

Catalytic effect of Zr and Hf on hydrogen desorption/absorption of NaAlH₄ and LiAlH₄

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Abstract

The main objective of this work was to investigate the effect of two transition metals (0–9 mol% ZrCl₄ and HfCl₄) on hydrogen desorption/absorption of NaAlH₄ and LiAlH₄. The hydrogen desorption was carried out over a wide temperature range of 25–280 °C while the hydrogen absorption took place at 125 °C and between 50–125 °C for NaAlH₄ and LiAlH₄, respectively, with the same pressure of 11 MPa. The result revealed that the transition metals (Zr and Hf) could improve the kinetics of the hydrogen desorption on NaAlH₄. NaAlH₄ doped with HfCl₄ released hydrogen at the lower temperature than that of ZrCl₄-doped NaAlH₄. In addition, the rate of hydrogen desorption increased with increasing the amount of HfCl₄ doping. However, the maximum hydrogen capacity of ~ 5.5 wt% was obtained from the first desorption, and dropped to 2.2–2.6 wt% in the subsequent cycles. This may be because of, after the hydrogen desorption, the hydrides melt due to the high temperature resulted in agglomeration of the hydrides and segregation of Al. XRD results showed the formation of NaCl after milling of NaAlH₄ with 4 mol% HfCl₄ and no evidence of any Hf-containing phase. However, with 10 mol% HfCl₄, the formation between Al and Hf in the form of Al₃Hf was observed. This compound may act as catalyst in the reversible hydrogen desorption/absorption. For LiAlH₄, ZrCl₄ or HfCl₄ also enhanced the kinetics of desorption of LiAlH₄. Moreover, it was observed that LiAlH₄ released hydrogen during the milling. After the hydrogen desorption from LiAlH₄, no hydrogen absorption was observed for the undoped hydride or that doped with HfCl₄ or ZrCl₄. This may be because of the instability of LiAlH₄. Moreover, milling and dopant may also destabilize the structure of LiAlH₄ causing the irreversibility of hydrogen desorption/absorption on LiAlH₄.

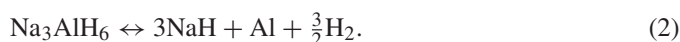
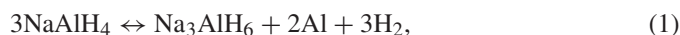
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1. Introduction

Alkali-metal aluminohydrides, like NaAlH₄ and LiAlH₄, have been considered as promising solid-state hydrogen storage materials for on-board fuel cell applications, in part, because of their high hydrogen content. NaAlH₄ decomposes into two steps, as shown in Eqs. (1) and (2). The first step releases 3.7 wt% hydrogen at 185 °C and the second one at

250 °C with 1.8 wt% hydrogen [1,2].

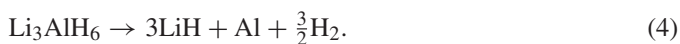
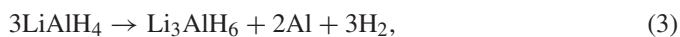


The material has become even more attractive, thanks to the results from Bogdanović and Schwickardi [3]. It was reported that NaAlH₄, mixed with Ti(OBuⁿ)₄, can desorb 3.5–4 wt% hydrogen and reabsorb hydrogen at 170 °C and 150 bar. After this breakthrough, attempts have been made to develop and modify hydrogen desorption/absorption in terms of its kinetics, capacity and reversibility of alkali-metal aluminohydrides.

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NaAlH₄ has been modified by doping with precious metals in different forms using different doping techniques [1,4–10]. However, more understanding on the desorption/absorption mechanism is still needed; especially the roles of metals. In that regard, two mechanisms have been proposed. The substitution of dopant in the lattice of NaAlH₄ has been believed to affect the activation and to be involved in the lattice distortions. And it is this distortion that results in the significant increase in hydrogen desorption kinetics of doped NaAlH₄ [11]. Another proposed mechanism by Graetz et al. using Ti K-edge X-ray absorption near-edge spectroscopy suggests that there is no bulk lattice substitution of Ti, and the metal is not in the form of Ti metal but present in the form of amorphous TiAl₃ [12].

