



CHAPTER I INTRODUCTION

According to the environmental concern of greenhouse gas emissions from the combustion of fossil fuels and finding alternative energy resources for the running out of fossil fuels, it is significantly important to switch to cleaner and renewable fuels. The most promising alternative fuel is hydrogen. It has high potential to be an energy carrier, and can be converted to electricity by reacting with oxygen in PEM fuel cells. However, hydrogen has a very light weight, which leads to the difficulty in storing hydrogen for on-board applications.

Hydrogen storage techniques include gaseous hydrogen storage, liquid hydrogen storage, and solid state hydrogen storage. The first two methods have been utilized to a certain extent while the last one is being developed. The drawbacks of the gaseous hydrogen storage include a very high pressure required to compress hydrogen and safety concern. For the liquid hydrogen storage, a large amount of energy needed for hydrogen liquefaction (Züttel, 2004). Therefore, the first two techniques seem to be inconvenient to be employed for on-board applications.

For the solid state hydrogen storage, hydrogen is stored in/on solid media by absorption or adsorption such as active carbons and carbon nanostructures, metal-organic frameworks, polymers with intrinsic microporosity, zeolites, and metallic hydrides (Van der Berg and Areán, 2007). This technique is considered as a promising method to employ for on-board hydrogen storage. On the other hand, there are some disadvantages such as low hydrogen capacity, very high hydrogen desorption/adsorption temperature, low kinetic rate and low reversibility. Many attempts have been made to improve and identify materials that can be applied to store hydrogen for on-board fuel cell applications. Metallic hydrides are one of the most interesting materials in that aspect due to their high hydrogen capacity.

To develop the high-performance solid state hydrogen storage materials for on-board applications, recently, amide-based materials have been focused due to their high H_2 capacity, particularly lithium amide ($LiNH_2$) (11.5 wt% H_2) (Chen *et al.*, 2002). However, its slow kinetics and high stability are big challenges, which have to be overcome (Leng *et al.*, 2008). Moreover, the formation of NH_3 as a by-

product during the decomposition of LiNH_2 at 300°C is a problem, which impairs the performance of the catalyst in a polymer membrane electrolyte fuel cell and loses the storage materials itself as the constituent nitrogen disappears from the system. However, there has been reported that mixing LiNH_2 with some metal hydrides such as lithium hydride (LiH) can suppress the release of NH_3 (Chen *et al.*, 2003).

Lithium aluminum hydride (LiAlH_4) is another promising metal hydride due to its ability in suppressing the NH_3 emission of LiNH_2 . The decomposition of LiAlH_4 produces both LiH and H_2 . It releases H_2 at low temperatures, $150\text{-}160^\circ\text{C}$, and releases hydrogen up to 5.3 wt% H_2 (Zaluski *et al.*, 1999). It was found that the increasing kinetics and destabilization of LiNH_2 can be accomplished by partial substitution of LiNH_2 by Mg . That resulted in the decrease in the H_2 desorption temperature (Luo and Sickafoose, 2006). There have been reports that magnesium hydride (MgH_2) can suppress NH_3 released from nitrogen-containing hydrides, moreover, MgH_2 also has high hydrogen capacity. Thus, MgH_2 and LiH seem to be a good compound to prevent NH_3 emission and to improve the reversible hydrogen capacity of LiNH_2 (Fujii and Ichikawa, 2006)

To further prevent the NH_3 ammonia released and improve the H_2 desorption of LiNH_2 , in this study, the investigation of adding LiAlH_4 and MgH_2 into LiNH_2 was carried out. $\text{LiNH}_2/\text{LiAlH}_4/\text{MgH}_2$ mixtures are prepared by mechanical ball-milling. Investigation on the hydrogen desorption/re-absorption of the mixtures including, hydrogen capacity, desorption temperature, and reversibility was carried out. Moreover, the effects of Ti compounds (TiO_2 , TiCl_3 , and Ti) on the desorption-absorption of the mixtures and their phase transformation were also studied using information from the X-ray diffraction technique. Results from adding carbon nanotube into the hydride mixture was also reported.