THE EFFECTS OF NANONICKEL ADDITIVE ON THE DECOMPOSITION OF COMPLEX METAL HYDRIDES

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Introduction

On board hydrogen storage for supplying fuel cell powered cars is one of the most important technical problems remaining to be solved if the future Hydrogen Economy is to become successful. Hydrogen storage in solid state hydrides [1] is the most attractive one as it provides better volumetric capacity of hydrogen than gaseous or liquid storage. High gravimetric capacities can be achieved by using complex hydrides based on low density metals such as Li, Mg and Al, and light nonmetals such as B and N. However, high capacity hydrides have usually higher hydrogen desorption temperatures than those generated by the waste heat of a fuel cell (~80°C) and have sluggish desorption kinetics [1]. Nanostructuring by ball milling combined with some catalytic additives have been found to vastly improve the hydrogen storage characteristics of high capacity hydrides [1].

In the present work we report the effects of experimental nano nickel (n-Ni) catalytic additive produced by Vale Inco, Mississauga, Ontario, on the hydrogen desorption behavior of two low-density complex metal hydrides: lithium alanate-$LiAlH_4$ (theoretical capacity 10.6wt.%H_2) and lithium amide-$LiNH_2$ (8.8wt.%H_2). The n-Ni has a filamentary shape with the average size of 42±16 nm and the specific surface area, SSA=14.5 m^2/g. Ball milling was used to intimately mix the n-Ni additive with respective hydride powders.

Results and discussion

Fig.1(a) shows the DSC trace of $LiAlH_4$ powder (97% purity) milled for 1h in the magneto-mill Uni-Ball-Mill 5 [1]. In principle, ball milling does not change the shape of a DSC curve with respect to that obtained without milling [1]. The first small exothermic peak at ~140°C is, most likely, due to an interaction with hydroxyl impurities and is unrelated to the hydrogen desorption. The first endothermic peak (1) is due to the melting of $LiAlH_4$. The second exothermic peak (2) at 189.5°C is due to the following reaction in liquid:
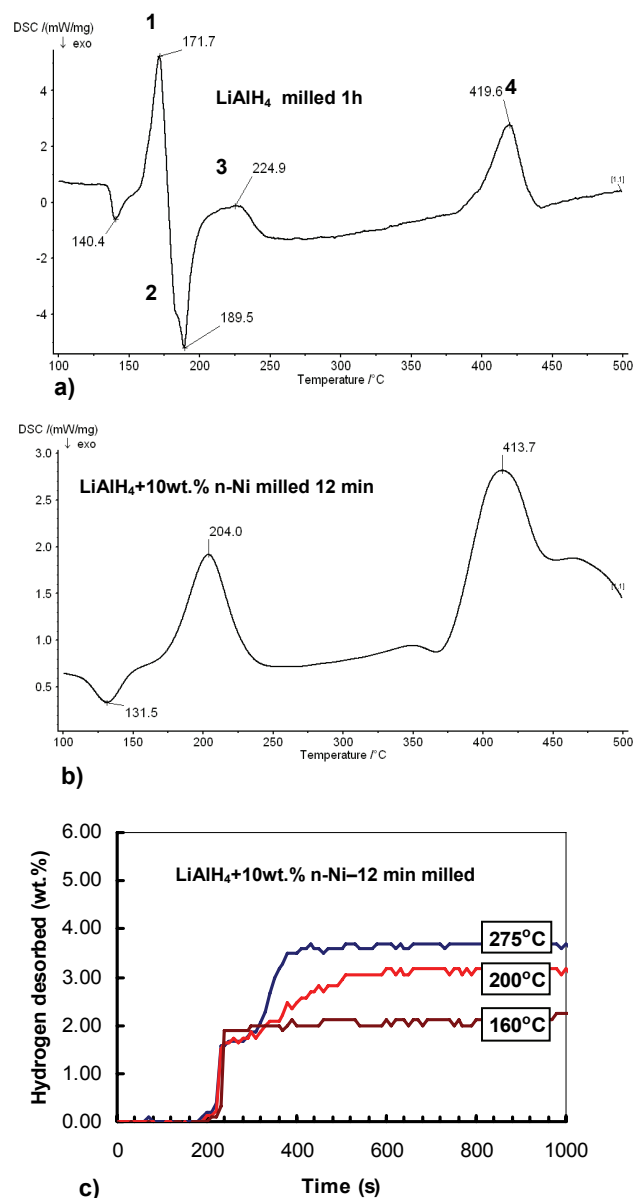$LiAlH_4$ (liquid) $\rightarrow$ 1/3Li_3AlH_3 + 2/3Al + H_2. This

