$ and other metal borohydrides [26]. It is possible that the intermediate closo-borane will down grade to simple boron hydride gases such as B_2H_6 or BH_3. We believe that the widely cited decomposition

$LiBH_4 \rightarrow LiH + B + 1.5H_2$ (13 wt% H_2)

may not reflect the true mechanism of the complicated process. Here we propose a decomposition path as:

$LiBH_4$ (s) $\rightarrow Li^+ + [BH_4]^-$ (l) $\rightarrow LiH(s) + 0.83B(s) + 1.25H_2$ (g) $+ 0.17BH_3$(g) (11 wt% H_2).

It is supported by our experimental data such as 11 wt% of H_2 desorption, amorphous B formation and BH_3 emission. It also indicates that the partial reversibility of LiBH4 demonstrated in limited cycles may not be sustainable because of gradual boron loss and slow recombination of amorphous B, LiH and H_2.

4.2 Metal oxide doped $LiBH_4$

As Fig. 6 shows before, the rehydriding capacity of $LiBH_4$ 75%+TiO_2 25% decreased from 8.5wt% to 4.5wt% in three dehydriding-rehydriding cycles. XRD identified LiH, LiOH, Li_7B_6 and TiB_2 in the dehydrided $LiBH_4$ 75%+TiO_2 25%. After rehydriding, XRD detected $LiBO_3$, TiB_2 and Li_7B_6. From this data we infer the additive TiO_2 reacted with LiBH4 in the dehydriding process and formed Li_7B_6 and TiB_2. XRD was not capable of detecting amorphous B and $LiBH_4$ in dehydrided and rehydrided $LiBH_4$, respectively. However, the formation of the stable compounds, TiB_2 and Li_7B_6, will prevent boron from recombining with LiH and H_2 and forming $LiBH_4$. This is the one of the possible reasons for unsustainable reversibility, in addition to possible diborane formation, for $LiBH_4$.

