

Destabilized LiBH₄/MgH₂ for reversible hydrogen storage

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Abstract

DOE and FreedomCAR technical targets of 6.0 and 9.0 wt.% are set forth capacities to realize a “holy grail” for hydrogen storage systems for 2010 and 2015 respectively. Alkali metal complex hydrides with high theoretical hydrogen capacity, for example: LiBH₄ (18 wt.%), are being investigated for their properties to store large quantities of hydrogen. The catalytic doping of SiO₂, seems to enhance the performance of LiBH₄. However, the poor cyclic reversibility due to thermodynamic barrier limits their wide usage. Recently, a destabilization mechanism was adopted in order to improve the cycling capacity of LiBH₄ by the addition of MgH₂. We have successfully synthesized the complex hydride mixtures LiBH₄ + ½MgH₂ + Xmol% ZnCl₂ catalyst (X=2, 4, 6, 8 and 10) by an inexpensive mechano-chemical process. The structural characterization by X-ray powder diffraction profiles exhibit the presence of LiCl, MgH₂ and LiBH₄ as majority and minority phases. Besides, the LiCl peaks relative intensity increases with increase of ZnCl₂ concentration. The thermal decomposition (gravimetric weight loss) and heat flow measurements have been performed by simultaneous DSC and TGA techniques. An earlier decomposition temperature of 270° C has been observed for the 10mol% ZnCl₂ doped LiBH₄/MgH₂ in comparison to the pristine LiBH₄ compound. The pressure-composition-temperature isotherms of the destabilized LiBH₄ show an extended plateau pressure around 4-5 bars at 350° C with a good cyclic stability.

Introduction

Light weight, high hydrogen storage capacity materials like LiBH₄, with a theoretical gravimetric and volumetric hydrogen storage capacities of 18.5 wt.% and 121 kgH₂/m³, accomplishes the DOE and FreedomCar targets [1]. Doping SiO₂ as a catalyst thus enables to decrease the dehydrogenating temperature of LiBH₄ [2]. A recent report indicates a dehydrogenation-rehydrogenation cycle improvement and reducing the reaction enthalpy of LiBH₄ by the addition of MgH₂ in a ratio of 2LiBH₄ / MgH₂ [3]. The addition of MgH₂ destabilizes LiBH₄ which in consequence increases the hydrogen equilibrium pressure. Moreover, recent investigations reveal an improvement in the reversibility of LiBH₄ with the addition of metal oxides such as TiO₂, V₂O₅ [4]. Further investigation of LiBH₄ should provide its feasibility as a candidate hydride for PEM fuel cells powered vehicles [5, 6]. The present research is focused on improving the overall kinetics of LiBH₄ by ad-mixing metal halide (e.g. ZnCl₂) catalyst to the mixture of LiBH₄ + ½MgH₂ [7, 8]. An extensive characterization has been carried out by using XRD, DSC, TGA and PCT analytical procedures.

Experimental Details

Materials such as LiBH₄ (95%) and MgH₂ (98%) were obtained from Alfa Aesar. Dopant material like ZnCl₂ (99%) and TiCl₃ (99%) were obtained from Sigma Aldrich and all used without purification. All mixing, transfers and weighing were performed in a nitrogen filled glove box. The mixture LiBH₄ + ½MgH₂ + Xmol% ZnCl₂ (X=2, 4, 6, 8 and 10) and for Xmol%

TiCl₃ (1, 2, 3 and 4) was mixed in a stainless steel bowl (80 ml) and sealed the specially designed lid (www.globalgilson.com) with a viton O-ring under nitrogen filled glove box. Before removing the bowl from the glove box, it was evacuated in the antechamber to remove any residual oxygen and/or moisture. The stainless steel bowl with the mixture was purged and pressurized with hydrogen (~ 1 atm) prior to ball milling process using the specially designed valves. A high energy Fritsch pulverisette planetary mono mill was employed to mechano-chemically mix the reactants. A ball to powder weight ratio of 20:1 and a milling speed of 300rpm were set to optimize the process over a varied range of milling time. After the mechano-chemical process, the as-prepared complex hydrides were immediately transferred to the glove box for further analysis.

