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REVIEW

Materials design and modification on amide-based composites for hydrogen storage

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Abstract Amide-based composite system has the potential to meet the needs of onboard hydrogen storage for fuel cell vehicles due to its relatively high hydrogen capacity and tunable thermodynamics. A large number of amide–hydride and amide–complex hydride composites have been developed in the past decades. This article reviews the state-of-the-arts of amide–hydride composite systems with the focus on the materials design and modification.

1. Introduction

The ever-increasing consumption of energy, dwindling fossil fuel and the growing environment concerns to urge the development of efficient, clean, safe and renewable energy system. Hydrogen energy offers a potential solution due to its transportable, storable, convertible properties and environmental compatibility [1,2]. To employ the hydrogen fuel cell technologies, the US Department of Energy (DOE) set up the targets of hydrogen storage system [3] (see Table 1). To allow small-size vehicles to achieve a driving range of 300 miles, a system capacity with gravimetric and volumetric densities of 4.5 wt% H_2 and 2.8 kg H_2/L, respectively, is basically required. More challenging targets (by year 2015) have been designated to enable the same driving range for mid-size vehicles. It is worthy of noting that these targets are for an integral hydrogen storage system (including auxiliary parts associated with the hydrogen

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Table 1 DOE targets for onboard hydrogen storage systems for light-duty vehicles [3].

Storage parameter	Units	2010	2015	Ultimate
System gravimetric capacity	kWh/kg	1.5	1.8	2.5
	(kg H_2/kg)	(0.045)	(0.055)	(0.075)
System volumetric capacity	kWh/L	0.9	1.3	2.3
	(kg H_2/L)	(0.028)	(0.040)	(0.070)
Storage system cost	\$/kWh	4	2	TBD
	(\$/kg H_2)	(133)	(67)	
Durability/operability operating ambient temperature	°C	−30/50	−40/60	−40/60
Min/Max delivery temperature	°C	−30/80	−40/85	−40/85
Cycle life(1/4tank–full)	cycles	1000	1500	1500
Charging/discharging rates				
System fill time(for 5 kg H_2)	min	4.2	3.3	2.5
	kg H_2/min	(1.2)	(1.5)	(2.0)
Minimum full-flow rate	(g/s)/kW	0.02	0.02	0.02

TBD: to be determined.

storage system). Hence, the material-based hydrogen storage capacities should exceed the above-mentioned values. Apart from these, the temperature range of hydrogen delivering from materials to fuel cell (−45 to 85 °C) is also restricted due to the operating temperature limit of the fuel cell.

The current storage methods based on high-pressure and cryogenic hydrogen are somehow unable to meet all the criteria for vehicular applications due to cost, energy efficiency, safety and volumetric constraints. Such a technical issue stimulates a global research effort on the development of solid hydrogen storage systems. In the past decades, a variety of promising solid state hydrogen storage materials have been intensively studied which include metal hydrides [4–7], chemical hydrides [8–11], carbonaceous materials [12,13], porous materials with large surface area [14–16] and complex hydrides [17–20]. The typical complex hydrides are composed of light metal cations (mainly include alkali or alkaline earth metals Li, Na, Mg, Ca, etc.) and hydrogen-containing anions in which hydrogen atoms are covalently bonded to central atoms, such as B, Al and N [20]. Among these materials, the amide–hydride and amide–complex hydride composite systems have attracted considerable attention since the report on reversible hydrogen storage over lithium nitride (Li_3N) and lithium imide (Li_2NH) in 2002 [21]. The present review focuses on the recent progress in amide–hydride and amide–complex hydride composite systems, e.g. Li–N–H, Li–Mg–N–H, Li–Al–N–H and Li–B–N–H etc., with focus on the materials design and modification.

2. Materials design

Alkali-metal amides such as $LiNH_2$, $NaNH_2$ and KNH_2 etc. are used to be applied in organic synthesis [22,23]. Since their thermolysis liberate only ammonia, they had not been considered as hydrogen storage materials before the introduction of $LiNH_2$–LiH composite [21]. Such an amide–hydride combination was resulted from the observation that Li_3N can absorb hydrogen with maximum capacity of ~10.5 wt% (as shown in Fig. 1) and yield $LiNH_2$. The intermediates Li_2NH and LiH can also reversibly store 6.5 wt% H_2 at elevated temperatures. The whole process relevant to the interactions among imide/amide/hydride can be described by the following equation:

