

## Effect of catalyst $\text{LaCl}_3$ on hydrogen storage properties of lithium alanate ( $\text{LiAlH}_4$ )

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### Abstract

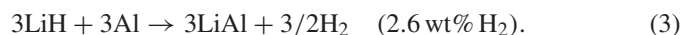
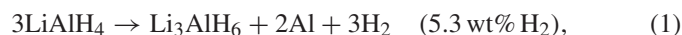
$\text{LiAlH}_4$  doped with  $\text{LaCl}_3$  additives were studied by PCT experiment and X-ray diffraction (XRD). Doping with 1 mol%  $\text{LaCl}_3$  resulted in a great decrease in the amount of hydrogen release associated with the first and second dehydrogenation steps. Increasing the amount of  $\text{LaCl}_3$  from 1 to 6 mol% caused such marked changes in behavior that the total amount of hydrogen release increased first and then decreased. The study on the first rehydrogenation cycle showed that  $\text{LiAlH}_4$  doped with 2 mol%  $\text{LaCl}_3$  presents the greatest absorption of hydrogen of about 0.8 wt%. The results from XRD spectra analysis indicated the reversibility of  $\text{Li}_3\text{AlH}_6$ .

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**Keywords:**  $\text{LiAlH}_4$ ;  $\text{LaCl}_3$  additives; Hydrogen release

### 1. Introduction

Hydrogen storage has been the subject of intensive research in recent years since hydrogen is pollution free and can readily be produced from renewable energy resources [1,2]. Complex hydrides, such as  $\text{NaAlH}_4$  and  $\text{LiAlH}_4$ , are attractive as hydrogen storage compounds due their high hydrogen content and low weight. In 1997, Bogdanović and Schwickardi [3] demonstrated that the addition of Ti compounds and other transition metal compounds enhances the desorption kinetics of  $\text{NaAlH}_4$  and, furthermore, that rehydrogenation is possible under moderate conditions. This finding has created an entirely new prospect for complex hydrides based on Al as promising reversible hydrogen storage media. Theoretically,  $\text{NaAlH}_4$  can reversibly store 5.6 wt%  $\text{H}_2$ . However, at below 200 °C the theoretical capacity of  $\text{LiAlH}_4$  is 7.9 wt% hydrogen. Hydrogen release occurs in three stages upon heating with 5.3, 2.6 and 2.6 wt% release of hydrogen, respectively.



The last reaction takes place at above 400 °C and is not considered available for practical purposes. The decomposition temperatures are reported to be between 150 and 175 °C for reaction (1) (Eq. (1)), and 180–220 °C for reaction 2 (Eq. (2)) [4–6].

In recent years, research has established that adding catalysts can have a distinct effect on the decomposition of  $\text{LiAlH}_4$ . The principal catalysts studied were elemental titanium,  $\text{TiCl}_4$ ,  $\text{TiCl}_3$ ,  $\text{AlCl}_3$ ,  $\text{FeCl}_3$ , elemental iron, elemental nickel, vanadium and carbon black [7–10]. The results found that the addition of  $\text{TiCl}_3$  and  $\text{TiCl}_4$  to  $\text{LiAlH}_4$  eliminated the first step of hydrogen evolution and significantly lowered the decomposition temperature of the second step. Doping with elemental iron caused only a slight decrease in the amount of hydrogen released and did not eliminate the first step of hydrogen evolution. In addition, the study by Blanchard [11] showed that ball-milling of  $\text{LiAlH}_4$  and  $\text{VCl}_3$  or  $\text{TiCl}_3 \cdot \frac{1}{3}\text{AlCl}_3$  reduced the thermal decomposition temperatures for Eq. (1) by 50–60 °C. By far the most reports concern the desorption reaction of catalyzed  $\text{LiAlH}_4$  and  $\text{Li}_3\text{AlH}_6$  [11–13]. However, reversibility in these two systems has not yet been realized [14].

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In this work we chose  $\text{LaCl}_3$  as additive because it has been found to have a favorable influence on the performance of some materials [15,16]. X-ray diffractometer (XRD) and pressure–composition–temperature (PCT) apparatus have been used to study the decomposition process of  $\text{LiAlH}_4$  doped with  $\text{LaCl}_3$  and to investigate the reversibility of  $\text{Li}_3\text{AlH}_6$ .