LiAlH₄ decomposes at 160 °C with 5.3 wt% hydrogen and at 200 °C with 2.6 wt% hydrogen, as shown in Eqs. (3) and (4) [13–15]:



Although less has been reported for LiAlH₄, it has also been investigated and improved for its stability and activity of hydrogen desorption using high energy ball-milling for up to 35 h without a catalyst [14]. Effects of transition metals (Ti and Fe) on hydrogen desorption from LiAlH₄ have been reported [15,16]. Balema et al. show that using mechanical ball-milling can transform LiAlH₄ and TiCl₄ to Al₃Ti, which is responsible for the increase in the hydrogen desorption kinetics [17]. The result was also substantiated using a different form of Ti salt by Chen et al., i.e. TiCl₃ can be reduced with LiAlH₄ via the

vibrating-mill technique to form microstructure composites, including Al₃Ti [15]. Despite the high hydrogen storage capacity of LiAlH₄, its reversibility casts some doubt for further applications [18,19].

The main objective of this work was to focus on the effects of adding transition metal on hydrogen desorption/absorption of NaAlH₄ and LiAlH₄. ZrCl₄ and HfCl₄ were used in various amounts for the study. Both effects of the catalysts and reversibility of the hydrides were investigated to understand the role of doped transitions in the hydrides.

2. Experimental

All experiments in this study were performed under nitrogen atmosphere for NaAlH₄ (90%, Aldrich Chemical) and argon for LiAlH₄ (95%, Fluka). Metal hydride samples were doped with ZrCl₄ (> 99.9%, Aldrich Chemical) or HfCl₄ (98%, Aldrich Chemical) using a centrifugal ball-mill (Retsch ball-mill model S100, agate vial size 250 ml, 5 and 2 agate balls with 1 and 2 cm diameters, respectively) for 20 min for NaAlH₄ with a speed of 500 rpm. For LiAlH₄, a mortar and pestle were also used as a means of mixing for 10 min. Amounts of dopant were varied between 0–9 mol%. For comparison purpose, undoped samples were also milled with the aforementioned time and methods. Immediately after mixing, approximately one gram of a sample was placed into the thermovolumetric apparatus. The high pressure stainless steel reactor (316SS) was heated from room temperature to 280 °C with the heating rate of 7 °C min⁻¹ via a furnace controlled by a PID temperature controller. The K-type

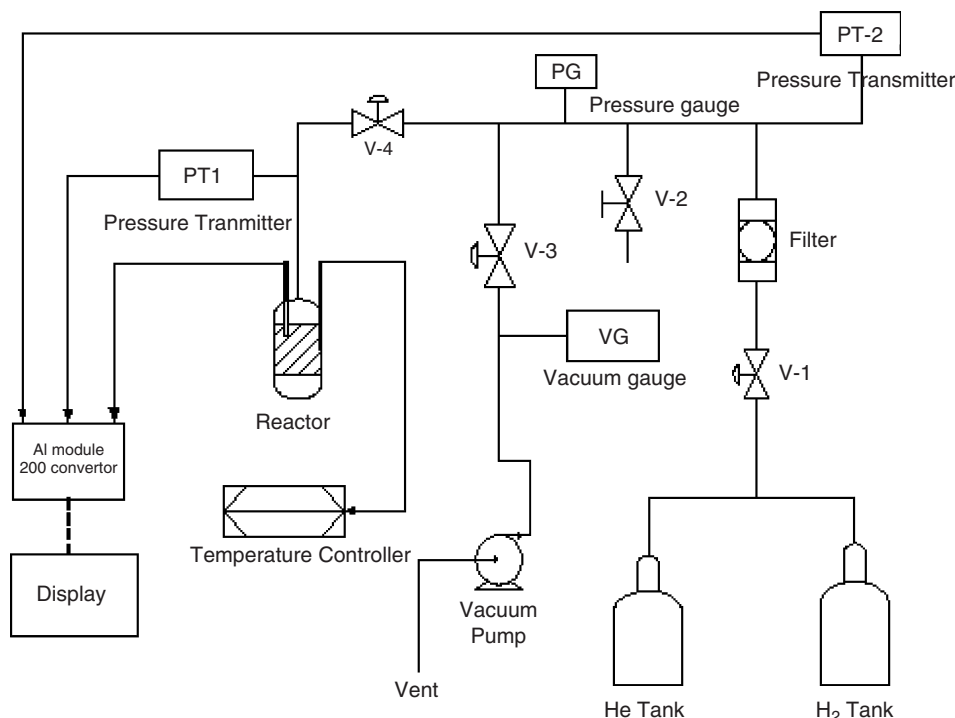


Fig. 1. Schematic diagram of experimental set-up.

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