Characterization of deposited Ti-doped lithium aluminium hydride thin film using dip coating method

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Abstract. Lithium aluminium hydride (LiAlH₄) is an outstanding complex metal hydride as a hydrogen storage material. The hydrogen storage capacity of LiAlH₄ is about 5-7 wt%. In this study, LiAlH₄ concentration of 20 g/l doped with various titanium (Ti) concentration by dip coating method was examined. The titanium dioxide (TiO₂) powder at 10 mol %, 25 mol % and 40 mol % was used as the Ti source. Instruments used to analyze Ti-doped LiAlH₄ were X-ray powder diffraction (XRD) and scanning electron microscope (SEM). XRD was used for phase and crystallite size analysis and SEM was used for surface morphology investigation. The experimental results reveal that at the LiAlH₄ concentration of 20 g/l with 40 mol% of TiO₂, the smallest crystallite size with rather dense surface was shown. The small crystallite size can improve the desorption of hydrogen from its surface area. Therefore, the addition of titanium might be advantageous in improving the hydrogen storage efficiency of LiAlH₄.

1. Introduction

Hydrogen is a clean energy and classified as non-toxic gas. When hydrogen is stored, it can be used and transported anywhere. Additionally, the hydrogen storage solves two main renewable energy problems i.e., the valorization of excess energy and a long-term clean energy storage system [1]. At present, the hydrogen storage technologies can be divided into 4 categories i.e., compressed hydrogen, liquid hydrogen, chemical hydrogen and solid-state hydrogen storage. The hydrogen storage improvement concerns about safety, reliability, compactability and low-cost with acceptable efficiency. The metal hydride in solid-state hydrogen storage development reveals many properties including hydrogen storage capacity, kinetics, cyclic behavior, toxicity, pressure and thermal response [2].

There are materials in solid-state hydrogen storage group. These are such as lithium aluminium hydride (LiAlH₄), sodium aluminium hydride (NaAlH₄), lithium amide and sodium borohydride (NaBH₄). The LiAlH₄ properties corresponding with the hydrogen storage improvement has the maximum hydrogen gravimetric density of around 10.6 wt% and the minimum desorption temperature of 180 °C.

For the solid-state hydrogen storage synthesis method, there were several methods including ball-milling, sputtering and electrophoretic deposition (EPD) [3]. For the high-energy ball-milling of LiAlH₄, good stability of the complex aluminohydride for up to 35 h was reported [4]. Additionally, the dehydrogenation kinetic of LiAlH₄ into Li₃AlH₆ and LiH was analyzed by ball milling. A relationship between crystallite size and dehydrogenation kinetics of LiAlH₄ and Li₃AlH₆ were found. On the
contrary, the kinetic of LiH was independent of crystallite size. This can be implied that the reaction of LiH is limited by the intrinsic kinetics while the reaction of LiAlH₄ and Li₃AlH₆ is limited by mass transfer [5]. The adsorption-desorption of Pd/Mg films formation in various sputtering conditions through the changing the RF coil has been investigated. They found that the dehydriding temperature decreased with decreasing degree of crystallization [6]. The hydrogen storage capacity of nickel particles deposited on carbon nanotubes using EPD was studied. The results showed that with increasing the number of cycles at a constant current, the capacity was increased and reached a constant value. Additionally, the post-annealing led to higher strength of the surface [3].

The titanium shows its important role in the hydrogen storage capacity. This is because small quantity of proper titanium catalyst can speed up the reaction, which makes it a suitable catalyst for practical hydrogen storage applications [7]. Additionally, the effort of LiAlH₄ production has been investigated by doping of LiAlH₄ with different Ti precursors such as titanium (Ti), titanium dioxide (TiO₂), and titanium chloride (TiCl₃) [8]. TiO₂ is of interest in this study because of its higher short-term stability than Ti and TiCl₃ with comparable desorption temperature and activation energy [8].

In this paper, the amount of TiO₂ at 0 mol%, 10 mol%, 25 mol % and 40 mol % mixed with the LiAlH₄ at the concentration of 20 g/l using the dip coating method was studied. TiO₂ was used as the Ti source. The dip-coating method is a simple method and low development cost for higher hydrogen storage capacity.

2. Materials and methods
2.1 Chemicals and substrates
All chemicals used in this study are LiAlH₄ powder grade (95% reagent), titanium dioxide nanopowder (anatase, 99.5% reagent) and dimethyl ether (DME) (99% or above solvent) supplied from Sigma-Aldrich. Before used, the solvent was pre-dried with 3A molecular sieve. Glass slide substrates (25x25 mm²) were used. Each substrate was cleaned by acetone followed by isopropanol (IPA). The substrates were heated at 105°C for at least 1 hour before dip coating in a controlled humidity and inert nitrogen atmosphere.

2.2 Methods
2.2.1 Precursor and thin film preparation
The precursor preparation and thin film coating process of LiAlH₄ doped with TiO₂ is shown in Figure 1. LiAlH₄ powder of 1.0 g was mixed with 0 mol%, 10 mol%, 25 mol% and 40 mol% of TiO₂ in a 50 ml Pyrex bottle to the LiAlH₄ concentration of 20 g/l with TiO₂ doping. The solution preparation was operated under the controlled humidity and nitrogen atmosphere. Additionally, it was ultrasonicated for 1 hour and stirred with magnetic stirrer for 30 min. The dip coating was conducted under the same controlled humidity and inert nitrogen atmosphere for 10 times. The next dip coating was 3 s after the previous dip-coating.
Figure 1. The process of Ti-doped LiAlH₄ thin film preparation under the controlled humidity and inert nitrogen atmosphere.

