Viewpoint Paper

Metal–N–H systems for the hydrogen storage

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Abstract—The hydrogen storage in metal–N–H systems is reviewed. Exemplary systems including Li–N–H, Mg–N–H, Li–Mg–N–H and Li–Al–N–H are highlighted. Analyses and discussions are focused on the thermodynamics and kinetics of the respective systems.
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1. Introduction

The demand for highly efficient solid-state hydrogen storage materials for the coming hydrogen economy has encouraged tremendous efforts worldwide in the research and development of novel storage systems [1–8]. Hydrogen can be stored in solid media either through physical or chemical processes. For chemical storage, the process can be either reversible or irreversible, depending on the thermodynamic nature of the corresponding reactions.

A variety of promising storage systems are currently being intensively investigated. Complex hydrides [2,3], chemical hydrides [4,5], carbonaceous materials [6] and nanocomposites [7] are among the systems being focused on. Material with a high H content is attractive because it allows more space for subsequent optimization.

Studies on the hydrogen storage in metal–N–H systems were initiated when researchers noticed accidentally that the mixture of metallic lithium and carbon nanotubes pretreated in a purified N_2 atmosphere could absorb a large amount of hydrogen at temperatures above 150 °C [8]. The hydrogenated solid-state sample was identified as containing $LiNH_2$, LiH and unreacted carbon nanotubes. Further investigations revealed that the N_2 treated Li–C mixture was actually composed of Li_3N and carbon nanotubes. The hydrogen storage in Li_3N follows the B-1 reaction (see Table 1). The subsequent dehydrogenation is via the chemical reaction between $LiNH_2$ and LiH, indicating that there must be a driving force for the reaction to be taken place. N, like O, can bond with H and form –NH, $–NH_2$ and NH_3. H bonded with N normally exhibits a positive oxidation state ($H^{\delta+}$) [9]. N can also bond with metals and metalloids. When both H and metal bond to N, imides ($M(NH)_n$) and amides ($M(NH_2)_n$) may form. Amides are analogous to NH_3 but with considerable changes in the structure and electronic properties [10]. The H content of amides is relatively high, especially when M is Li and Mg. However, the direct decomposition of amides will not generate hydrogen but rather, NH_3. On the contrary, the H in hydrides, especially ionic hydrides, is negatively charged ($H^{\delta-}$) [11]. The abnormal high potential of the union of $H^{\delta+}$ and $H^{\delta-}$ to H_2 may induce amides and hydrides to react with each other. The significant implication of this interaction lies in that similar reactions between a variety of amides and hydrides combination may occur which will lead to the development of new chemical processes/materials for hydrogen storage. In this paper, investigations on hydrogen storage in metal–N–H systems were reviewed based on the works published since 2002. The chemical processes involved are summarized in Table 1.

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Table 1. Summary of the chemical reactions between various amides and hydrides

Systems		Reactions	Refs.
Binary	B-1	$LiNH_2 + 2LiH \leftrightarrow Li_3N + 2H_2$	[8,12,13]
	B-2	$LiNH_2 + LiH \leftrightarrow Li_2NH + H_2$	[8,12,13]
	B-3	$Mg(NH_2)_2 + MgH_2 \rightarrow 2MgNH + H_2$	[17]
	B-4	$Mg(NH_2)_2 + 2MgH_2 \rightarrow Mg_3N_2 + 4H_2$	[18]
	B-5	$2CaNH + CaH_2 \leftrightarrow Ca_3N_2 + 2H_2$	[21]
	B-6	$CaNH + CaH_2 \leftrightarrow Ca_2NH + H_2$	[8,21]
	B-7	$Ca(NH_2)_2 + CaH_2 \rightarrow 2CaNH + 2H_2$	[22]
Ternary	T-1	$2LiNH_2 + CaH_2 \leftrightarrow Li_2Ca(NH)_2 + 2H_2$	[23]
	T-2	$Mg(NH_2)_2 + 2LiH \leftrightarrow Li_2Mg(NH)_2 + 2H_2$	[23,24]
	T-3	$3Mg(NH_2)_2 + 8LiH \leftrightarrow 4Li_2NH + Mg_3N_2 + 8H_2$	[26]
	T-4	$Mg(NH_2)_2 + CaH_2 \rightarrow MgCa(NH)_2 + 2H_2$	[31]
	T-5	$2LiNH_2 + LiBH_4 \rightarrow Li_3BN_2 + 4H_2$	[32,33]
	T-6	$2LiNH_2 + LiAlH_4 \rightarrow Li_3AlN_2 + 4H_2$	[36]
	T-7	$LiNH_2 + 2LiH + AlN \leftrightarrow Li_3AlN_2 + 2H_2$	[36]
	T-8	$4LiNH_2 + 2Li_3AlH_6 \rightarrow Li_3AlN_2 + Al + 2Li_2NH + 3LiH + 15/2H_2$	[37]
Multinary	M-1	$NaNH_2 + LiAlH_4 \rightarrow NaH + LiAlNH + 2H_2$	[39]
	M-2	$3Mg(NH_2)_2 + 3LiAlH_4 \rightarrow Mg_3N_2 + Li_3AlN_2 + 2AlN + 12H_2$	[40]

