

MODIFIED LITHIUM BOROHYDRIDE FOR MOBILE HYDROGEN STORAGE

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ABSTRACT

Influences of fluorine containing compounds TiF_4 and ZrF_4 on hydrogen sorption properties of LiBH_4 have been investigated. Thermovolumetric measurements, titration, and XRD technique were used to characterize the samples. The results demonstrated a pronounced beneficial effect of both ZrF_4 and TiF_4 on the sorption properties of modified LiBH_4 . After hydrogenation at 400°C and 80 bar, formation of modified LiBH_4 was observed as a consequence of F dissolution in LiH ($\text{LiH}_{1-z}\text{F}_z$). Adding TiF_4 and ZrF_4 to LiBH_4 has been found to modify both thermodynamic and kinetic properties.

Keywords: Hydrogen storage; Complex hydride; Lithium borohydride; Fluorine doping

1. INTRODUCTION

Hydrogen is a promising candidate for zero emission fuel for mobile application. However, there are challenges to storing hydrogen because of its low density in ambient temperature as well as its low boiling temperature, i.e. -254°C . To date, in commercial use, hydrogen is stored in compressed or liquid form. However, both of these forms have significant problems in their efficiency and safety. Compressed hydrogen needs a large space in vehicles and must use a high pressure system which is not very safe. Due to the low boiling temperature of hydrogen, energy needed for its liquefaction is also high (Schlapbach & Züttel, 2001). Fortunately, hydrogen can also be stored in solid materials. In this kind of storage, hydrogen either occupies specific sites in the structure of solid materials or it reacts to form compounds. In addition to their high volumetric density, most solid storage materials have the potential to operate at ambient temperature and pressure, which is the goal of hydrogen storage research. Hence if these materials are successfully developed, it will fulfil both efficiency and safety requirements.

Complex metal hydrides based boron, LiBH_4 is considered as one of the most promising solid state hydrogen storage possibilities because of its high gravimetric density of up to 18 wt% H. However, because of its high enthalpy of formation, it tends to be very stable even at high temperature which is impractical for on-board application. Several investigations have been conducted on hydrogen desorption from LiBH_4 systems and it has been found that hydrogen desorption can only be achieved at above 500°C (Züttel et al., 2003; Orimo et al., 2005). Several attempts have been made to modify the properties of LiBH_4 . One approach is the so called destabilization process in which LiBH_4 is mixed with elements or compounds which result in an intermediate compound that forms during the dehydrogenation process.

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This intermediate compound emits exothermic energy during its formation thereby reducing the total heat of the dehydrogenation of LiBH_4 .

Another method to modify LiBH_4 is by cation doping in which an element with high electro negativity like Magnesium can be used to substitute Li (Lee et al., 2010). Besides cation doping, it is suggested theoretically that the anion doping concept can also be applied to modify hydrogen sorption properties of complex hydrides. An Ab-initio calculation based on the potential density method suggests that F can be used to modify the anions of the LiBH_4 system. Calculation by Yin et al. (2008) show that ΔH will reduce to -20 to -40 kJ/mol of H_2 depending on the number of H side substituted. That amount of enthalpy is in the range of practical application (between -30 to -50 kJ/mol) needed to achieve a desorption temperature of around 100°C at 1 bar. In this paper, experimental investigations on the hydrogen sorption properties of LiBH_4 by addition of transition metal fluoride will be presented. It was hypothesized that addition of TiF_4 and ZrF_4 in LiBH_4 would give F anion doping effects on the LiBH_4 .

2. METHODOLOGY/ EXPERIMENTAL

Powders of lithium borohydride, and metal fluorides used in this work are listed in Table 1.

Table 1 List of the materials used in this work

Compound	Particle Size	Purity	Producer
LiBH_4	$< 44 \mu\text{m}$	95%	Alfa Aesar
TiF_4	$< 44 \mu\text{m}$	98%	Alfa Aesar
ZrF_4	$< 44 \mu\text{m}$	98%	Sigma Aldrich

Milling of LiBH_4 +10% metal tetrafluorides was done in the SPEX 8000 milling machine. Three grams of sample were placed in a stainless steel vial, milled for 60 minutes with a powder to ball ratio of 1:10. Milling and handling of the materials were carried out in a glove box with continuously purified Ar atmosphere.