The powder X-ray diffraction analysis was carried out by a Philips X'pert diffractometer with CuK α radiation of $\lambda = 5.4060 \text{ \AA}$ with incident and diffraction slit width of 1° and 2° respectively. The XRD results were analyzed using PANalytical X'pert Highscore software, version 1.0e to identify phase and crystalline size. A polyethylene clear plastic wrap was used to cover the mixture once it has been placed in the sample holder in order to avoid contact with air.

An SDT (Simultaneous DSC and TGA) Q-600 model from TA Instruments was used to analyze the weight loss and heat flow characteristics for the reaction during decomposition with a temperature ramp rate of 5° C/min. The SDT calibration was performed as per TA instructions with empty pan and standard sapphire disc. The measurement for isothermal volumetric sorption was performed by a Hy-Energy's PCT Sievert's type apparatus.

Results and Discussion

Figure 1A shows different TGA results for the pristine 95% LiBH₄ and mixtures of LiBH₄ + ½MgH₂ + X mol% ZnCl₂ (X = 2,4,6,8,10) ball milled for 2 hours under H₂ pressure.

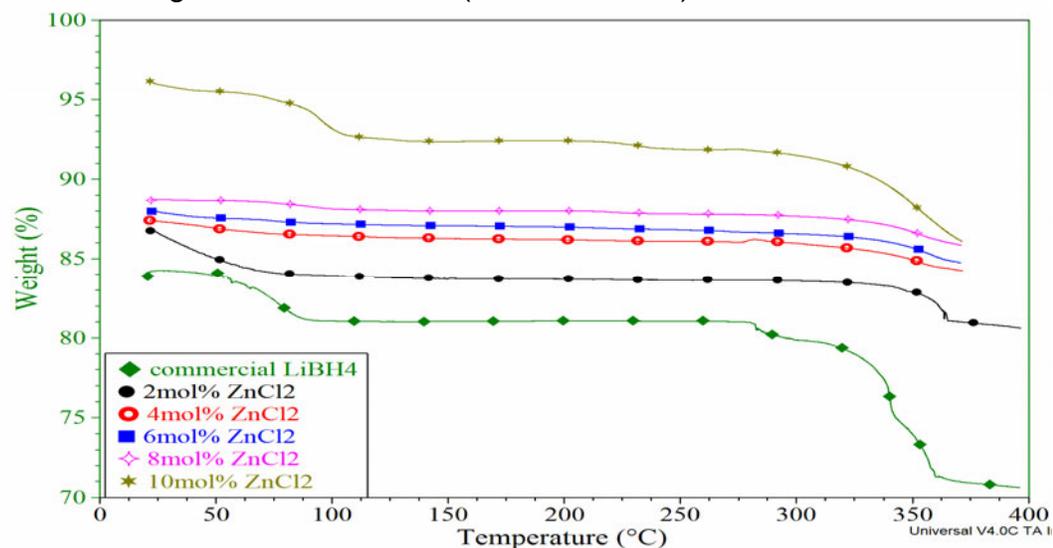


Fig. 1(a). TGA curves for LiBH₄ + ½MgH₂ + 2,4,6,8,10 mol% ZnCl₂ ball milled for 2 hours under H₂ pressure.

A slight weight loss of around 1.2% during the melting process of non-ball milled LiBH₄ between the peaks 275-300° C [2, 9, 10] was observed (refer to Figure 1(a)). A significant

exothermic peak around 75° C with weight loss since the beginning of the analysis [11] indicates a possible hydrolysis [12-13] for the pristine LiBH₄ sample due to moisture and a total weight loss around 13.6wt% (see Figure 1(b)) below.