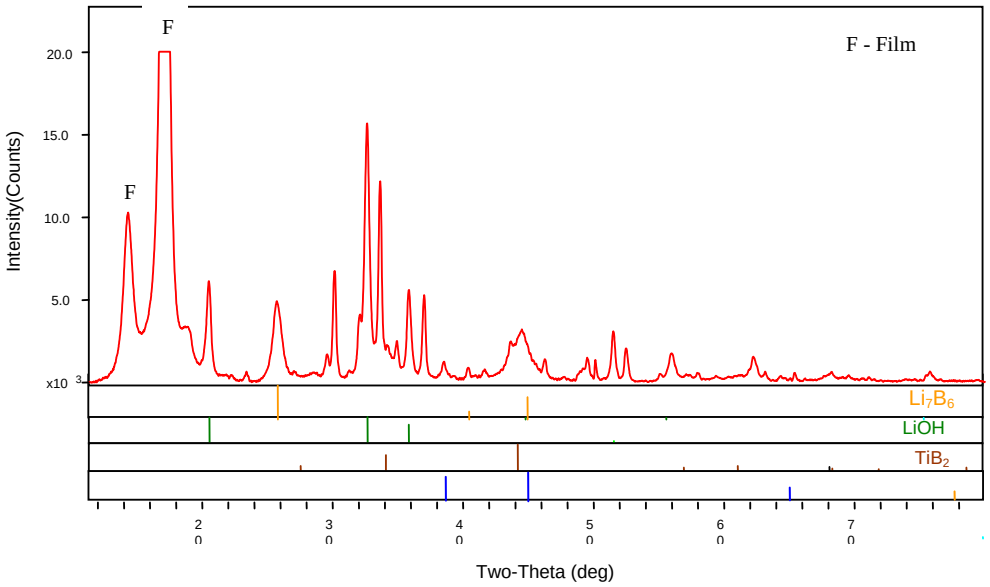

Fig.8 The XRD of the dehydrided $LiBH_4$ 75%+TiO_2 25%

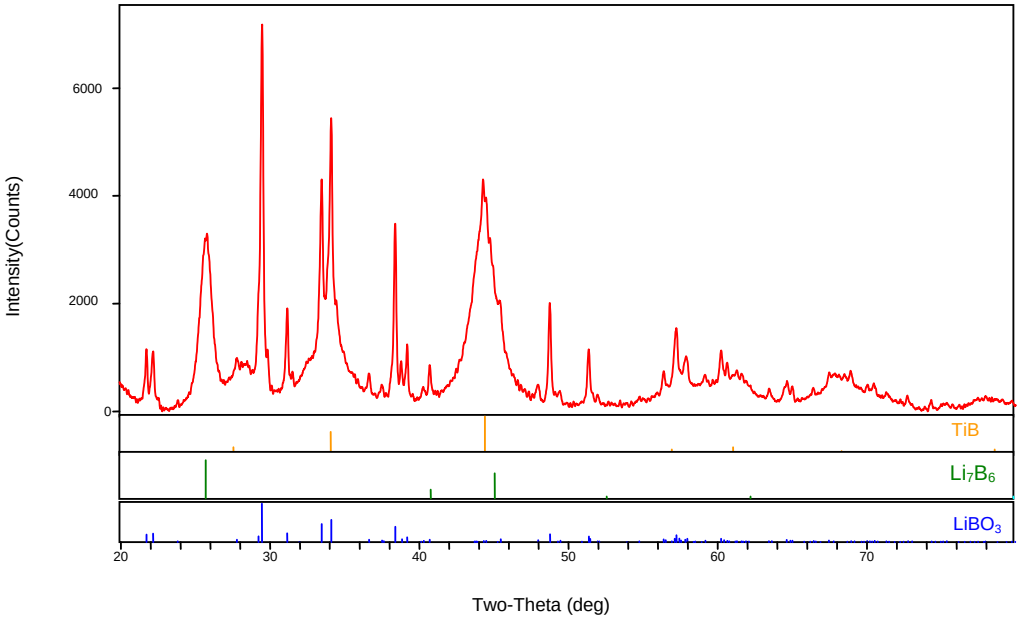

Fig.9 The XRD of the rehydrided $LiBH_4$ 75%+TiO_2 25%

4.3 Metal halide modified $LiBH_4$

Doping with metal halides made $LiBH_4$ very unstable, releasing H_2 even at 60^oC (Fig.4). Unfortunately, it also made $LiBH_4$ irreversible (Fig.7). What are the reasons? It was assumed that the additives $TiCl_3$, TiF_3, ZnF_2 and AlF_3 react with $LiBH_4$ and form unstable metal borohydrides $Ti(BH_4)_3$, $Al(BH_4)_3$ and $Zn(BH_4)_2$ that decompose at room temperature and release H_2 and B_2H_6 (Fig.5-6). For example, $LiBH_4$ could first react with $TiCl_3$ as $3LiBH_4+TiCl_3 \rightarrow 3LiCl + Ti(BH_4)_3$. The unstable $Ti(BH_4)_3$ could then decompose immediately even at room temperature as $Ti(BH_4)_3 \rightarrow TiH_2 + 2.5B + 0.25B_2H_6 + 4.25H_2$. This reaction is not reversible. The stoichiomestry to convert all $LiBH_4$ to $Ti(BH_4)_3$ is $LiBH_4/ TiCl_3 = 3/1$. A portion of $LiBH_4$ probably was not converted to $Ti(BH_4)_3$ in samples $LiBH_4+0.1TiCl_3$ and $LiBH_4+0.1TiF_3$ that show some of rehydrogenation capacity. When the ratio of additive $TiCl_3$, TiF_3 and ZnF_2 were increased to 0.5 moles, the doped $LiBH_4$ are irreversible because of unrecoverable boron loss caused by B_2H_6 emission (Fig.7). For this reason, “boron retention” is a key for long term reversible dehydriding and rehydriding.

5. CONCLUSION

It was verified that the commercially pure $LiBH_4$ is partially reversible in limited dehydriding-rehydriding cycles. The decomposition of $LiBH_4$ is accompanied by borane emission that causes unrecoverable boron loss. The gradual decrease of rehydriding capacity indicates that the partial reversibility is not sustainable.

Doping with metal oxides (TiO_2, ZrO_2, V_2O_3, SnO_2) and halides ($TiCl_3$, TiF_3, ZnF_2 and AlF_3) reduced the dehydriding temperature of $LiBH_4$ remarkably. However, the possible cation exchange reactions of lithium borohydride and the additives produced unstable transition metal borohydrides that decompose and released diborane gas during the interaction.

Historically, the transition metal borohydride were made for the generation of diborane because of their volatility. For this reason, attempt to develop transition metal borohydrides, or doping with transition metal compounds, will lead to disappointment. It is challenging to make metal borohydrides reversible, if not impossible.

Acknowledgement

This project is financially supported by NNSA PDRD program and General Motors Corporation. Savannah River National Laboratory is operated by Savannah River Nuclear Solution for US Department of Energy under contract DE-AC09-08SR22470.

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