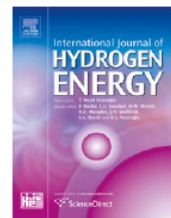


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## The effects of ball milling and nanometric nickel additive on the hydrogen desorption from lithium borohydride and manganese chloride ( $3\text{LiBH}_4 + \text{MnCl}_2$ ) mixture

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### ABSTRACT

A mixture of  $[3\text{LiBH}_4 + \text{MnCl}_2]$  was processed by high energy ball milling in ultra-high purity hydrogen gas for 0.5 and 1 h. The XRD patterns of milled powders show the sole diffraction peaks of LiCl. The reaction occurring during milling of  $[3\text{LiBH}_4 + \text{MnCl}_2]$  seems to have all characteristics of the metathesis-type reactions occurring between borohydrides ( $\text{LiBH}_4$  and  $\text{NaBH}_4$ ) and metal chlorides ( $\text{MCl}_n$ ) induced in a solid state by a mechano-chemical activation synthesis (MCAS). Under pressure of 0.1 MPa  $\text{H}_2$  (atmospheric) the ball milled  $[3\text{LiBH}_4 + \text{MnCl}_2]$  mixture is able to desorb  $\sim 4.0$  wt.%  $\text{H}_2$  at  $100^\circ\text{C}$  within 21,000 s and  $\sim 4.5$  wt.%  $\text{H}_2$  at  $120$  and  $200^\circ\text{C}$  within 8000 s and 4000 s, respectively. The addition of n-Ni with  $\text{SSA} = 60.5$   $\text{m}^2/\text{g}$  allows desorption of  $\sim 3.7$  wt.%  $\text{H}_2$  within 8,700 s at  $100^\circ\text{C}$ . This is one of the highest  $\text{H}_2$  desorption capacities obtained for a complex hydride at  $100^\circ\text{C}$  under atmospheric pressure of  $\text{H}_2$  taking into account the fact that the microstructure contains some amount of a useless LiCl constituent. The activation energy of hydrogen desorption for a ball milled undoped  $[3\text{LiBH}_4 + \text{MnCl}_2]$  is  $\sim 102$  kJ/mol and  $\sim 98$  and  $92$  kJ/mol after doping with 5 wt.% of nanometric Ni having specific surface area (SSA) of 9.5 and  $60.5$   $\text{m}^2/\text{g}$ , respectively. After volumetric desorption from  $100$  to  $450^\circ\text{C}$  the XRD patterns show only LiCl. The n-Ni additive slightly lowers the total quantity of desorbed  $\text{H}_2$ . Re-absorption tests, under pressure of 10 MPa  $\text{H}_2$  at  $200^\circ\text{C}$ , show that the system is, most likely, irreversible. Flammability studies show that the ball milled  $[3\text{LiBH}_4 + \text{MnCl}_2]$  mixture can be ignited by scraping the cylinder walls with a metal tool as well when it is thrown and dispersed in air in a powder form. It also reacts violently in contact with water and a nitric acid.

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