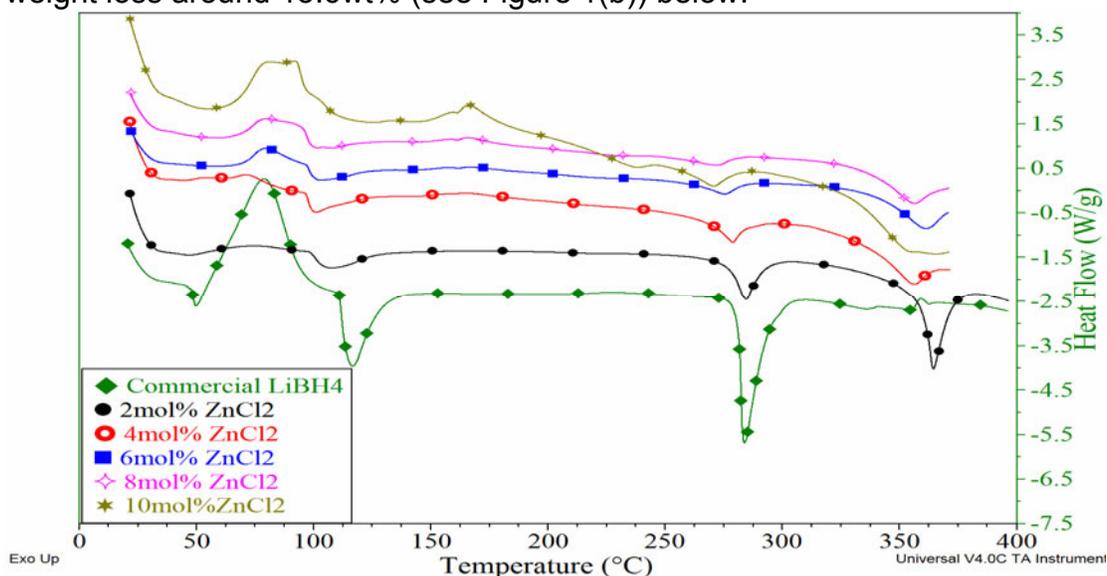


Fig. 1(b). DSC profiles for LiBH₄ + ½MgH₂ + 2,4,6,8,10 mol% ZnCl₂ ball milled for 2 hours under H₂ pressure.

In addition, a slight shift in the melting peak from approximately 283°C to 270°C was observed when contrasting DSC profiles to the non-ball milled LiBH₄. This effect could be more associated with the concentration of ZnCl₂ than with the ball milling time and/or the addition of MgH₂. Moreover, the presence of desorption peaks [1-3], which are endothermic peaks around 350-365°C for the ZnCl₂ doped mixtures, indicates the effectiveness of ZnCl₂ as a catalyst by slightly lowering the desorption temperature with higher concentration of ZnCl₂.

According to Figure 2, the desorption rate of LiBH₄ + ½MgH₂ + 2mol%ZnCl₂ ball milled for 2 hours increases with increasing temperature. Desorption rate at 350°C is around 5 times faster than the desorption rate at 300°C. The dramatic desorption difference when comparing the plots for 350° C and 300° C indicates a range to locate the significant desorption process. An additional observation, assuming the reaction products are: LiH + ½MgB₂ + 2H₂, the H₂ total weight percent in the product mixture will decrease with increasing concentration of ZnCl₂. Assuming the later product mixture, for the following ZnCl₂ concentrations an approximate theoretical total H₂ weight percentage would be obtained (see Table 1). These weight percentages include the weight of ZnCl₂ since it is not eliminated from the mixture. Additional analysis must be performed to the reaction products to determine gas composition.

Table 1: Reduction effect in the theoretical total H₂ wt% by ZnCl₂ addition.

