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# Catalytic effects of nano-sized TiC additions on the hydrogen storage properties of $LiAlH_4$

Rafi-ud-din*, Lin Zhang, Li Ping, Qu Xuanhui

*State Key Laboratory for Advanced Metals and Materials, School of Materials Science and Engineering, USTB, Beijing 100083, China*

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ABSTRACT

The catalytic effect of TiC nanopowder addition in varying proportions on the hydrogen storage properties of $LiAlH_4$ has been investigated by pressure-composition-temperature (PCT) experiments, thermogravimetry (TG), and differential scanning calorimetry (DSC). The results indicate that doped samples are able to dehydrogenate at much lower temperatures; for example, the onset of dehydrogenation is 85 °C for $LiAlH_4$–2 mol% TiC, and the majority of hydrogen (~6.9 wt.%) can be released by 188 °C. About 5 out of 6.9 wt.% of $H_2$ can be released in the range of 85–138 °C (heating rate 4 °C $min^{-1}$). Isothermal desorption results at 115 °C reveal that doped alanate exhibits dehydriding rate 7–8 times faster than that of pure $LiAlH_4$. DSC measurements indicate that enthalpies of decomposition in $LiAlH_4$ decrease significantly with doping. From Kissinger analysis, the apparent activation energies are estimated to be 59 kJ/mol, 70 kJ/mol and 99 kJ/mol for the decompositions of $LiAlH_4$, $Li_3AlH_6$ and LiH, respectively. The results of first rehydrogenation indicate that 5 mol% dopant exhibits the maximum absorption of about 1.9 wt.%. XRD, FESEM, EDS, FTIR, and XPS analyses are utilized to put forward a possible catalytic mechanism of nano-sized TiC in ameliorating the dehydriding/rehydriding characteristics of doped $LiAlH_4$.

## 1. Introduction

The major obstacle to the transition from a carbon-based/fossil fuel energy system to a hydrogen-based economy is the identification of efficient and cost-effective means for on-board storage of hydrogen. Despite the decades of intense research efforts, so far none of the materials has satisfied the performance targets specified by automotive industry with respect to gravimetric density, hydrogenation/dehydrogenation kinetics, and thermodynamic properties. Recently, complex hydrides such as alanates ($AlH_4^-$), amides ($NH_2^-$), and borohydrides ($BH_4^-$) have attracted considerable attention, as they inevitably provide extremely high gravimetric storage capacities compared to that of conventional metal hydrides [1–14]. But, the practical utility of most of these complex hydrides is limited by their poor kinetics and difficulty in reversing the hydrogen under the moderate conditions. Alanates of the general form $MAlH_4$, where M is a light weight alkaline metal (Li, Na or K), have a high gravimetric density of hydrogen, which is essential for their potential use as hydrogen storage materials. Following the breakthrough work on Ti-doped $NaAlH_4$ [15], lithium alanates ($LiAlH_4$) as well as alanates of other alkali-and alkaline-earth-metal-based complex aluminum hydrides have received a great deal of attention as possible candidate materials because of their light weight and high inherent storage capacity [16,17]. Among the alanates, the hydrogen content of two alkali metal aluminohydrides, $LiAlH_4$ and $NaAlH_4$, are 10.5 wt.% and 7.3 wt.% $H_2$, respectively. However, the relatively low hydrogen content of sodium aluminohydrides (5.6 wt.% H when $NaAlH_4$ decomposes to NaH, Al and $H_2$) renders them inferior to other hydrides such as lithium aluminohydrides (7.9 wt.% H when $LiAlH_4$ decomposed to LiH, Al and $H_2$) and magnesium hydride (7.6 wt.% $H_2$). Upon heating, the decomposition of $LiAlH_4$ takes place in three steps [1] with 5.3 wt.%, 2.6 wt.% and 2.6 wt.% release of hydrogen, respectively.

$$3LiAlH_4 \rightarrow Li_3AlH_6 + 2Al + 3H_2 \quad (1)$$

$$Li_3AlH_6 + 2Al \rightarrow 3LiH + 3Al + 3/2H_2 \quad (2)$$

$$3LiH + 3Al \rightarrow 3LiAl + 3/2H_2 \quad (3)$$

Reaction (3) occurs above 400 °C and is not considered viable for practical purposes. The decomposition temperature ranges for reactions (1) and (2) are 150–175 °C and 180–220 °C, respectively [1].

Lithium alanate ($LiAlH_4$) hydrid indeed exhibits among the highest hydrogen capacity, but its high capacity is plagued by some of its drawbacks such as the presence of exothermic decomposition reaction, extremely high plateau pressure at relatively low

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* Corresponding author. Tel.: +86 10 62332700; fax: +86 10 62334311.
*E-mail address:* rafi_682@yahoo.com ( Rafi-ud-din).

