Abstract

Thermodynamic and kinetic modification for $LiBH_4$ and its composite with MgH_2
（$LiBH_4$ および MgH_2 との複合化材料の熱力学的および動力学的改良）

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The present study was focused on to lower the decomposition temperature of $LiBH_4$ and its composite system $2LiBH_4$-MgH_2 by tuning their thermodynamics and kinetics. According to the issues associated with $LiBH_4$ (hard thermodynamics) and $2LiBH_4$-MgH_2 (sluggish kinetics), the thesis was structured with two objectives.

First objective was to focus on the $2LiBH_4$-MgH_2 composite, where the thermodynamics of $LiBH_4$ was modified by the addition of MgH_2 but this composite system possess serious kinetic issues. In this work, KH was added as catalyst to the $2LiBH_4$-MgH_2 system in order to enhance the kinetics. A reduction in the temperature was observed for the first hydrogen desorption reaction, but no effect could be seen in the second dehydrogenation. However, an interesting phenomenon of eutectic melting was observed during the thermal heating of this system. By addition of 5 mol% KH, the melting point was shifted to lower temperature, which was continuously decreased with increase in the amount of KH from 0 to 55 mol%. For 55 mol% KH i.e. at eutectic composition $0.45(2LiBH_4$-$MgH_2)$-0.55KH the lowest melting temperature was observed as 79^oC. Eutectic melting is an interesting phenomenon and happens if two or more components sustain their liquid state below the melting points of their pure components. In this work, kinetic enhancement was achieved due to the occurrence of eutectic melting on adding KH as additive. The enhanced ionic mobility must be the driving force to desorb hydrogen at lower temperature in comparison of $2LiBH_4$-MgH_2 composite, thus caused a kinetic enhancement on addition of KH. Reduced melting point for some complex hydrogen

storage systems behaves as eutectic melts and can be utilized for refueling of vehicles. A pseudo-binary phase diagram between the $2LiBH_4$-MgH_2 composite and KH was discussed and was explained in terms of degree of freedom.

The second objective of the thesis was to modify the thermodynamics of pure $LiBH_4$ by the addition of Bi_2X_3 chalcogenides and study their decomposition properties. This work was initiated with a curiosity during an electrochemical experiment on Bi_2X_3 chalcogenides as anode materials for all-solid-state Li-ion battery in a recent work by our group. $LiBH_4$ was used as solid electrolyte in the cell with Bi_2Te_3 nanostructures as anode material. An interesting issue of cell opening during the charging – discharging motivated us to investigate the effect of Bi_2X_3 (X = S, Se and Te) addition on the decomposition properties of $LiBH_4$. An efficient destabilization of $LiBH_4$ could be achieved by addition of chalcogenides (Bi_2S_3, Bi_2Se_3 and Bi_2Te_3), which could tune the thermodynamic properties of $LiBH_4$ decomposition by alloying with Li. The hydrogen desorption temperature of $LiBH_4$ was reduced to below 150 ℃ by the addition of bulk Bi_2X_3. The detailed mechanism was established for the reaction of $LiBH_4$ with the Bi_2Te_3 (similar reaction steps were found for other two composites as well, i.e. $LiBH_4$-50wt%Bi_2Se_3 and LiBH4-50wt%Bi_2S_3) using several techniques and was proposed as follows:

$$38\mathrm{LiBH_4} + \mathrm{Bi_2}Te_3 \rightarrow \mathrm{Li_2}Te + 25\mathrm{LiBH_4} + 7LiH + 2\mathrm{Bi} + 12B + 22.5\mathrm{H_2}$$

$$\rightarrow 2\mathrm{Li_3Bi} + 17\mathrm{LiBH_4} + 2LiH + 8B + 15\mathrm{H_2}$$

$$\rightarrow 13\mathrm{LiH} + 4\mathrm{Li} + 17\mathrm{B} + 27.5\mathrm{H_2}$$

A further reduction in the decomposition temperature was achieved using nanostructured Bi_2X_3, which must be due to kinetic enhancement due to better solid-solid contact between $LiBH_4$ and Bi_2X_3 that promotes a faster reaction between the components.

All the work was compiled in Chapter 1 to 6. Chapter 1 describes the introduction of the field, need of research, and associated challenges. Based on the background discussed in chapter 1, the objectives are described in chapter 2, which comprises the aim of the thesis and motivation behind the research work. All the methods and materials adopted for the preparation as well as characterization of composite materials used in this work are covered in chapter 3. Chapter 4 is the explanation of our first objective i.e. improving the kinetics of $2LiBH_4$-MgH_2 system by the addition of potassium hydride (KH) as a catalyst. The results on the destabilization of $LiBH_4$ by the infusion of Bi_2X_3 (X = S, Se, Te) are presented in chapter 5. At last, chapter 6 summarizes the results and suggests overall conclusion of the thesis and proposes the future direction of research.