Mol% ZnCl ₂	Total H ₂ wt%
2	10.34
4	9.359
6	8.549
8	7.867
10	7.286

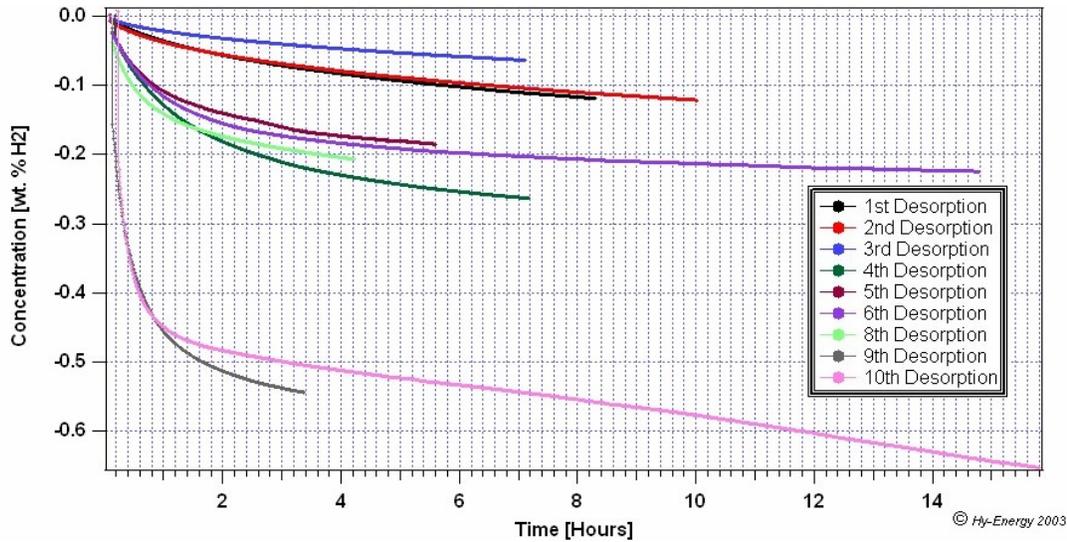


Fig. 2. Desorption data collected on a PCT for $\text{LiBH}_4 + \frac{1}{2}\text{MgH}_2 + 2\text{mol}\%\text{ZnCl}_2$ ball milled 2 hours under H_2 ambient. Desorptions were performed at various temperatures: 1-3 cycles at 250°C ; 4-6 cycles at 300°C ; 8-10 cycles at 350°C .

The PCT diagram (Figure 3), shows two different desorption curves at 250°C and 350°C for $\text{LiBH}_4 + \frac{1}{2}\text{MgH}_2 + 2\text{mol}\%\text{ZnCl}_2$ ball milled 2 hours under H_2 pressure. An absence plateau pressure for the 1st desorption cycle curve at 250°C is an indication of no hydrogen being absorbed by the mixture at that temperature. As for the 11th desorption cycle curve at 350°C , a plateau pressure at around 4-5 bars was observed with a total desorption of 3 wt.%.

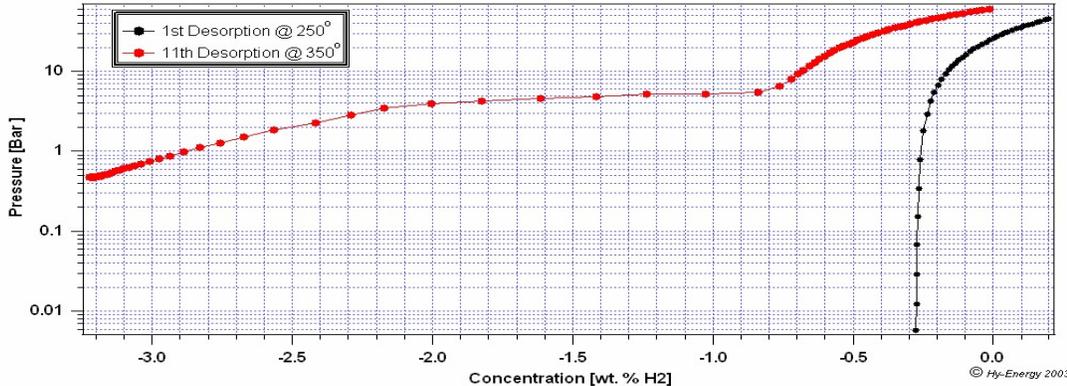


Fig. 3: PCT desorption plots at 250°C and 350°C for the mixture $\text{LiBH}_4 + \frac{1}{2}\text{MgH}_2 + 2\text{mol}\%\text{ZnCl}_2$ ball milled 2 hours under H_2 pressure.

