The effects of the micrometric and nanometric iron (Fe) additives on the mechanical and thermal dehydrogenation of lithium alanate (LiAlH₄), its self-discharge at low temperatures and rehydrogenation

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ABSTRACT

LiAlH₄ containing 5 wt.% of nanometric Fe (n-Fe) shows a profound mechanical dehydrogenation by continuously desorbing hydrogen (H₂) during high energy ball milling reaching $\sim$3.5 wt.% H₂ after 5 h of milling. In contrast, no H₂ desorption is observed during *low energy* milling of LiAlH₄ containing n-Fe. Similarly, no H₂ desorption occurs during high energy ball milling for LiAlH₄ containing micrometric Fe (μ-Fe) and, for comparison, both the micrometric and nanometric Ni (μ-Ni and n-Ni) additive. X-ray diffraction studies show that ball milling results in a varying degree of the lattice expansion of LiAlH₄ for both the Fe and Ni additives. A volumetric lattice expansion larger than 1% results in the profound destabilization of LiAlH₄ accompanied by continuous H₂ desorption during milling according to reaction: LiAlH₄ (solid) → 1/3Li₃AlH₆ + 2/3Al + H₂. It is hypothesized that the Fe ions are able to dissolve in the lattice of LiAlH₄ by the action of mechanical energy, replacing the Al ions and forming a substitutional solid solution. The quantity of dissolved metal ions depends primarily on the total energy of milling per unit mass of powder generated within a prescribed milling time, the type of additive ion e.g. Fe vs. Ni and on the particle size (micrometric vs. nanometric) of metal additive. For thermal dehydrogenation the average apparent activation energy of Stage I (LiAlH₄ (solid) → 1/3Li₃AlH₆ + 2/3Al + H₂) is reduced from the range 76 to 96 kJ/mol for the μ-Fe additive to about 60 kJ/mol for the n-Fe additive. For Stage II dehydrogenation (1/3Li₃AlH₆ → LiH+1/3Al + 0.5H₂) the average apparent activation energy is within the range 77–93 kJ/mol, regardless of the particle size of the Fe additive (μ-Fe vs. n-Fe). The n-Fe and n-Ni additives, the latter used for comparison, provide nearly identical enhancement of dehydrogenation rate during isothermal dehydrogenation at 100 °C. Ball milled (LiAlH₄ + 5 wt.% n-Fe) slowly self-discharges up to $\sim$5 wt.% H₂ during storage at room temperature (RT), 40 and 80 °C. Fully dehydrogenated (LiAlH₄ + 5 wt.% n-Fe) has been partially rehydrogenated up to 0.5 wt.% H₂ under 100 bar/160°C/24 h. However, the rehydrogenation parameters are not optimized yet.

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1.   Introduction

One of the major challenges to the implementation of the widespread hydrogen economy is the development of an efficient hydrogen storage technology for various industrial sectors and particularly for transportation/automotive applications. For a long-term development, solid state hydrogen storage in hydrides is more preferable than gaseous or liquid hydrogen storage which both have some serious drawbacks [1]. In general, solid state hydrogen storage systems based on hydrides require certain attributes such as reasonably high volumetric and gravimetric densities of hydrogen, the operating dehydrogenation/rehydrogenation temperature compatible with the waste heat generated by a fuel cell stack (<100 °C), fast dehydrogenation/rehydrogenation rates, possible reversibility and a reasonably low price. The relative importance of these factors depends on a perceived application in a selected industrial sector.

One of the most interesting hydrides for solid state hydrogen storage is a complex metal hydride $LiAlH_4$ (lithium alanate) since it can liberate a relatively large theoretical quantity of 7.9 wt.% H_2 below 250 °C [1]. However, the PCT plateau pressure of $LiAlH_4$ has been reported to be very high which could make $LiAlH_4$ irreversible under practical conditions of temperature/pressure. For instance, Brinks et al. [2] reported that the plateau pressure for the first stage dehydrogenation reaction of $LiAlH_4$ into Li_3AlH_6, Al and H_2 [1] is higher than 99 and 87 bar at 53 and 80 °C, respectively. Mulana and Nishimiya [3] estimated the enthalpy (ΔH) and entropy (ΔS) for the first stage dehydrogenation reaction (Stage I) of $LiAlH_4$ into Li_3AlH_6, Al and H_2 and the second stage dehydrogenation reaction (Stage II) of Li_3AlH_6 into LiH, Al and H_2, as being equal to $\Delta H = 17.5$ kJ/molH_2 and $\Delta S = 121.6$ J/molH_2 K, and $\Delta H = 11.1$ kJ/molH_2 and $\Delta S = 62.6$ J/molH_2 K, respectively. The equilibrium H_2 pressure for the hydrogen desorption/absorption plateau is related to temperature through the Van't Hoff equation [1]:

$$\ln(p/p_0) = -\Delta H/RT + \Delta S/R \qquad (1)$$

where p is the pressure (atm/bar), p_0 is the atmospheric pressure (1 atm/1 bar), ΔH and ΔS are the enthalpy and entropy changes in kJ/molH_2 and J/molH_2 K, respectively, R is the gas constant (8.314472 J/mol K) and T is the absolute temperature (K). One can estimate that for $\Delta H = 17.5$ kJ/molH_2 and $\Delta S = 121.6$ J/molH_2 K, the equilibrium pressure for Stage I dehydrogenation would amount to 1.88×10^3 and 19.6×10^3 atm at room temperature (24 °C = 297 K) and 170 °C (443 K), respectively. Apparently, the first dehydrogenation reaction appears to be completely irreversible due to extremely high pressures required for rehydrogenation. Assuming $\Delta H = 11.5$ kJ/molH_2 and $\Delta S = 62.6$ J/molH_2 K for Stage II, one obtains that at 170 °C the equilibrium pressure is around 82 atm. The latter pressure seems to be more reasonable for being achieved under practical conditions to induce reversibility. However, there is some discrepancy here because the computed stability diagrams for $LiAlH_4$/Li_3AlH_6/LiH show pressures on the order of 10^3 atm at 170 °C needed for the rehydrogenation of LiH/Al into Li_3AlH_6 (see ref. [4,5] and also Fig. 3.12 in [1]). In contrast, the experimental results

reported by Chen et al. [6] for $LiAlH_4$ ball milled with the $TiCl_3 \bullet 1/3AlCl_3$ additive showed reversibility of (LiH + Al) into Li_3AlH_6 at 40 bar and ~ 175 °C with the achieved reversible H_2 capacity of 1.8 wt.%. Recently, Rafi-ud-din et al. [7] reported that ball milled $LiAlH_4$ with 5 mol % TiC, dehydrogenated to (LiH + Al) (Stage II), could be successfully rehydrogenated to Li_3AlH_6 at 165 °C and 95 bar H_2 pressure with the achieved reversible H_2 capacity of 1.9 wt.%. These experimental results indicate that there is still a possibility of achieving at least a partial reversibility for $LiAlH_4$ containing catalytic additives using an appropriate window of temperature/pressure/time. It must also be added that it has recently been shown that $LiAlH_4$ doped with $TiCl_3$ and dehydrogenated to the (LiH + Al) mixture can be partially rehydrogenated back to $LiAlH_4$ at room temperature in low-boiling dimethyl ether under 100 bar H_2 pressure [8,9].

In order to decrease the dehydrogenation temperature and increase the dehydrogenation rate a number of additives were tested with $LiAlH_4$ and incorporated by ball milling. The effects of most common additives such as metal halides $AlCl_3$, $NiCl_2$, $TiCl_3$, $TiCl_3 \bullet 1/3AlCl_3$, $TiCl_4$, VCl_3, $ZrCl_4$, $ZnCl_2$ and VBr_3 on the dehydrogenation properties of $LiAlH_4$ are summarized in [10] (also see [1] for a more thorough review of pertinent works). Metal fluorides such as TiF_3 [2,11] and NbF_5 [12] were also tried as catalysts for $LiAlH_4$. The mechanism by means of which they act as catalytic additives is not fully elucidated. However, most papers report that they locally react with $LiAlH_4$ and form metal salts and free elemental metals or intermetallic compounds of nanometric sizes which most likely act as effective nano-metal catalysts [1,2,10–12]. A disadvantage of metal halides is the formation of a metal salt by-product which constitutes unnecessary ballast (deadweight) for the microstructure and reduces the total available hydrogen capacity. The addition of metallic and especially nanometric size metal catalysts to $LiAlH_4$ has not been investigated so extensively. Balema et al. [13] reported that the elemental Fe as a catalytic additive was much less effective than $TiCl_4$, Al_3Ti, $Al_{22}Fe_3Ti_8$ and Al_3Fe. They also reported that ball milling of $LiAlH_4$ with 3 mol% $TiCl_4$ for 5 min caused decomposition of $LiAlH_4$ into Li_3AlH_6, Al and H_2 by a rapid reduction of $TiCl_4$ by $LiAlH_4$ forming a LiCl salt. They did not observe any accelerated decomposition of $LiAlH_4$ during ball milling with Fe [13,14]. A partial decomposition of $LiAlH_4$ during ball milling was also observed with the TiF_3 [11] and $NiCl_2$ [15] additives. Resan et al. [16] concluded that the addition of elemental Ti, Fe and Ni did not cause the decomposition of $LiAlH_4$ during ball milling as did metal chlorides. Kojima et al. [17], besides metal chlorides and intermetallics, also added nanometric Ni as a catalyst to $LiAlH_4$. They found that both chlorides and nanometric Ni led to the decomposition of $LiAlH_4$ during ball milling for 24 h. Most recently, we reported that ball milling of $LiAlH_4$ containing 5 wt.% nanometric Ni did not cause any decomposition of $LiAlH_4$ up to at least 1 h of milling duration [18,19].

In the present work we report the results of the detailed studies on the catalytic effects of 5 wt.% micrometric iron (μ-Fe) and nanometric iron (n-Fe) on the dehydrogenation/rehydrogenation behavior of the ball milled $LiAlH_4$. The results obtained in the present work are compared to the