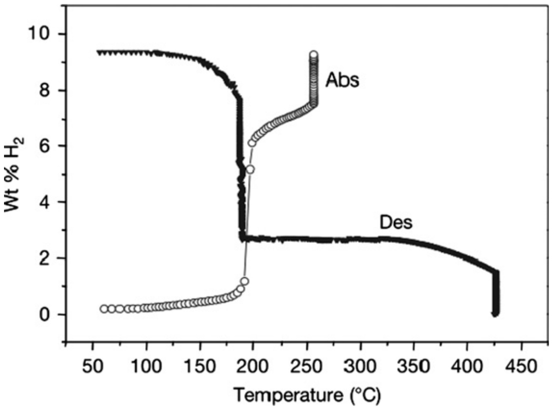

Fig. 1 Weight variations during hydrogen absorption and desorption processes over Li_3N samples. Abs: absorption; Des: desorption [21]. Copyright 2002, Nature Publishing Group.

$$LiNH_2 + 2LiH = Li_2NH + LiH + H_2 = Li_3N + 2H_2 \qquad (1)$$

Fig. 2 shows that the crystal structure of Li_3N is built by the Li and Li_2N layers [24]. When H_2 is introduced into the system, Li in the Li layer tends to separate from the Li_3N structure and combines with H to form LiH. At the same time, H substitutes for Li to bond with N and forms Li_2NH. Further hydrogenation results in the additional exchange between Li in Li_2NH (illustrated in Fig. 3; [25]) and H in H_2, and the formation of $LiNH_2$ and LiH.

A typical feature of the amide–hydride systems is the co-existence of oppositely charged hydrogens. It differs from hydrogen storage materials such as physisorption materials, metal/complex hydrides, organic liquids and hydrazine in which the valence state of H atom are either constant or monotonously changed.

It is well known that hydrogen can bond with nitrogen to form –NH, –NH_2 and NH_3. H bonded to N normally exhibits a positively charged state ($H^{\delta+}$) as that performed by metals. When both H and metal simultaneously bond to N, imides

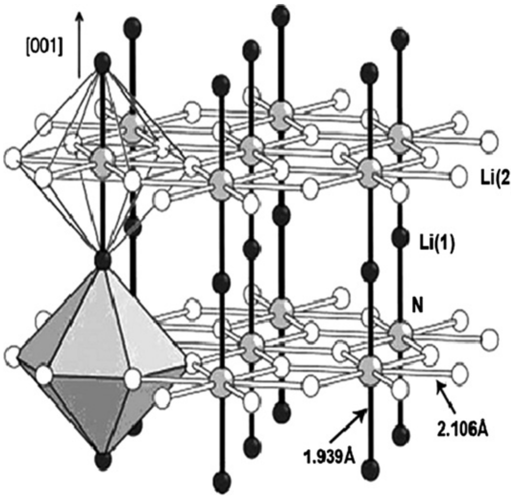

Fig. 2 Crystal structure of Li_3N [24]. Reproduced by permission of the American Institute of Physics.

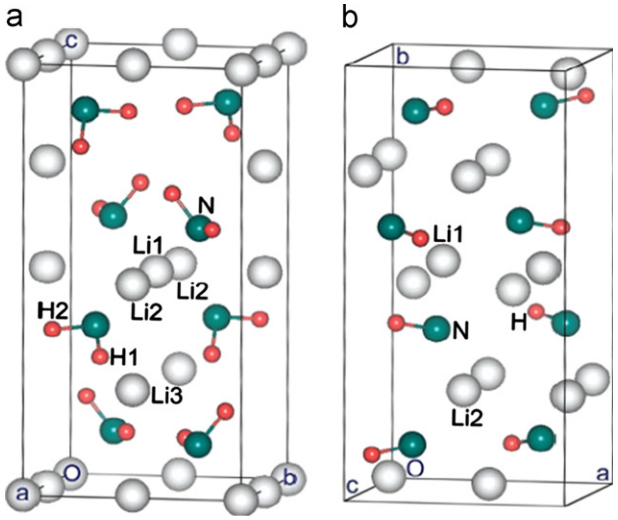

Fig. 3 Relaxed structures of: (a) tetragonal $LiNH_2$ and (b) orthorhombic Li_2NH. Large (gray) spheres are Li, medium (blue) spheres are N, and small (red) spheres are H. In equivalent, atoms are labeled as H1, H2, Li1, Li2 and Li3 [25]. Copyright (2012) by the American Physical Society.