Moreover, the hydrogen storage capacity increases with increasing number of cycles. It was proven the MgH_2 effects in reducing the reaction enthalpy by $25 \text{ kJ}/(\text{mol H}_2)$ by destabilizing LiBH_4 [1].

The XRD profiles shown in Figure 4 correspond to the mixture of $\text{LiBH}_4 + \frac{1}{2}\text{MgH}_2 + X\text{mol}\%\text{ZnCl}_2$ ball milled under an ambient of H_2 gas for 30 minutes. The presence of LiCl after ball milling for 30 minutes indicates a reaction between ZnCl_2 and LiBH_4 taking place while the mixture is being pulverized. In addition, the peak corresponding to LiCl increases with increasing concentration of ZnCl_2 while at the same time the peaks corresponding to MgH_2 and LiBH_4 decreases. No presence of MgB_2 was found.

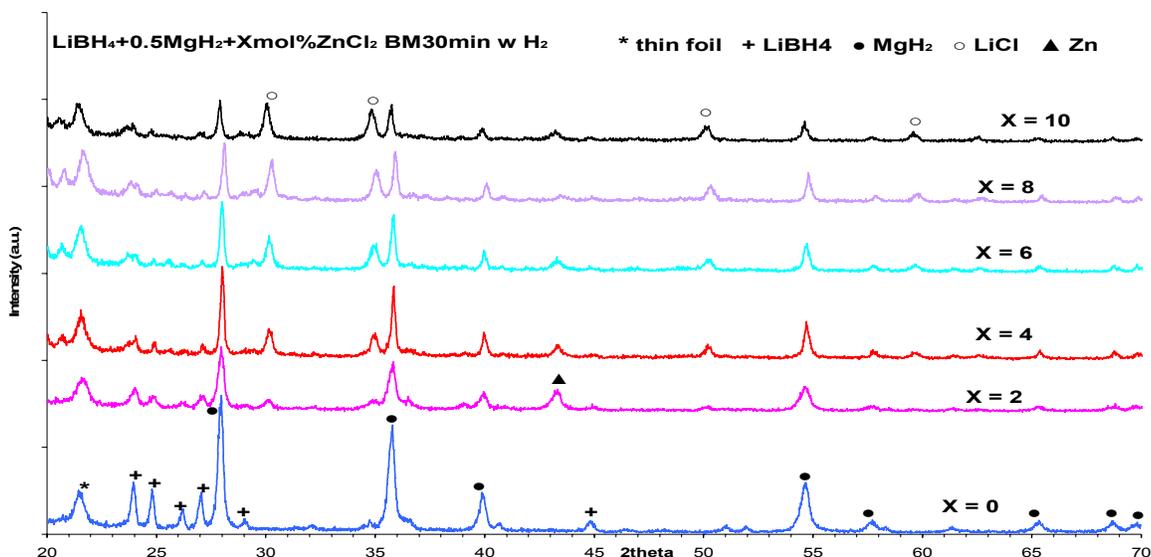


Fig. 4: XRD profiles of $\text{LiBH}_4 + \frac{1}{2} \text{MgH}_2 + X \text{mol}\% \text{ZnCl}_2$ ball milled for 30 minutes under a H_2 gas ambient.

The XRD profiles shown on Figure 5 correspond to the mixture of $\text{LiBH}_4 + \frac{1}{2} \text{MgH}_2 + X \text{mol}\% \text{TiCl}_3$ ball milled under an ambient of H_2 gas for 30 minutes.