## 2. Experimental details

$\text{LiAlH}_4$  ( $\geq 96$  wt% pure) was purchased from Tianjin Beidouxing Fine Chemical Co., Ltd.  $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$  was obtained from the Central Iron and Steel Research Institute.  $\text{LiAlH}_4$  was used as received with no additional purification. Due to a mass of crystal water in  $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ , dehydration was carried out before  $\text{LiAlH}_4$  was mixed with  $\text{LaCl}_3$  in order to prevent the effect of the crystal water on  $\text{LiAlH}_4$ .  $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$  was heated to  $150^\circ\text{C}$  and then kept at that temperature for 3 h. All operations on the samples were done under dry argon atmosphere in a glove box to prevent reaction with moisture and oxygen in the air.  $\text{LiAlH}_4$ , usually 2 g, was mixed with 1, 2, 3, 4, 5 and 6 mol%  $\text{LaCl}_3$ , respectively, by ball-milling for 20 min at a gyration rate of 200 rpm using a Spex mill. Three hardened steel vials sealed under argon with 14 steel balls (1 g each) were used. Air-cooling of the vials was employed to prevent their heating during the ball-milling process. The ball-milled samples were then transferred to 3-ml glass bottles in a glove box under dry argon atmosphere.

Hydrogen desorption experiments were carried out in PCT apparatus. This can be operated up to 10 MPa and at  $600^\circ\text{C}$ . The pressure of hydrogen released in relation to volume was displayed by a pressure transducer. The experimental studies were done by a reactor. This consisted of two parts: heater and sample vessel. The former was used to connect with the pressure transducer and thermocouple. It had a 2.2 cm outside diameter (OD), 0.5 cm wall and 20 cm internal length. It was loaded with the sample vessel (1 cm OD, 0.1 cm wall and 5 cm internal length). The sample vessel was loaded with about 0.2 g of  $\text{LiAlH}_4$ . The reactor was heated with an air furnace. During heating, the hydrogen released overflowed from the sample vessel firstly into the heater and then into the transit pressure transducer. The value of hydrogen pressure could be clearly read.

Rehydrogenation studies were carried out with  $\text{LiAlH}_4$  doped with 1, 2, 3, 4, 5 and 6 mol%  $\text{LaCl}_3$ . After the first complete dehydrogenation (first two reactions), the samples were kept at  $180^\circ\text{C}$  under  $\sim 8$  MPa hydrogen pressure for 2 h. The uptake of hydrogen for the samples is evident from the gradual decrease of pressure in this closed system. The change of hydrogen pressure was recorded by the pressure transducer.

The phase structure was determined by an MXP21VAHF XRD (XRD with  $\text{Cu K}\alpha$  radiation). XRD was done at a tube voltage of 40 kV and a tube current of 200 mA. A small amount of sample was spread evenly in the sample holder. The samples were placed in a sealed container which was filled with argon before they were measured. The X-ray intensity was measured over a diffraction angle from  $10^\circ$  to  $90^\circ$  with a velocity of  $0.02^\circ$  per step. XRD was used to analyze phase

composition and to obtain the precise lattice parameters of samples.

## 3. Results and discussion

In this study, samples of  $\text{LiAlH}_4$  doped with 1, 2, 3, 4, 5 and 6 mol%  $\text{LaCl}_3$  were milled for 20 min. In order to calculate and allow for the effects of ball-milling on the results, a sample of undoped  $\text{LiAlH}_4$  was also milled for 20 min. The hydrogen release capacity of  $\text{LiAlH}_4$  doped with 1, 2, 3, 4, 5 and 6 mol%  $\text{LaCl}_3$  was studied by PCT experiments. Fig. 1 presents the hydrogen desorption of  $\text{LiAlH}_4$  and  $\text{LiAlH}_4$  doped with 1 mol%  $\text{LaCl}_3$ .  $\text{LiAlH}_4$  began to decompose at  $148^\circ\text{C}$  and continued up to  $176^\circ\text{C}$ . In the first step, about 3.9 wt% hydrogen was released and in the second step about 2.1 wt% hydrogen, so a total of about 6.0 wt% hydrogen was released from the  $\text{LiAlH}_4$ . Doping with 1 mol%  $\text{LaCl}_3$  increased the decomposition temperature. The decomposition reaction started at about  $150^\circ\text{C}$  and was completed at about  $185^\circ\text{C}$ , which is different from the results reported for other catalysts. Resan et al. [10] found that doping  $\text{LiAlH}_4$  with  $\text{Ti}_3\text{Al}$ ,  $\text{TiAl}_3$  and elemental aluminum reduced the temperature required for hydrogen release. The study of Ti- and V-based additives by Blanchard et al. [11] proved that ball-milling of  $\text{LiAlH}_4$  in the presence of  $\text{VCl}_3$  or  $\text{TiCl}_3 \cdot \frac{1}{3}(\text{AlCl}_3)$  can reduce its thermal decomposition temperatures by 60 and  $50^\circ\text{C}$ , respectively.