Sorption experiments were carried out using the HERA titration machine in which dehydrogenation and rehydrogenation can be measured. Data acquisition was done using LabVIEW software. Thermovolumetric desorption was conducted in the dynamic mode in which powder was heated in the reaction chamber from room temperature to the 450°C with a $3^\circ\text{K}/\text{minute}$ heating rate. Data of pressure change in the reaction chamber and, therefore, weight loss versus temperature were recorded. Desorption was carried out under 10^{-2} bar. Absorption was conducted in isothermal condition at 440°C , 80 bar. Absorbed and desorbed powders were examined using a D-80 Advance XRD instrument made by Bruker AXS with Cu-K α monochromatic radiation source with wavelengths of 1.505 \AA .

3. RESULTS AND DISCUSSIONS

It has been known that some metal halide compounds can decrease the desorption temperature of LiBH_4 and create partial reversibility (Cho et al., 2006; Barkhordarian et al., 2007; Au et al., 2008; Zhang & Liu, 2010). For example, TiCl_3 and TiCl_4 were found to be good additives in this respect. However, there is not much research on the effect of fluorides on this system. Previous investigations on the function of fluoride compounds on the hydride systems showed

that they affect hydrogen sorption properties of single hydrides. For example, in magnesium hydride, TiF_3 , NbF_5 and other transition metal fluorides were proved beneficial (Jin et al., 2007; Ma et al., 2007; Luo et al., 2008). In NaAlH_4 , TiF_3 was used, showing good results compared to the TiCl_3 (Kang et al., 2007).

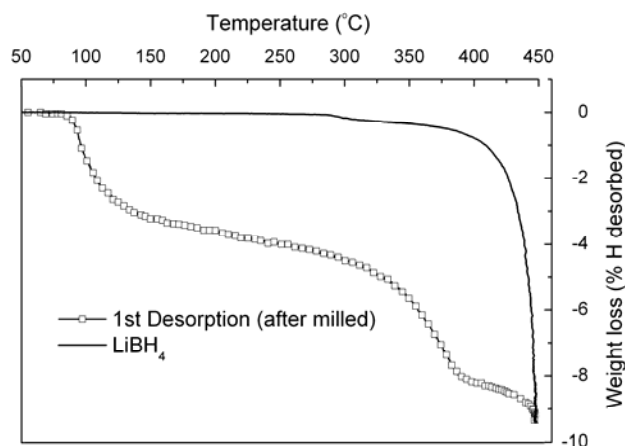
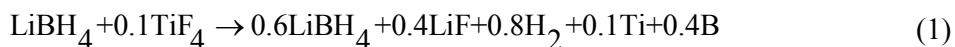


Figure 1 Thermovolumetric measurements on the 1st desorption of $\text{LiBH}_4+0.1\text{TiF}_4$ at 10^{-2} bar. Sample was heated from room temperature to 450°C at $3\text{K}/\text{min}$

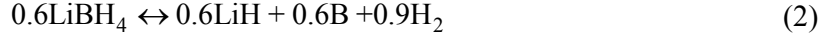
Figure 1 shows the 1st desorption curve of $\text{LiBH}_4+0.1\text{TiF}_4$ compared with pure LiBH_4 . Powder was heated from room temperature to 450°C with $3\text{K}/\text{minute}$ heating rate. Desorption was done at 10^{-2} bar. As can be seen in Figure 1, the $\text{LiBH}_4+0.1\text{TiF}_4$ sample released hydrogen in several consecutive stages. First, at a low temperature of about 80°C , TiF_4 most likely reacted with LiBH_4 in which Li and F form a stable compound, LiF . This LiF formation was confirmed from the XRD pattern of desorbed sample as shown in Figure 2(a). It can be seen that there were strong peaks of LiF beside LiH . This reaction of Li from LiBH_4 and fluorine was accompanied by a fast hydrogen release rate which can be seen on the curve in temperatures ranging between $80\text{--}150^\circ\text{C}$. In the next stage, at around 150°C , the hydrogen desorption rate, shown by the gradient of the curve began to decrease. The gradient was less sharp when compared with the first desorption stage. This stage continued until a temperature of around $300\text{--}320^\circ\text{C}$ was reached. At above 320°C , hydrogen desorption was faster until it reached a capacity of $8\text{ wt}\%$ at 390°C . After that, the rest of the LiBH_4 desorbed hydrogen at a very slow rate.