Fig.1. DSC trace at 10°C/min for (a) $LiAlH_4$ milled for 1h and (b) $LiAlH_4$+10 wt.% n-Ni milled for 12 min. (c) Desorption curves in a Sieverts-type apparatus up to 160, 200 and 275°C for $LiAlH_4$+10 wt.% n-Ni milled for 12 min.

reaction proceeds with a theoretical hydrogen release of 5.3 wt.%. The third endothermic peak (3) at 224.9°C is due to the following reaction: $1/3Li_3AlH_3 \rightarrow LiH+1/3Al+0.5H_2$ which releases 2.6 wt.% H_2. The fourth (4) endothermic peak at 419.6°C is most likely due to the decomposition of LiH which releases 2.6 wt. % H_2. The XRD pattern of $LiAlH_4$ milled for 1h (not shown here) revealed that a very small amount of $LiAlH_4$ already decomposed to Li_3AlH_3 and Al (reaction (2)) in a *solid state* without going through the liquid phase.

Fig.1(b) shows the DSC trace of $LiAlH_4$ doped with 10 wt.% n-Ni and milled for 12 min. Apparently, instead of separate peaks (1), (2) and (3) as observed for the unmilled $LiAlH_4$, there is only one endothermic peak at 204°C. Peak (4) at 413.7°C remains the same as for the unmilled material in Fig.1a. XRD pattern of $LiAlH_4+10$wt.%n-Ni milled for 12 min (not shown here) contains only peaks of Li_3AlH_3, Al and Ni. This clearly shows that the addition of n-Ni catalyzed the first stage of the decomposition of $LiAlH_4$ to the extent that it occurred completely during milling in a *solid state*. Therefore, the single endothermic peak at 204°C in Fig.1b is most likely due to the second stage of the decomposition of Li_3AlH_3 into LiH, Al and ~2.6 wt.% H_2 as shown above. Decomposition during milling of $LiAlH_4$ doped with n-Ni is observed for the first time although it has been reported in the literature that the addition of metal chlorides to $LiAlH_4$ and among them $NiCl_2$ [2] also induces the decomposition of lithium alanate during ball milling. However, in view of the present results it seems that the accelerated decomposition of metal chloride doped $LiAlH_4$ is induced by the nanometric metals released from the chlorides rather than by the chlorides themselves.

Fig.1(c) shows that the ball milled mixture of $LiAlH_4+10$ wt.% n-Ni desorbs much less than 5.3 wt.%H_2 from 160 to 275°C which confirms that only Li_3AlH_3 is decomposing according to the reaction (3) above.

Fig. 2 presents the DSC traces of as received, milled and n-Ni doped $LiNH_2$. It can be seen that ball milling even for such a long duration as 25h does not change the DSC trace corresponding to the as received powder. A single endothermic peak corresponds to melting and simultaneous decomposition into Li_2NH (lithium imide) and NH_3 (ammonia) [1]. The latter is detrimental to a Proton Exchange Membrane fuel cell and should be avoided. We anticipated that the addition of n-Ni would greatly reduce the release of NH_3. Unfortunately, as can be seen the addition of 5 wt.% n-Ni introduces a peak doublet on a DSC curve but does not change the fundamental desorption characteristic of $LiNH_2$ which still decomposes through melting and release of NH_3.
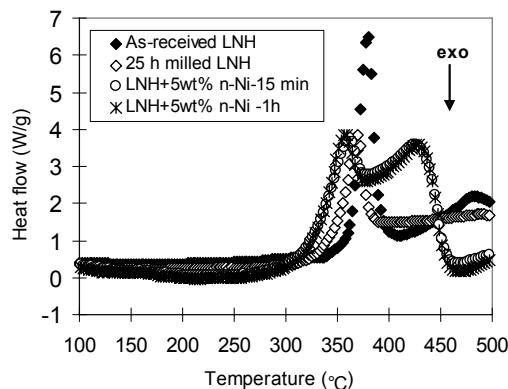

Fig.2. DSC traces of $LiNH_2$ (LNH) as received, milled and doped with n-Ni.

Conclusions

The addition of n-Ni to $LiAlH_4$ catalyzes its first stage of decomposition to the extent that the $LiAlH_4+$n-Ni mixture decomposes to Li_3AlH_3, Al and H_2 in a *solid state* during ball milling. This result strongly suggests that the accelerated decomposition of $LiAlH_4$ doped with metal chlorides reported in the literature is induced by the nanometric metals released from the chlorides rather than by the chlorides themselves. The addition of n-Ni to a complex hydride $LiNH_2$ does not change its fundamental desorption characteristics which still involve melting and the release of NH_3.

References

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2. Sun T, Huang CK, Wang H, Sun LX, Zhu M. The effect of doping $NiCl_2$ on the dehydrogenation properties of $LiAlH_4$. Int J Hydrogen Energy 2008;33:6216-6221.