2.2.2 LiAlH₄ thin film analysis
Scanning electron microscope (SEM) was used for surface analysis. The SEM used is Carl Zeiss the EVO® HD at 20 kV and magnification at 1000x. The phase of the Ti-doped LiAlH₄ thin films were characterized using X-ray diffraction (XRD). The XRD was operated at 30 mA and 40 kV with a graphite - monochromated Cu Kα radiation (λ = 1.54180 Å), X-ray tube with Cu, velocity of 0.02 ° per step (2 min⁻¹) and scan axis at 10 deg – 80 deg with Theta/2-Theta. The crystallite size were calculated from Scherrer equation as written in Equation 1:

\[ D = \frac{K\lambda}{\beta \cos \theta} \]  

Where D is the crystallite size, K is the Scherrer constant (0.9), λ is wavelength of the X-ray source (0.15406 nm), β is the full width at half maximum (FWHM) at the peak solution and θ is the Bragg angle by 11.855° for lithium aluminium hydride (LiAlH₄), 19.035° for lithium hexahydroaluminate (Li₃AlH₆) and anatase titanium dixoide (TiO₂) for 12.15°. The LiAlH₄, Li₃AlH₆ and TiO₂ peaks were identified by JCPDS file No. 12-0437, 47-1157 and 84-1286, respectively.

3. Results and discussion
3.1 Phase and crystallite size
As can be seen in Figure 2, the peak intensity of Ti-doped LiAlH₄ (002) peak at 23.71° is higher than any other peaks. The peak intensity of LiAlH₄ are (002), (031), (013) and (231) peaks and there are three peak intensity of Li₃AlH₆, which is (113), (302) and (401) peak. When considering the calculated crystallite size as summarized in Table 1, the crystallite size with the use of TiO₂ concentrations of 0 mol%, 10 mol%, 25 mol% and 40 mol% are 86.20 nm, 75.42 nm, 52.60 nm and 34.22 nm, respectively. It is obvious that the XRD highest peak and minimum crystallite size were obtained at the LiAlH₄ concentration of 20 g/l with 40 mol% TiO₂. This can be implied that the doping with Ti enhances the kinetics of hydrogen storage [10]. The kinetics of hydrogen loading and releasing are a function of the
crystallite size. Moreover, it was found that the hydrogenation efficiency increases with the decreasing crystallite size [10]. This is because the smaller crystallite size was found to improve the desorption kinetics of hydrogen storage from the higher surface area [11].

**Table. 1** Calculated crystallite size of Ti-doped LiAlH₄ thin film at various TiO₂ concentrations.

| TiO₂ concentration (mol %) | 0%   | 10%  | 25%  | 40%  |
|----------------------------|------|------|------|------|
| Crystallite size (nm)      | 86.20| 75.42| 52.60| 34.22|

**Figure 2.** XRD patterns of the deposited Ti-doped LiAlH₄ thin film at the LiAlH₄ concentration of 20 g/l and TiO₂ concentrations of (a) 0 mol%, (b) 10 mol%, (c) 25 mol% and (d) 40 mol%.

3.2 Surface morphology

The SEM images in Figure 3 show the surface morphology of Ti-doped LiAlH₄ at the concentration of 20 g/l with various TiO₂ concentrations. For the LiAlH₄ without TiO₂, cracks and holes on the surface was found. Less cracks and smaller holes were observed with the use of the Ti-doped LiAlH₄ with TiO₂ at 10 mol% concentration. The Ti-doped LiAlH₄ with 40 mol% TiO₂ concentration has rather dense surface without holes. From such a surface morphology observation, it can be implied that the dense surface without any cracks was improved with the incorporation of increasing amount of the TiO₂ [12,13]. This is because the amount of TiO₂ reduces the solvent evaporation rate [14]. In this study, the optimal condition is then the deposition of the Ti-doped LiAlH₄ with the 40 mol% TiO₂ concentration.
4. Conclusions
The dip coating method was applied to fabricate the Ti-doped LiAlH$_4$ at the concentration of 20 g/l with the various TiO$_2$ concentrations of 0 mol%, 10 mol %, 25 mol% and 40 mol%. The LiAlH$_4$ (002) peak is the most intense peak in the XRD pattern. When considering the crystallite size corresponding with (002) peak, the crystallite size at 0 mol%, 10 mol %, 25 mol% and 40 mol% TiO$_2$ concentration were 86.20 nm, 75.42 nm, 52.60 nm and 34.22 nm, respectively. The small crystallite size improved the kinetics of hydrogen storage. Therefore, the Ti-doped LiAlH$_4$ at the TiO$_2$ concentration of 40 mol% is expected to produce the largest amount of hydrogen in this study. Moreover, the SEM also showed the dense surface without any cracks of Ti-doped LiAlH$_4$ at the TiO$_2$ concentration of 40 mol%. Therefore, it might be suggested that increasing the amount of Ti doping increase the efficiency of hydrogen storage.

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