In addition, doping with 1 mol%  $\text{LaCl}_3$  caused an obvious decrease in the amount of hydrogen release. In the first step, about 3.5 wt% hydrogen was released and in the second step about 1.7 wt% hydrogen, a total of about 5.2 wt% hydrogen. The slopes of the curves indicate that doping with  $\text{LaCl}_3$  decreased the rate of hydrogen release in the first step.

It is interesting that increasing the amount of  $\text{LaCl}_3$  from 1 to 6 mol% caused such marked changes in behavior that the total amount of hydrogen release increased first and then

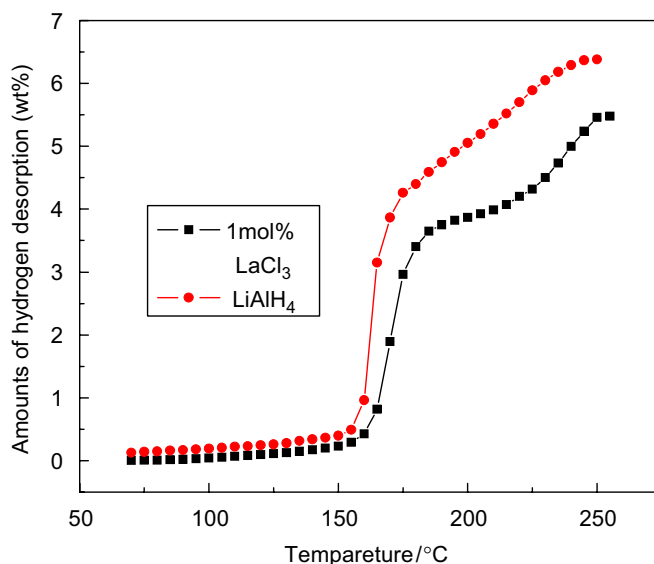


Fig. 1. Thermal desorption of  $\text{LiAlH}_4$  and  $\text{LiAlH}_4$  doped with 1 mol%  $\text{LaCl}_3$ .

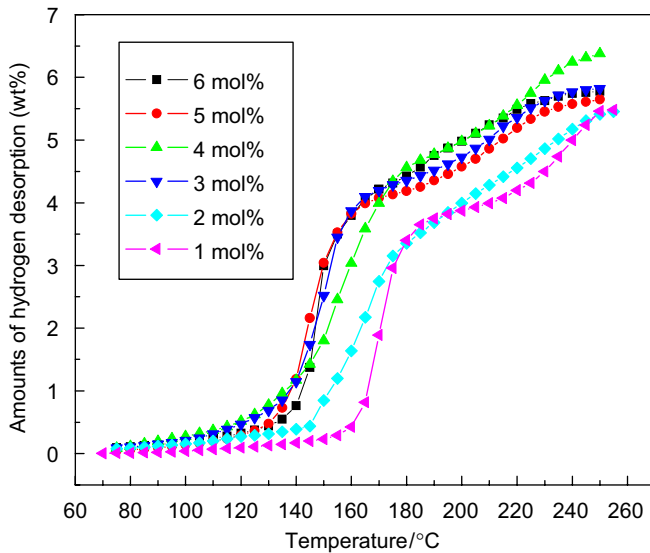


Fig. 2. Thermal desorption of  $\text{LiAlH}_4$  doped with 1, 2, 3, 4, 5 and 6 mol%  $\text{LaCl}_3$ .