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temperatures which makes the hydride practically irreversible and relatively slow hydrogen desorption kinetics. Recent studies have indicated that both ball-milling and doping with various catalysts have not only rendered the low-temperature decomposition of lithium aluminohydride into lithium hexahydroaluminate, aluminum, and hydrogen but also to some extent has caused the partial reversibility of reaction (2) by eliminating the kinetic restrictions. It is documented that by using $TiF_3$ [18], Ce $(So_4)_2$ [19,20], $TiCl_3$ [21], $TiCl_3 \cdot (1/3)(AlCl_3)$ [22,23], $LaCl_3$ [20,24], $VBr_3$ [25], Ni [19,20], Fe [26], Ti, Sc, V [20,26,27], $NiCl_2$ [28], $NbF_5$ [29], $VCl_3$, and carbon nanofibers [30], a significant reduction in the decomposition temperatures of the first and the second steps can be achieved. In addition, partial reversibility of reaction (2) has been claimed by $LaCl_3$ [20,24], Ni [19,20], Ti [20], Ce $(SO_4)_2$ [19,20], $VCl_3$ [30], carbon nanofibers [30], and $TiCl_3$ [23]. However, the most of these catalysts induce the reduction in hydrogen storage capacity during the ball-milling. Therefore, there have been persistent efforts to find new effective catalysts that can enhance the reaction kinetics while maintaining the high hydrogen capacity.

Tailoring nanophase structure by using foreign scaffolds is found to dramatically improve kinetics and thermodynamics of hydrogen exchange reactions of the complex hydride materials. The nanostructured catalytic dopants may offer several advantages for the physicochemical reactions such as surface interactions, adsorption in addition to bulk absorption, rapid kinetics, low-temperature sorption, hydrogen atom dissociation, and molecular diffusion via the surface catalyst [31–34]. TiC is well known for its high degree of hardness and stability due to its high Ti–C bond enthalpy. Recently, Xuezhang et al. [35] have reported the role of TiC as a catalyst in the improvement of hydriding/dehydriding properties of the sodium alanate. In the present work, the efficacy of TiC nanoparticles is evaluated by subjecting the doped samples to the dehydrogenation and rehydrogenation experiments by pressure-composition-temperature (PCT) apparatus, thermogravimetry (TG), and differential scanning calorimetry (DSC). TiC nanopowder, in varying proportions, has been incorporated into $LiAlH_4$ by high-energy ball-milling.

## 2. Experimental details

$LiAlH_4$ (≥95%, average 325 mesh) and TiC (≥99%, <30 nm) were purchased from Sigma–Aldrich Co. and Hefei Kaier Development Co., Ltd. (China), respectively. Both the materials were used as-received without any further purification. All material handlings (including weighing and loading) were performed in high purity argon filled glove box, with low oxygen and water vapour content. $LiAlH_4$ (typically 1–2 g) was mixed with 1 mol%, 2 mol%, 3 mol%, 4 mol% and 5 mol% TiC and ball-milled for 30 min by using a high-energy Spex mill. All the samples were loaded into the hardened steel vial under an argon atmosphere in a glove box. Steel balls (1 g and 3 g) were added with a ball to powder weight ratio of 15:1. Air-cooling of the vial was employed to prevent its heating during the ball-milling process.

Hydriding/dehydriding properties of the as-received and doped samples were investigated by using a pressure-composition-temperature (PCT) apparatus. The details of apparatus are given in our previous report [36]. The apparatus can be operated up to the maximum pressure of 10 MPa and 600 °C. About 0.5 g of sample was loaded into the sample vessel. For dehydrogenation (first two steps) measurements, the samples of $LiAlH_4$ doped with 1 mol%, 2 mol%, 3 mol%, 4 mol% and 5 mol% TiC were heated up to 250 °C at a heating rate of 4 °C $min^{-1}$ under a controlled vacuum atmosphere. During the heating process, all the temperature and pressure data were documented and the curves for the two-stage process were drawn by using computer software. Following the first complete dehydrogenation (first two steps), the samples were subjected to rehydrogenation studies at 165 °C under 9.5 MPa for 3 h. The pressure drop with time in the closed system testified the rehydrogenation of the samples. Subsequently, the rehydrogenated samples were dehydrogenated at similar temperature.

The simultaneous DSC and TG analyses were conducted by using NETZSCH STA 449C. All measurements were carried out under a flow (50 ml $min^{-1}$) of high purity argon (99.999%). Sample mass was typically 5 mg. Heating runs were performed at different rates (4 °C $min^{-1}$, 7 °C $min^{-1}$ and 10 °C $min^{-1}$) from 35 °C to 500 °C.