It can be seen in Figure 1 that the maximum hydrogen capacity that can be desorbed was $9.4\text{ wt}\%$. Theoretically, if all hydrogen in the $\text{LiBH}_4+0.1\text{TiF}_4$ can be extracted, powder will release $11.8\text{ wt}\%$ hydrogen. Since maximum temperature in this measurement was 450°C , some hydrogen remained in LiH . Nevertheless, it is interesting to note that at around 390°C there was already $8\text{ wt}\%$ of hydrogen released, which can not be achieved with pure LiBH_4 at that temperature.

Based on the above discussion, the decomposition reaction of $\text{LiBH}_4+0.1\text{TiF}_4$ can be described as two main reactions.



Reaction 1 yields 4.8wt% hydrogen. It can be seen that there is only 0.4% mol of LiBH_4 reacted in this reaction step. The rest of the LiBH_4 will react according to reaction 2, which is typical decomposition of LiBH_4 .



Reaction according to Equation (2) releases 5.8wt% H from the sample. Therefore, according to this reaction scenario, the total hydrogen which can be desorbed is about 10.6 wt%. The rest of hydrogen is still bound in LiH, which is 1.2 wt%. This calculation agrees with experimental data where maximum hydrogen capacity is 9.4 wt%.

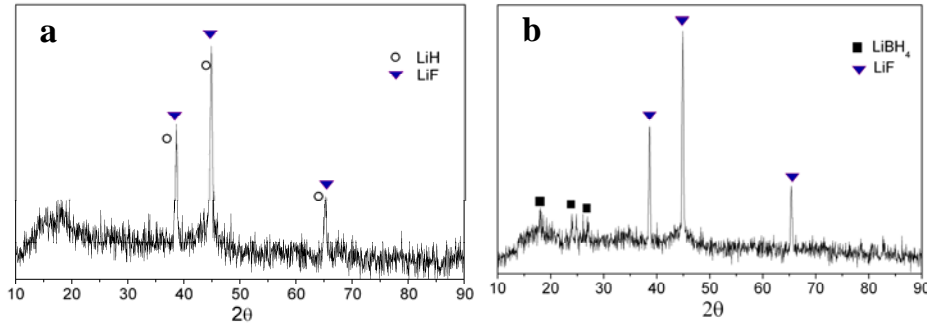
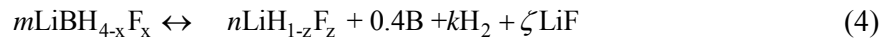
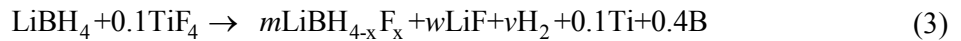


Figure 2 (a) XRD pattern of sample ($\text{LiBH}_4+0.1\text{TiF}_4$) after dynamic desorption in vacuum. (b) The ($\text{LiBH}_4+0.1\text{TiF}_4$) system after 1st absorption at 440°C, 80 bar

It is interesting to observe that if the first reaction in Equation (1) proceeds completely in the range of 80-150°C, the system releases about 4.8 wt% hydrogen. In addition, the hydrogen desorption rate does not significantly decrease unless 4.8 wt% hydrogen is released. It can also be seen that the desorption rate slows when hydrogen reaches 2.6 wt%, which is below the value mentioned above (4.8 wt% H_2). Another interesting point is that the dissociation of LiBH_4 through reaction 2 occurred at below 400°C, which did not happen in pure LiBH_4 . This can be explained by the existence of fluorine in the system and the formation of $\text{LiBH}_{4-x}\text{F}_x$. LiH and LiF have similar cubic NaCl type structures with close lattice parameters, i.e. LiF is 4.0270 Å and LiH is 4.0830 Å. As a result, the formation of this $\text{LiBH}_{4-x}\text{F}_x$ phase is indeed very likely. $\text{LiBH}_{4-x}\text{F}_x$ may have lower dissociation temperature than that of pure LiBH_4 . Based on this, the reactions in Equations (1) and (2) can be modified as Equations (3) and (4), respectively. Due to the difficulty on determining the exact quantification of dissolved F in the structure, in these equations the reaction coefficients are written as variables.



