

CHAPTER I

INTRODUCTION

For decades, the world has been concerned with limited fossil fuel reservoirs. And an increase in the fossil-fuel consumptions causes global environmental issues due to CO₂ emissions. As the most promising alternative fuel, hydrogen is attractive as a clean energy source. Unlike petroleum, hydrogen can be produced from renewable sources such as water, sunlight, and biomass, thereby reducing a growing dependence on fossil fuels (Becker, 2001, http://www.cenonline.org). In addition, it can generate electricity by reacting with oxygen in PEM fuel cells with only water as the by-product without greenhouse gases emissions for hydrogen-fueled vehicles. To store hydrogen for on-board applications, however, is difficult because of its physical characteristics such as its very light weight.

Hydrogen storage is a big key challenge in developing hydrogen economy. To be competitive with current vehicles, the hydrogen storage system must achieve a driving distance more than 300 miles on a single fill near-ambient operation while meeting packing, cost, safety, and performance requirements. The conventional hydrogen fuel storage methods of pressurized hydrogen gas and cryogenic liquid hydrogen do not meet future on-board application goals (http://www.hydrogen.energy.gov/storage). The gaseous hydrogen storage requires a very high pressure to compress hydrogen not to mention the safety concern, while the liquid hydrogen storage needs a large amount of energy for hydrogen liquefaction (Zhou, 2004). As a result, these two techniques are not practical for transportation applications. Alternatively, solid-state hydrogen storage (materials-based hydrogen storage) has been considered as a promising method to employ for on-board hydrogen storage.

The solid-state hydrogen storage is the method that stores hydrogen in/on materials via absorption, adsorption, or chemical reaction. Even these materials have been researched for decades, their poor operating conditions need to be enhanced such as low hydrogen storage capacity, low kinetic rate, low reversibility, and very high desorption/adsorption temperature. Identifying the candidate materials for the most promising on-board hydrogen storage has been an issue of extensive study.

According to previous works, Li-based complex hydrides such as lithium borohydride (LiBH₄) and lithium aluminum hydride (LiAlH₄) have been considered as the promising hydrogen storage materials due to their high theoretical hydrogen capacity about 18.5 and 10.5 wt%, respectively (Jin *et al.*, 2008; Blanchard *et al.*, 2004; Isobe *et al.*, 2005). Recently, Jin *et al.* (2008) reported that LiBH₄ and LiAlH₄ mixture added with 3 mol% TiF₃ stored hydrogen up to 7.2 wt% with the decomposition temperature between 177 and 247°C. LiAlH₄ with the presence of TiCl₃.1/3(AlCl₃) and VCl₃ could reduce its decomposition temperature by 50 and 60°C, respectively (Blanchard *et al.*, 2004).

In this work, LiBH₄ and LiAlH₄ were selected as the based materials for hydrogen storage. The mixtures of these hydrides were prepared by mechanical ball-milling. A small amount of catalysts such as Ti-based compounds (TiCl₃ and TiO₂), VCl₃, and ZrCl₄ were added during the milling process to study the effects on hydrogen storage capacity, decomposition temperature, kinetics, and reversibility of hydrogen desorption/absorption. Phase transformations during the hydrogen desorption/absorption were also investigated.