The phase structure of the sample following the ball-milling, dehydrogenation, and rehydrogenation was determined by a MXP21VAHF X-ray diffractometer (XRD with CuKα radiation) at room temperature. XRD was done at a tube voltage of 40 kV and a tube current of 200 mA. The X-ray intensity was measured over a diffraction angle from 10° to 90° with a velocity of 0.02° per step. The samples were covered with the liquid paraffin to prevent the oxidation during the XRD test.

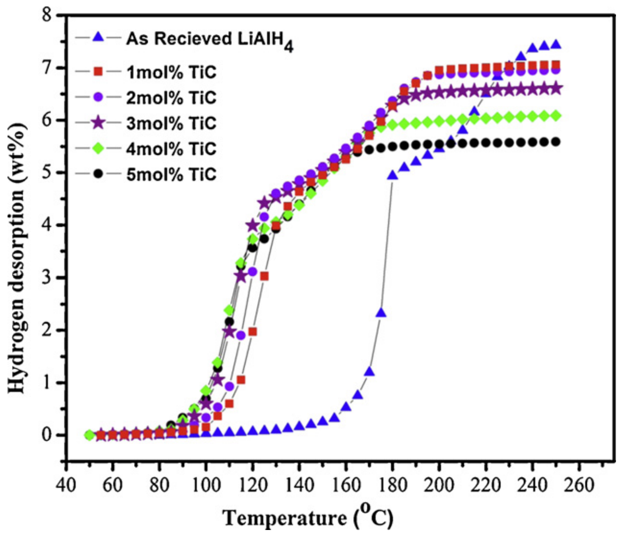

**Fig. 1.** Thermal desorption profiles of as-received $LiAlH_4$ and $LiAlH_4$ doped with 1 mol%, 2 mol%, 3 mol%, 4 mol%, and 5 mol% TiC. The samples are heated up to 250 °C at the heating rate of 4 °C $min^{-1}$.

FTIR spectroscopy was performed by using an infrared spectrophotometer (NEXUS670). The spectral resolution was 4 $cm^{-1}$. Scans were done between 2000 $cm^{-1}$ and 800 $cm^{-1}$ under an argon atmosphere. X-ray photoelectron spectroscopy (XPS) was performed with a PHI-5300 XPS spectrometer.

The as-received, doped, and dehydrogenated samples were examined by a field emission scanning electron microscope (FESEM-6301F) coupled with energy dispersive spectroscopy (EDS). Sample preparation for the FESEM measurement was carried out inside the glove box and, moreover, the samples were transferred to the SEM chamber by means of a device maintaining an Ar overpressure.

## 3. Results and discussion

Fig. 1 exhibits the non-isothermal dehydrogenation performances of the as-received $LiAlH_4$, and the $LiAlH_4$ doped with 1 mol%, 2 mol%, 3 mol%, 4 mol%, and 5 mol% TiC nanopowders. The desorption curves clearly depict that the $LiAlH_4$ samples balled milled with nano-sized TiC have rendered quite striking effects not only on the dehydrogenation characteristics of the first reaction (1) but also on the second reaction (2). Obviously, the onset temperature of dehydrogenation for all the Li alanate/carbide composite samples is below 100 °C, a significant reduction compared with neat $LiAlH_4$, in which dehydrogenation starts at around 150 °C. The pure $LiAlH_4$ starts to decompose at around 150 °C for the first stage and desorbs about 4.9 wt.% hydrogen. In the second stage, it initiates to dehydrogenate at 180 °C, and about 2.5 wt.% hydrogen is released. Hence the total dehydriding capacity of pure alanate is about 7.4 wt.%. $LiAlH_4$ with 1 mol% TiC releases about 6.96 wt.% hydrogen in a desorption temperature range between 100 °C and 200 °C. The addition of 2–3 mol% TiC nanopowders further reduces the first decomposition temperature of $LiAlH_4$ by the factor of around 60–65 °C, and the second decomposition temperature by the factor of around 50–55 °C, respectively. The sample of 2 mol% dopant initiates to decompose at 90 °C and terminates at 130 °C for the first stage, whilst the sample with 3 mol% dopant starts the decomposition at 85 °C and concludes at 125 °C. The second stage of the decomposition of 2 mol% and 3 mol% samples terminates at 190 °C and 185 °C, respectively. The hydrogen release contents in the first and second steps, for the sample doped with 2 mol%, are 4.60 wt.% and 2.25 wt.%, respectively. However, the desorption capacity with 3 mol% addition degrades, and amounts to 4.41 wt.% and 2.06 wt.% in the first and second stages, respectively. Further raising the doping amount to 5 mol% shortens the desorp-