Formation of modified LiBH_4 can be deduced by comparing the hydrogen desorption behaviour of the sample with TiF_4 and without this additive at the values higher than 4.9 wt%. Based on the discussion above, if all TiF_4 reacts with LiBH_4 , 4.9 wt.% hydrogen can be desorbed; hydrogen higher than this value must be released from LiBH_4 . Since the desorption curves of these two cases are obviously different, so the presence of F modified LiBH_4 can be concluded.

Desorption products of $\text{LiBH}_4+0.1\text{TiF}_4$ were isothermally rehydrogenated at 440°C, 80 bar. It can be seen in Figure 3 that at the 1st rehydrogenation about 5 wt% hydrogen was absorbed in

30 minutes. The XRD pattern of absorbed sample in Figure 2(b) shows formation of LiBH_4 . It is worth mentioning that synthesis of LiBH_4 from LiH and B without any additives is only possible if 600°C and 350 bar are applied (Züttel et al., 2003; Mauron et al., 2008). This is further verification of $\text{LiBH}_{4-x}\text{F}_x$ formation during hydrogenation. However, this was not observed in XRD pattern, either due to similarity of the fluoride and hydride structures or to the amount of F in the structure of LiBH_4 . In the same line one can conclude that the reactants during hydrogenation have also been different than LiH and B . As indicated by Equations (3) and (4), the most likely reactants are $\text{LiH}_{1-z}\text{F}_z$ and boron. Because of identical crystal structures of LiH and LiF – with only 0.15% difference in cell parameters (Messer, 1970) - they can not be distinguished in the XRD pattern. Thus, it is clear that significant improvement has been achieved by the addition of TiF_4 .

From Figure 3, it can be inferred that maximum hydrogen capacity after rehydrogenation is 5.1 wt %. This capacity is less than the capacity predicted by Equation (2), which is 5.8 wt% H_2 . This can be explained by the presence of F in the LiBH_4 , which obviously reduces the hydrogen capacity to 5.1% as indicated by Equation (3).

Figure 4 shows all of the desorption curves of the $\text{LiBH}_4 + 0.1\text{TiF}_4$. The 2nd desorption started at 200°C which was higher than that of 1st desorption. In order to explain this, it is argued that during 2nd desorption the TiF_4 no longer existed. Accordingly, there was no reaction of Li from LiBH_4 with fluorine from TiF_4 . However, there was reaction between fluorine in $\text{LiBH}_{4-x}\text{F}_x$ and Li as discussed above. It can be also observed that there was no trace of LiBH_4 melting at 278°C in the curve. The 3rd desorption followed the same trend with the 2nd desorption. The slight differences is on the desorption rate, which is lower than that of the 2nd desorption. The possible reason for this may be the extraction of fluorine from the structure of LiBH_4 in the previous cycles. This is also consistent with the capacity observed in the 2nd and 3rd desorption. It can be seen that in the 3rd desorption, hydrogen capacity is less than that of 2nd desorption. This is because of LiF formation in the previous cycle.

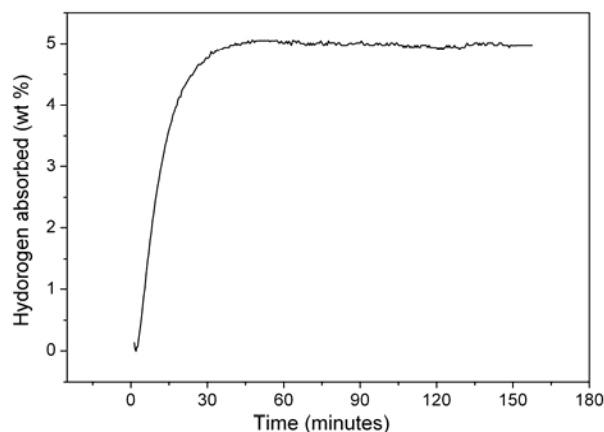


Figure 3 1st Absorption of ($\text{LiBH}_4 + 0.1 \text{TiF}_4$) desorbed products at 440°C , 80 bar