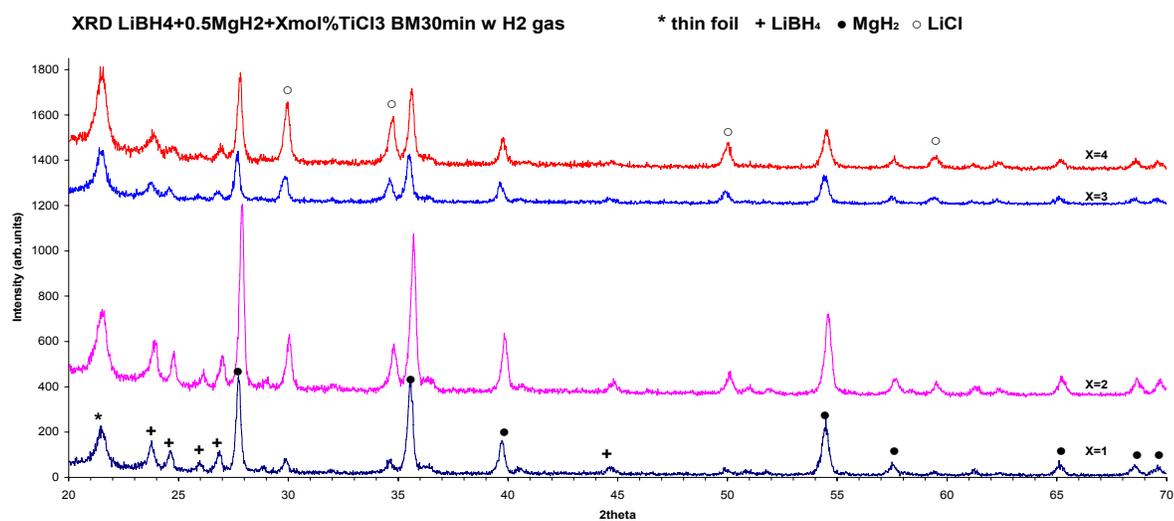


Fig. 5: XRD profiles of $\text{LiBH}_4 + \frac{1}{2} \text{MgH}_2 + X \text{mol}\% \text{TiCl}_3$ ball milled for 30 minutes under a H_2 gas ambient.

The presence of LiCl after ball milling for 30 minutes indicates a reaction between TiCl_3 and LiBH_4 . Besides, the peak corresponding to LiCl increases with increasing concentration of TiCl_3 while at the same time the peaks corresponding to MgH_2 and LiBH_4 decrease and no presence of MgB_2 was found. When comparing both diagrams, the peak at 43° is not present on this plot since it belongs to Zn .

Conclusion

In summary, we have successfully prepared $\text{LiBH}_4/\text{ZnCl}_2$ mixture doping with different amounts of ZnCl_2 and TiCl_3 catalysts. DSC and TGA analysis shows a lower

decomposition/melting temperature of $\text{LiBH}_4/\text{MgH}_2$ mixture in the presence of ZnCl_2 . It concludes the predominance of thermodynamics over kinetics as limiting factor. The initial rate of hydrogen decomposition from $\text{LiBH}_4 + \frac{1}{2}\text{MgH}_2 + 2\text{mol}\% \text{ZnCl}_2$ increases with an increase of temperature. Moreover, the plateau pressure of 4-5 bars at 350°C indicates a lower energy level for dehydrogenation-rehydrogenation cycling with a volumetric capacity of 3.0wt%, such capacity increases per cycle. The XRD profiles indicate a reaction occurring during the mechano-chemical mixing with ZnCl_2 and TiCl_3 successfully showing the presence of LiCl as product. At this moment, the research is focused in identifying the gas composition during desorption employing a GC-MS and development of destabilized structures by dopant admixing catalyst. Identifying the gas composition during desorption might provide useful information regarding the reaction path and products. Further experimental analysis using different catalysts and amounts of reactants is currently under way to tailor the hydrogenation properties of the complex borohydride systems.

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