EVIDENCE OF FORMATION OF $LiBH_4$ BY HYGH ENERGY BALL MILLING OF LiH AND B IN HYDROGEN ATMOSPHERE

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Abstract

$LiBH_4$ is one of the most interesting and studied complex hydride for hydrogen storage, due to its high theoretical gravimetric hydrogen capacity (18.4 wt%). The problem of using $LiBH_4$ as a hydrogen storage material is the complexity of the recycling mechanism: the decomposition reaction is reversible only in extreme conditions. In this work the formation of $LiBH_4$ by high energy ball milling a mixture of LiH and crystalline B in hydrogen atmosphere is demonstrated. Thermal programmed desorption, X-ray diffraction and DSC measurements on produced samples showed that the released gas comes from amorphous $LiBH_4$. The white crystalline powder obtained by solvent separation from one of samples has been identified by X-ray diffraction as pure $LiBH_4$.

Preparation of samples

Samples of 1.0 g were obtained by mixing LiH powder (Sigma–Aldrich, 95% purity) and small (less than 1 cm size) B pieces (Sigma–Aldrich, >99% purity) in the stoichiometric ratio 1:1. Boron in pieces was used to reduce the natural passivating oxide layer that could reduce reactivity. The samples were processed in hydrogen atmosphere by high energy ball milling with a SPEX 8000M mill in a stainless steel vial using stainless steel or WC balls (ball to mixture ratio of 30:1).

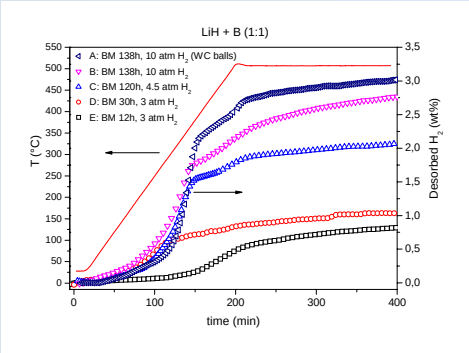
TPD measurements

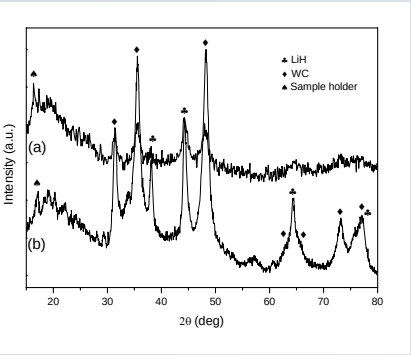
Thermal programmed desorption measurements showed that the amount of released gas increased by increasing milling time, hydrogen pressure into the vial and by using WC balls instead of stainless steel balls

X-ray diffraction

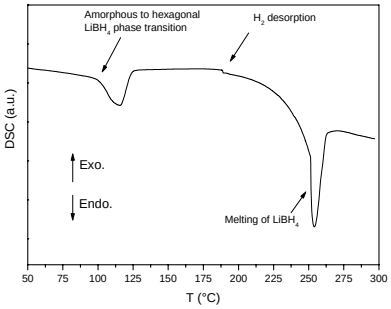
Diffraction patterns of the as milled sample (a) and decomposed sample A (b) are the same except peak intensities. WC is present as a contaminant (<0.05 vol%)

$$LiBH_4 \rightleftharpoons LiH + B + 3/2\ H_2$$





The desorbed hydrogen is reasonably coming from an amorphous hydrogenated phase like $LiBH_4$ formed during the reactive milling, as confirmed by DSC

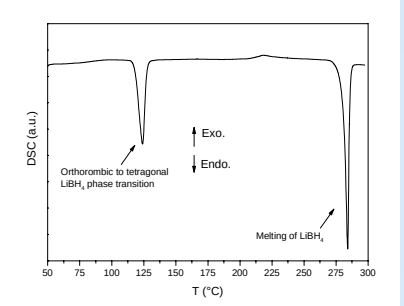


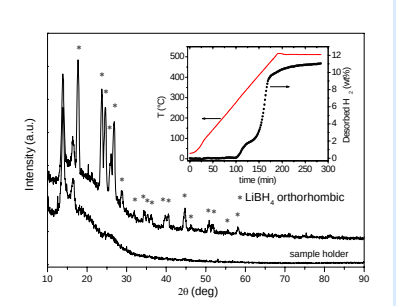
The amorphous-like state and/or the chemical surrounding (LiH and B acting as seeds) seem to enhance the decomposition reaction of $LiBH_4$

Solvent separation of $LiBH_4$

One g of milled sample A was put in 70 ml of methyl *tert*-butyl ether, in which $LiBH_4$ is soluble, and stirred for 12 h under argon atmosphere. Methyl *tert*-butyl ether was used due to its much lower tendency to form explosive organic peroxides with respect to other ethers like THF and moreover, it does not form adducts with $LiBH_4$. The suspension was then filtered and the obtained solution was evaporated under dynamic rotary pump vacuum. After the complete evaporation of solvent a white crystalline light powder was obtained.

DSC, TPD and X-ray diffraction confirmed that pure orthorombic $LiBH_4$ has been obtained.





Conclusions

- The formation of $LiBH_4$ during reactive high energy ball milling in hydrogen atmosphere of LiH and B, the decomposition products, is demonstrated.
- Increasing hydrogen pressure, time of milling and hardness of balls leads to increased release of hydrogen, probably due to the enhancement of the yield of formation of $LiBH_4$.
- The amorphous-like state of $LiBH_4$ and the chemical surrounding in the as milled samples seem to considerably enhance the decomposition shifting it at lower temperatures.