To obtain further insight on the effects of fluorine compounds on the sorption properties of LiBH_4 another tetrafluoride compound was tested. ZrF_4 was used as additive in the same amount as TiF_4 i.e. 10% mol. ZrF_4 differs from TiF_4 in terms of formation enthalpy. ZrF_4 has lower enthalpy of formation compared with the TiF_4 (it is more stable). This difference of the enthalpy of formation indicates that those compounds will react differently with LiBH_4 .

Figure 5 shows the 1st desorption curve of $\text{LiBH}_4+0.1\text{ZrF}_4$ compared with the pure LiBH_4 . The desorption was done at dynamic mode from room temperature to the 450°C at 3K/min with the pressure of 10^{-2}bar . It can be seen that 1st desorption of this system follows the same consecutive stages as the $\text{LiBH}_4+0.1\text{TiF}_4$ system. The first reaction of released hydrogen was the reaction of fluorine from ZrF_4 with Li from LiBH_4 to form LiF . The XRD pattern in figure 6(a) shows strong LiF peaks which means that a large quantity of LiF had been formed during 1st desorption.

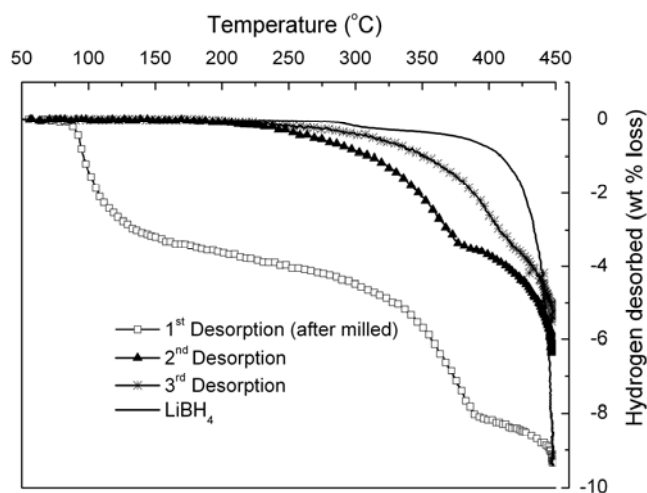


Figure 4 Thermovolumetric measurements on the desorption of $(\text{LiBH}_4+0.1\text{TiF}_4)$ at 10^{-2} bar. Sample was heated from room temperature to 450°C at 3K/min

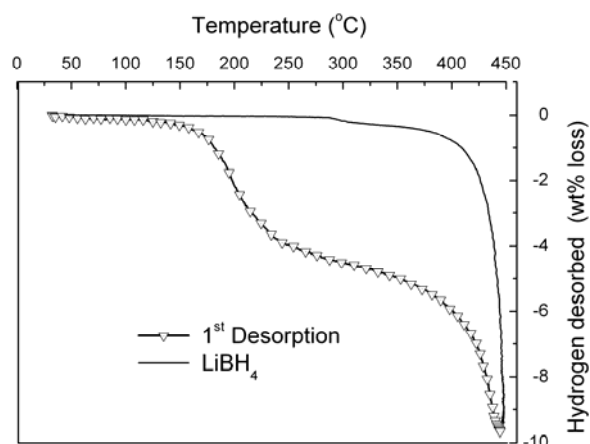


Figure 5 Thermovolumetric measurements on 1st desorption of $\text{LiBH}_4+0.1\text{ZrF}_4$ at 10^{-2} bar. Sample was heated from room temperature to 450°C at 3K/min

Onset temperature for hydrogen desorption in this system is slightly higher than that of $\text{LiBH}_4+0.1\text{TiF}_4$. As shown in the previous section, $\text{LiBH}_4+0.1\text{TiF}_4$ started releasing hydrogen at about 80°C . On the other hand, $\text{LiBH}_4+0.1\text{ZrF}_4$ began desorbing hydrogen at 100°C . Those differences on the onset of desorption temperature must be related to the stability (enthalpy of formation) of the fluoride compounds. TiF_4 has $\Delta H_f = -394.19\text{ kcal/mol}$ which is lower than that of ZrF_4 , which is $\Delta H_f = -456.80\text{ kcal/mol}$. Therefore TiF_4 reacts with higher driving force than ZrF_4 .

