Article ID: 1003－7837(2005)02,03－0405－04

Reversible hydrogen storage properties of Ti-doped lithium aluminium hydride

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Abstract: In this paper our work on lithium aluminium hydride doping with $Ti(OBu)_4$ by mechanical milling was showed. Its thermodynamic and kinetics were enhanced greatly and its reversible hydrogen storage capacity could reach 3.0% (mass fraction). From the X-ray diffraction (XRD) patterns, we found that a lot of $LiAlH_4$ had been decomposed to Li_3AlH_6 and Al. The catalyst $Ti(OBu)_4$ couldn't be found after ball-milling, instead $TiAl_3$ appeared. But the locations of Ti atoms are still not determined.

Key words: hydrogen storage; lithium aluminium hydride; mechanical milling

CLC number: TG113 **Document code**: A

1 Introduction

Traditional metal hydrides (AB_5, AB_2 and AB) are limited to only about 2%(mass fraction) reversible gravimetric H-capacity, far from the demand of some fields (for example fuel cell). International Energy Association (IEA) required that hydrogen storage materials could release 5%(mass fraction) hydrogen below 423K and the circle life could be beyond 1 000 times. That's a great challenge for traditional metal hydrides. For the reason above mentioned, research and development on hydrogen storage materials turns to materials with high hydrogen capacity in recent years, and complex hydride doped with catalyst is one of them.

Complex hydrides with the general formula $A_xM_yH_z$, where A is an alkali or alkaline earth metal and M is a nontransition or transition metal, have been synthesized and characterized by different methods. Because they contain lightweight elements such as lithium, sodium, and aluminum, nontransition complex hydrides (such as $LiAlH_4$ and Li_3AlH_6) offer the potential of much higher hydrogen capacities than the intermetallic hydrides do. However, hydride formation and decomposition in these complex hydrides are barely reversible, therefore it is impractical for them to be used. This situation has not been changed until Bogdanovic and his partners who pioneered the demonstration that upon doping with selected titanium compounds in 1997, the dehydriding of $NaAlH_4/Na_3AlH_6/Na_2LiAlH_6$ could be kinetically enhanced and rendered reversible under moderate conditions in the solid state. Researches on complex hydrides now focus on $NaAlH_4$ and $LiAlH_4$. The kinetic characters of rehydriding and dehydriding are remarkably enhanced by

Received date: 2005－06－30

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doping with Ti, Zr based catalyst and the reversible hydrogen capacity can reach 3.1%—4.2%(mass fraction).

Lithium aluminium hydride ($LiAlH_4$) was firstly synthesized in 1947 and has been used as a powerful reducing agent. It is one of the new potential hydrogen storage materials and its total capacity is approximately 10.6%(mass fraction) desorbed in a three-step decomposition reaction:

$$LiAlH_4 \longrightarrow \frac{1}{3}Li_3AlH_6 + \frac{2}{3}Al + H_2 \quad (5.3\%H_2, \text{ mass fraction}) \tag{1}$$

$$\frac{1}{3}Li_3AlH_6 + \frac{2}{3}Al + H_2 \longrightarrow LiH + Al + \frac{3}{2}H_2 \quad (2.6\%H_2, \text{ mass fraction}) \tag{2}$$

$$LiH \longrightarrow Li + \frac{1}{2}H_2 \quad (2.6\%H_2, \text{ mass fraction}) \tag{3}$$

But like sodium aluminium hydride, the problem is the rather slow hydriding and dehydriding kinetics of these reactions and these reactions are reversible only under excessively rigor conditions. The first two of these reactions proceed around 160—210℃ and liberate 5.3% and 2.6%(mass fraction)of hydrogen, respectively. The dehydrogenation of LiH occurs only at very high temperatures(400℃) and is normally not considered as a source of hydrogen available from $LiAlH_4$.

In this paper we doped $LiAlH_4$ with $Ti(OBu)_4$ by ball-milling which greatly enhanced thermal and kinetic performance.

2 Experimental

The purities of the starting materials lithium aluminium hydride ($LiAlH_4$) and Titanium butoxide ($Ti(OBu)_4$) are 95% and 98% respectively. All reactions and operations were performed in an argon glove box to prevent samples and starting powers from oxidation and hydroxide formation. To prepare Ti-doped $LiAlH_4$, there have been employed 2 %(mol fraction) $Ti(OBu)_4$, 98%(mol fraction) $LiAlH_4$ and steel balls of 8 mm in diameter which were sealed in a stainless steel ball mill tank, and then were high energy ball milled for 4h by using a high energy SPEX 8000 ball mill(the ratio of ball weight to powder weight was 10 : 1, hydrogen protected).

Pressure composition thermal (PCT) experiments were carried out to study the dehydriding and hydriding characters. Structure and phase impurities on samples in this investigation were analyzed by X-ray diffraction (XRD) using a XD—2 X-ray diffractmeter (made by Peiking University). The power of X-ray generator is 40 kV, 30 mA, the scanning rate of 2θ angle is 2°/min.

3 Results and discussion

3.1 2% (mol. fraction) $Ti(OBu)_4$ doped $LiAlH_4$

Fig. 1 shows the XRD patterns of raw $LiAlH_4$, raw $LiAlH_4$ milled and the 2% $Ti(OBu)_4$(mol fraction) doped $LiAlH_4$ through ball-milling. It showed us that $LiAlH_4$ milled without catalyst barely transformed, only some peaks were relatively broader because nonacrystallites were formed. The 2% $Ti(OBu)_4$ (mol. fraction) doped $LiAlH_4$ decomposed after ball-milling because the reaction (1) had taken place. Li_3AlH_6 and Al were formed and trifle $TiAl_3$ appeared which is consistent with correlated reports. It was previously reported that polycrystalline $LiAlH_4$ was completely transformed into polycrystalline Li_3AlH_6 during short mechanochemical treatment with 3% $TiCl_4$(mol. fraction). After ball-milling under the same condition, $LiAlH_4$ without catalysts didn't decompose but $LiAlH_4$ doped with catalysts decomposed. This means the Ti-catalyst enhanced the thermodynamics of $LiAlH_4$ greatly, reduced the reaction enthalpy thus

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it could decompose under a comparatively low temperature.