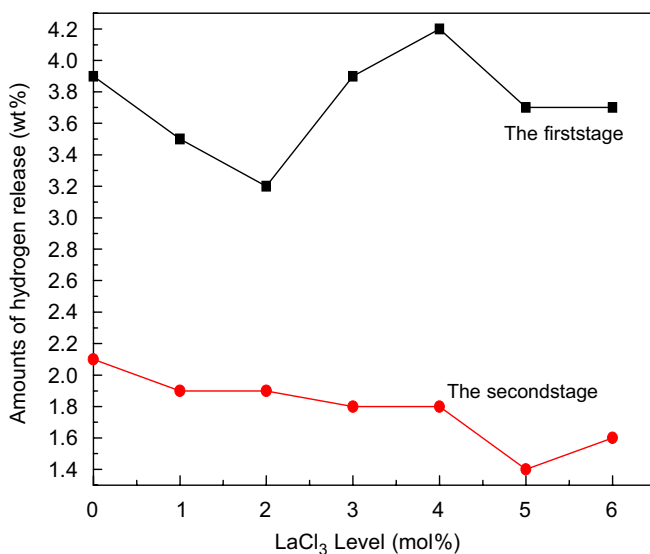


Fig. 3. Dehydrogenation for  $\text{LiAlH}_4$  in the first and second steps as a function of added  $\text{LaCl}_3$ .

decreased (Fig. 2). The sample doped with 4 mol%  $\text{LaCl}_3$  presented the largest amount of hydrogen release. In addition, the first-step decomposition temperature showed a significant decrease. Compared to  $\text{LiAlH}_4$ , the first dehydrogenation temperature of doping with 4 mol%  $\text{LaCl}_3$  was substantially lower by about 27 °C and the second was lower by about 10 °C. The rate of hydrogen release was lower than that of  $\text{LiAlH}_4$  and  $\text{LiAlH}_4$  doped with 1 mol%  $\text{LaCl}_3$ .

Fig. 3 shows the dehydrogenation amount of  $\text{LiAlH}_4$  in the first and second stages as a function of the  $\text{LaCl}_3$  concentration. In the first stage, the samples doped with 2 and 4 mol%  $\text{LaCl}_3$  present the lowest and largest amount of hydrogen release, while the samples undoped and doped with 5 mol%  $\text{LaCl}_3$

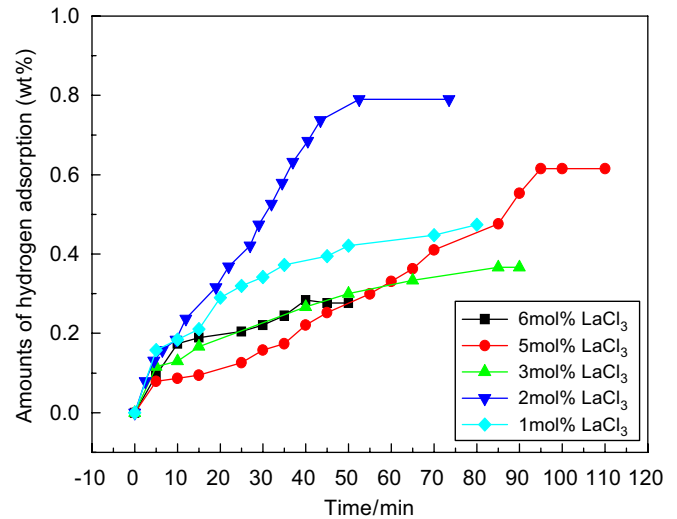


Fig. 4. Rehydrogenation curves of samples doped with  $\text{LaCl}_3$ .

present the largest and least dehydrogenation in the second stage, respectively.

Although  $\text{LiAlH}_4$  has shown very impressive dehydrogenation kinetics at a reasonable dehydrogenation temperature, the reversible storage of hydrogen in  $\text{LiAlH}_4$  has not been demonstrated conclusively. In addition, recent results have shown no reversibility of reaction in Eq. (2) under similar conditions [12–14,17,18]. Therefore, the main aim of this work was to study dehydrogenation of  $\text{Li}_3\text{AlH}_6$ . Fig. 4 compares the adsorption process of the samples doped with  $\text{LaCl}_3$  during the first rehydrogenation cycle carried out in PCT at 180 °C under 8 MPa after being discharged of hydrogen at 270 °C.  $\text{LiAlH}_4$  doped with 2 mol%  $\text{LaCl}_3$  presents the greatest absorption of hydrogen about 0.8 wt%. The rehydrogenation amount of samples doped with 1 and 5 mol%  $\text{LaCl}_3$  was about 0.5 and 0.6 wt%, respectively. However, the rehydrogenation amount of the sample doped with 6 mol%  $\text{LaCl}_3$  registers only a slight increase.