In the next stages, desorption of hydrogen from LiBH_4 comprised two simultaneous reactions: Reaction of rest of ZrF_4 with the LiBH_4 and decomposition of modified LiBH_4 . Identical to the $\text{LiBH}_4+0.1\text{TiF}_4$ system that modified LiBH_4 is fluorine dissolved LiBH_4 in the form of $\text{LiBH}_{4-x}\text{F}_x$.

Analogues to the $\text{LiBH}_4+0.1\text{TiF}_4$ system, dehydrogenation of $\text{LiBH}_4+0.1\text{ZrF}_4$ mainly contain two reactions. The first reaction, written as equation 5, will release 3.9 wt% hydrogen from the sample. The second reaction (Equation (6)) will desorb 5.2 wt% hydrogen. The sum of the hydrogen released will be less than the $\text{LiBH}_4+0.1\text{TiF}_4$, since the molecular weight of the ZrF_4 is much higher.

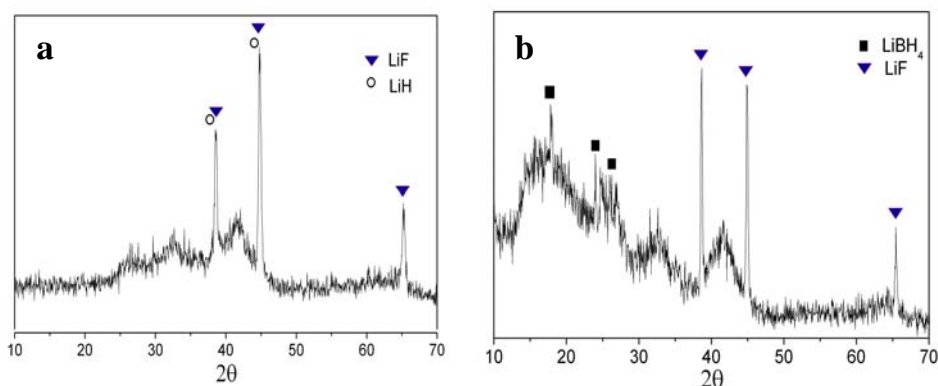
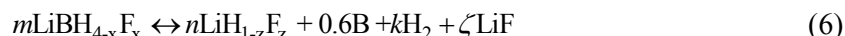
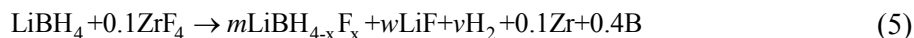


Figure 6 (a) XRD pattern of sample ($\text{LiBH}_4+0.1\text{ZrF}_4$) after dynamic desorption in vacuum. (b) The ($\text{LiBH}_4+0.1\text{ZrF}_4$) system after 1st absorption at 440°C, 80 bar

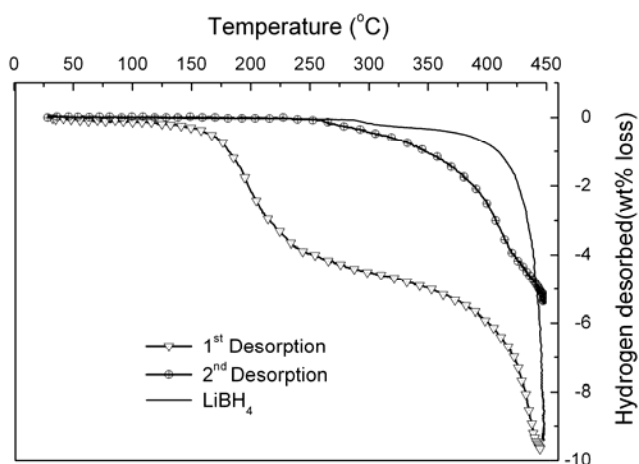


Figure 7 Thermovolumetric measurements on desorption of $\text{LiBH}_4+0.1\text{ZrF}_4$ at 10^{-2} bar. Sample was heated from room temperature to 450°C at 3K/min