Fig. 2 shows the hydrogen desorption curves of the raw material $LiAlH_4$ and the 2% $Ti(OBu)_4$ (mol fraction) doped $LiAlH_4$ after ball-milling. The raw material $LiAlH_4$ nearly decomposed completely in 12 h at 175℃ but the 2% $Ti(OBu)_4$ (mol. fraction) doped $LiAlH_4$ after ball-milling released hydrogen in 2 h at 80℃. This means the kinetics of catalyst doped $LiAlH_4$ was improved markedly in addition to the thermodynamics.

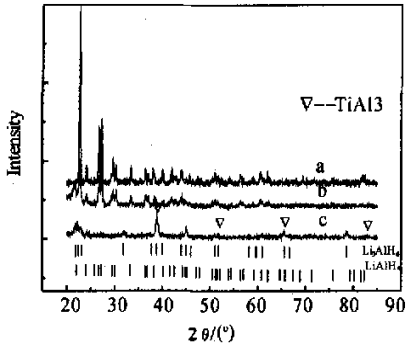

Fig. 1 XRD Patterns of (a) $LiAlH_4$ (b) $LiAlH_4$ milled for 4h (c) 2% $Ti(OBu)_4$ + 98% $LiAlH_4$ (mol fraction) milled for 4 h

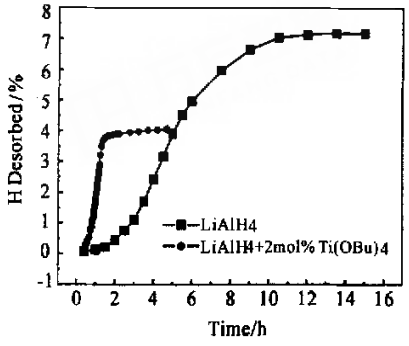

Fig. 2 Hydrogen desorption curves of (a) raw material $LiAlH_4$ at 175℃ (b) 2% Ti $(OBu)_4$ (mol fraction) doped $LiAlH_4$ after ball-milling at 80℃

Fig. 3 shows the cycling characters of hydriding and dehydriding at 175℃. The reversible hydriding capacity could be 3% (mass fraction) but the reversible dehydriding capacity was only 2% (mass fraction) and decreased to 1.33% (mass fraction) rapidly. This was due to the difference between the kinetics of hydriding and dehydriding. The kinetics of hydriding was favorable but the kinetics of dehydriding was poor so the reversible dehydriding capacity was considered to be only 1% (mass fraction). As Fig. 4 showed us, the hydriding capacity was 3.3% (mass fraction) in 1h at 11th cycling number but the kinetics of dehydriding was so poor that it could only release 1% (mass fraction) hydrogen in 2 h. In all, the Ti-catalyst's effects were obvious and the kinetics of hydriding was enhanced greatly contrarily the kinetics of dehydriding not distinctly.

3.2 Discussion of catalytic mechanism

Trifle $TiAl_3$ appeared in the XRD patterns of 2%$Ti(OBu)_4$ (mol fraction) doped $LiAlH_4$ after ball-milling which is consistent with correlative reports. Redox took place between $Ti(OBu)_4$ and powerful reducing agent $LiAlH_4$. Ti^{4+} transformed into active $TiAl_3$ alloy dispersed in the sample which decreased the activation energy of this reaction, thus kinetics of the reaction was enhanced.

4 Conclusion

The ball-milling technique is a successful way for producing $Ti(OBu)_4$ doped $LiAlH_4$ powders: (1) nanocrystallites $LiAlH_4$ and Li_3AlH_6 were formed; (2) the reversible absorption capacity could be 3.0wt% and the kinetics was excellent , but the reversible desorption capacity and the desorption kinetics was still poor which should be improved further; (3) Ti-catalyst existed in the form of $TiAl_3$ alloy which enhanced the kinetics, but the concrete mechanism still demands further research.

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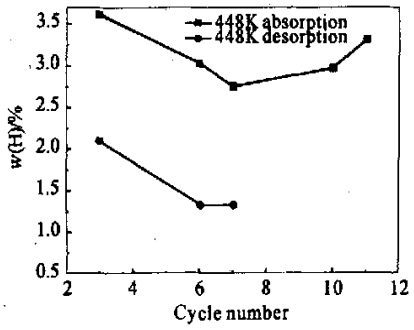

Fig 3 Cycling kinetics of 2% Ti(OBu)$_4$ (mol. fraction) doped $LiAlH_4$ after ball-milling at 175℃

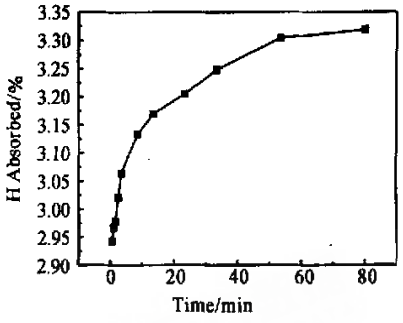

Fig. 4 Hydrogen absorption kinetics of 2% Ti(OBu)$_4$ (mol. fraction) doped $LiAlH_4$ at 175℃ (11th)

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