XRD measurements were carried out in order to verify the dehydrogenation/rehydrogenation characteristics of 3 mol%  $\text{LaCl}_3$ -doped  $\text{LiAlH}_4$ , and hence to study the structural changes to the phases. The results are presented in Fig. 5. It can be seen that the major phases presented in the XRD pattern of the decomposed sample were  $\text{LiH}$  and  $\text{Al}$ , with no noticeable  $\text{LiAlH}_4$  and  $\text{Li}_3\text{AlH}_6$  phases (curve a). In addition, diffraction peaks from  $\text{LaCl}_3$  are not observed because only a small amount of  $\text{LaCl}_3$  catalyst was added. This result indicated that the first and second reactions went to completion. Fig. 5 (curve b) shows the XRD pattern of the sample rehydrogenated. The additional peaks of micro-crystalline  $\text{Li}_3\text{AlH}_6$  indicate slow composition of  $\text{LiH}$ ,  $\text{Al}$  and  $\text{H}_2$  into  $\text{Li}_3\text{AlH}_6$  according to the following reaction:



This result proves that the  $\text{Li}_3\text{AlH}_6$  is reversible.

In addition, this study analyzed the reproducibility of these dehydrogenation and rehydrogenation results. The dehydrogenation and rehydrogenation process of the doped samples presented good reproducibility under similar testing conditions.

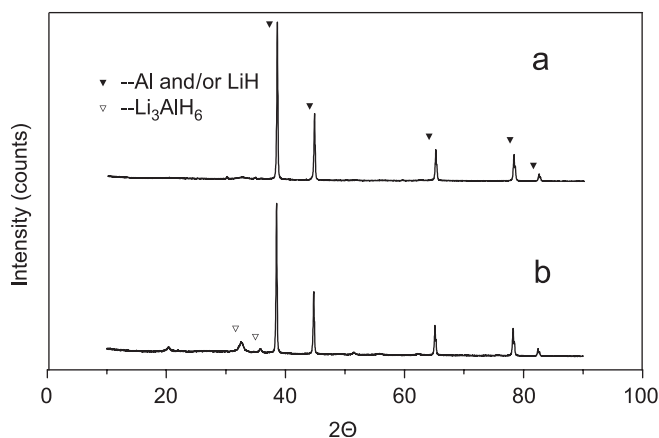


Fig. 5. XRD data for  $\text{Li}_3\text{AlH}_6$  doped with 3 mol%  $\text{LaCl}_3$  during one dehydrogenation (a) rehydrogenation and (b) cycle.

According to our earlier report [19], the decomposition amount and the first dehydrogenation process of the  $\text{LiAlH}_4$  presented good reproducibility even under different heating rates.

#### 4. Conclusion

The effect of doping with  $\text{LaCl}_3$  on the hydrogen release capacity of  $\text{LiAlH}_4$  was studied by PCT experiment. Doping  $\text{LiAlH}_4$  with 1 mol%  $\text{LaCl}_3$  resulted in a marked decrease in the amount of hydrogen release, and an obvious increase in the temperature associated with the first and second hydrogen release steps. Increasing the amount of  $\text{LaCl}_3$  from 1 to 6 mol% caused such marked changes in behavior that the total amount of hydrogen release increased first and then decreased. The samples doped with 4 mol%  $\text{LaCl}_3$  presented the largest amount of hydrogen release. The results of the first rehydrogenation cycle showed that  $\text{LiAlH}_4$  doped with 2 mol%  $\text{LaCl}_3$  presents the greatest absorption of hydrogen of about 0.8 wt%. In addition, the XRD pattern of the rehydrogenated sample doped with 3 mol%  $\text{LaCl}_3$  indicated the reversibility of  $\text{Li}_3\text{AlH}_6$ .

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