The sample was hydrogenated isothermally at 440°C, 80 bar. The XRD pattern can be seen in figure 6b, which shows that there is formation of LiBH_4 . This provides proof that this system is reversible. Figure 7 shows the second desorption of $\text{LiBH}_4+0.1\text{ZrF}_4$. It can be seen that the desorption temperature was lower than the pure LiBH_4 . The sample started released hydrogen at

about 250°C. The capacity was 5.2 wt%, which is the same as the expected value in reaction 6. Thus, it can be said that there is improvement of the system in terms of desorption temperature. Analogous to the system with TiF₄, less hydrogen was released during the 2nd desorption. The formation of LiF and the possible hydrogenation product, LiBH_{4-x}F_x are probably the reason for this.

Based on the above results, the good hydrogen sorption properties of fluoride doped LiBH₄ can be attributed to the presence of F in the structure of LiBH₄. The existence of F during sorption is illustrated in Figure 8. During the 1st dehydrogenation of the TiF₄/ZrF₄ doped LiBH₄ system there was formation of LiBH_{4-x}F_x which lead to the formation of LiH_{1-z}F_z products after desorption. This LiH_{1-z}F_z was more reactive than LiH during rehydrogenation and it lead to the formation of LiBH_{4-x}F_x. As illustrated in Figure 8, the LiBH_{4-x}F_x is reversible if the F still exists in LiH_{1-z}F_z. However during the next sorption cycles, F gradually exits the reaction by LiF formation. As a result, upon cycling the LiH_{1-z}F_z degraded to normal LiH, which is less reactive and does not react to form LiBH₄ at the same experimental condition.

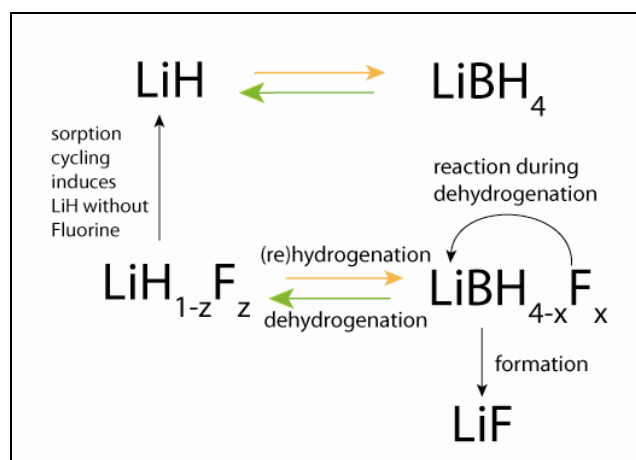


Figure 8 Illustration of LiBH₄ system containing fluorine in which LiH is modified as LiH_{1-z}F_z which induces the formation of LiBH_{4-x}F_x

4. CONCLUSION

The addition of 10% mol of TiF₄ and ZrF₄ to the LiBH₄ was found to be beneficial for both desorption and absorption. First dehydrogenation of LiBH₄ with ZrF₄ or TiF₄ additives started at very low temperatures. During the first dehydrogenation of both systems, the reaction started in the temperature range of 80-100°C. At temperatures below 400°C, up to 8 wt %, H₂ was released. On both systems onset temperatures for the 2nd desorption were higher in the range of 200-250°C. Moreover, the reactions showed reversibility at low temperatures and pressure, i.e. 440°C and 80 bar which is much lower than that of unmodified LiBH₄, (600°C, 300 bar). This can be explained by the formation of fluorine doped LiBH₄ in the form of LiBH_{4-x}F_x. In addition, the decomposition of LiBH_{4-x}F_x lead to the formation of LiH_{1-z}F_z, which was more reactive than normal LiH. This formation of LiH_{1-z}F_z brought about reversibility on these systems.

5. ACKNOWLEDGEMENT

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