

Single- and Double-Cations Borohydrides for Hydrogen Storage Applications

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We have systematically investigated the thermodynamical stabilities of single cation borohydrides $M(\text{BH}_4)_n$ ($M = \text{Li, Na, K, Mg, Ca}\sim\text{Mn, Cu, Zn, Al, Y, Gd, Dy, Zr}$ and Hf ; $n = 1\text{-}4$) and their intermediate phases by both first-principles studies and thermal desorption measurements [1-5]. Recently, new series of double-cation borohydrides $M\text{Li}_{m-n}(\text{BH}_4)_m$ ($M = \text{Zn, n} = 2$; $M = \text{Al, n} = 3$; $M = \text{Zr, n} = 4$; $n \leq m$) were also studied [6]. Thermal desorption measurements indicate that both $\text{ZnLi}(\text{BH}_4)_3$ and $\text{AlLi}(\text{BH}_4)_4$ disproportionate into $\text{Zn}(\text{BH}_4)_2^-$ (or $\text{Al}(\text{BH}_4)_3^-$) and LiBH_4 -based phases upon heating, respectively. However, no disproportionation reaction is observed in the case of $\text{ZrLi}_{m-4}(\text{BH}_4)_m$. The hydrogen desorption temperature T_d of $\text{ZrLi}_{m-4}(\text{BH}_4)_m$ increases from 440 K ($m = 4$) to 650 K ($m = 6$), and continuously approaches to 740 K (T_d of LiBH_4). That is, T_d of $\text{ZrLi}_{m-4}(\text{BH}_4)_m$, namely $MM'(\text{BH}_4)_n$, is closely related to the averaged electronegativity of M and M' , as what have observed in $M(\text{BH}_4)_n$. Consequently, the above-mentioned results indicate that the appropriate combination of cations is an effective method to precisely adjust the thermodynamical stability of metal borohydrides, similar to the conventional “alloying” method for hydrogen storage alloys. Microwave irradiation effects on selected metal borohydrides and their composites were also investigated experimentally [7, 8].

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