2. Binary metal–N–H systems

A few binary systems, such as Li–N–H [8,12–16], Mg–N–H [17–20] and Ca–N–H [21,22], are listed in Table 1. Hydrogen desorption from a $LiNH_2$ and LiH mixture (molar ratio = 1:2) is a two-step process [8,12]. As shown in Figure 1, the first desorption step occurs at temperatures above 150 °C. Approximately 6 wt.% of hydrogen is desorbed at 200 °C when a high vacuum was applied. The second desorption step occurs at temperatures above 320 °C. It takes a long time for complete desorption at temperatures around 420 °C. The subsequent hydrogenation takes place at temperatures above 150 °C. X-ray diffraction measurements have revealed that the half-dehydrogenated sample contains Li_2NH and LiH, whereas the fully dehydrogenated sample is red–brown Li_3N (see Fig. 2) [12]. Thermodynamic analyses have shown that hydrogen desorption from $LiNH_2$–2LiH and $LiNH_2$–LiH is a highly endothermic process, with the heat of desorption of 80 and 66 kJ mol^{-1} H$_2$ [8], respectively. Therefore, the operation temperature at 1.0 bar equilibrium desorption pressure is above 250 °C, which is too high for its practical application. It has also been reported that additives such
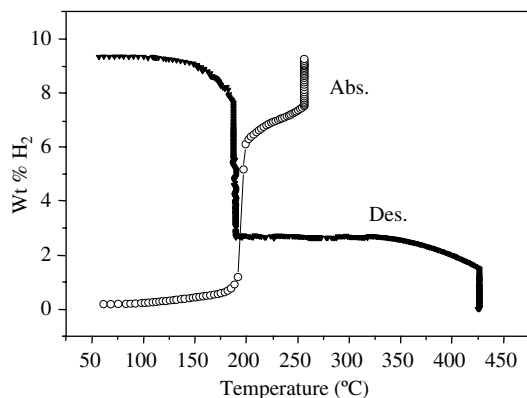
Figure 1. Weight variations during the hydrogen absorption and desorption processes of an Li_3N sample.
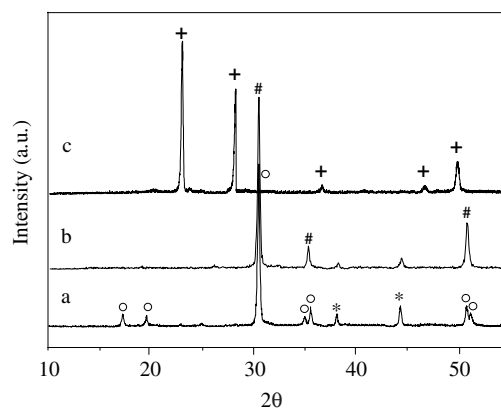
Figure 2. Structural changes during the dehydrogenation of an $LiNH_2$–LiH (1/2) sample: (a) pristine sample; (b) half-dehydrogenated sample; (c) fully dehydrogenated sample. (○) $LiNH_2$; (∗) LiH; (#) Li_2NH and (+) Li_3N.

as $TiCl_3$ and Li_2O can improve the kinetics of hydrogenation and dehydrogenation [13,14]. A few simulation studies have been performed on $LiNH_2$ and Li_2NH [15,16].

The Mg–N–H system, on the other hand, has relatively mild thermodynamics [17,18]. Hydrogen desorption from $Mg(NH_2)_2$ and MgH_2 (at either a 1:1 or 1:2 molar ratio, Reactions B-3 and B-4) can occur under a mechanochemical reaction condition, i.e. energetic ball milling. As shown in Figure 3, hydrogen evolved from the $Mg(NH_2)_2$–MgH_2 (1:2) mixture shortly after the ball milling [18]. The hydrogen desorption was accelerated after the mixture was ball milled for 5 h. The hydrogen release rate slowed down after about 20 h of milling. $Mg(NH_2)_2$ and MgH_2 are stable in the milling jar if ball milled alone, indicating that the hydrogen generation is due to the chemical reaction between these two chemicals. In total, 4 equiv. H2 per $[Mg(NH_2)_2 + 2MgH_2]$ were released at the end of ball milling [18]. As expected, the solid residue is Mg_3N_2. Thermodynamic analysis revealed that the average heat of desorption is ∼3.5 kJ mol^{-1} H$_2$ [18] for Reaction B-4, indicating that