($M(NH)_n$) or amides ($M(NH_2)_n$) may be formed. Amides differ from ammonia in the structures and electronic properties [26]. Opposite to amide, H in ionic metal hydrides is negatively charged ($H^{\delta-}$). When two starting chemicals (amides and hydrides) are mixed together, the high combination potential of $H^{\delta+}$ and $H^{\delta-}$ (see Eq. 2), together with the attractions between the electropositive metal cation and electron-rich nitrogen-based group, will trigger a series of interaction. H_2 is therefore liberated [27].

$$H^{\delta+} + H^{\delta-} = H_2 \qquad \Delta H = -17.37\ \text{eV} \tag{2}$$

The $H^{\delta+}$–$H^{\delta-}$ mechanism sheds light on the materials design for amide-based hydrogen storage systems, i. e., one can select different amides to mix with hydrides or complex hydrides to lead to the development of amide–hydride and amide–hydride complex systems.

3. Amide–hydride systems

The de/re-hydrogenation kinetics of the $LiNH_2$–LiH and $LiNH_2$–2LiH systems are sluggish and lead to unfavorable operating temperature. Introducing "catalytic" additives and reducing particle size were proven to be the effective ways to improve the kinetics. Ichikawa et al. revealed that the Li–N–H system doped with nano-sized Ti additives [28,29] has a superior catalytic effect over the pristine one. According to their results, the Ti-doped sample can desorb large amount of hydrogen (~5.5 wt%) and does not release any ammonia within the temperature range of 150–250 °C. On the other hand, however, Aguey-Zinsou et al. [30] argued that the chemistry of additives played more important role than their particle size in improving the kinetics. They believed that the micro-scaled BN particles served as an efficient catalyst to improve Li^+ diffusion and the kinetics of the reaction between $LiNH_2$ and LiH. In that case, hydrogen can be fully released within only 7 h at 200 °C due to the presence of BN in comparison with several days of BN-free sample. Recently, an interesting phenomenon was discovered by Lamb et al. [31] that partial substitution of H_2 by 20 mol% N_2 can significantly enhance the reversible capacity of Li_3N from ~3 wt% H_2 to 10 wt% H_2 after 516 cycles at 528 K. The improvement in cyclic stability is proposed to be due to the interaction between nitrogen with the formed metallic lithium in liquid and the formation of Li–N or Li–N–H compounds in the composite. Hu and Ruckenstein [32] found that partial oxidization over the surface layer of Li_3N, followed by a hydrogenation/dehydrogenation pretreatment, can yield a Li_2O/Li_3N composite material. It exhibited faster kinetics, larger reversible capacity and higher stability than pristine Li_3N. Introducing Li_2O into Li_3N system can also inhibit the temperature jump and prevent the agglomeration during the hydrogenation process. Mechanical milling also enhances the kinetics of the Li–N–H system [33,34], which can be ascribed to the reduced sizes of $LiNH_2$ and LiH particles.

Theoretical calculations [25,35–41] have been performed on the relevant phase analyses [42–44] and the reaction mechanism interpretation on the $LiNH_2/Li_2NH$ system. For example, the studies on native point defects of Li–N–H system by first-principles [25] found that both $LiNH_2$ and Li_2NH were liable to form Frenkel disorder on the Li sublattice. Lithium interstitials and vacancies have low formation energies and high mobility, and therefore, play important roles in mass transport and ionic conduction. Hydrogen interstitials and vacancies, on the other hand, are responsible for forming and breaking N–H bonds in the Li amide/imide reaction. Similar work was conducted by Hazrati et al. [36] in which first-principles and density functional theories were employed to study the native defects and dopants in $LiNH_2$. Both Li-related and H-related defects were charged in $LiNH_2$. Li-related defects can diffuse at moderate temperatures more easily than H-related defects due to its lower diffusion barriers (0.3–0.5 eV).

The $LiNH_2$–LiH and $LiNH_2$–2LiH composites suffer from unfavorable dehydrogenation enthalpies ($\Delta H = 66$ and 88 kJ/mol H_2, respectively). The temperature of minimum ca. 255 °C is necessary to attain equilibrium pressure of 1 bar during dehydrogenation. Such operating temperature is too high to be directly combined with fuel cells. Substitutions of $LiNH_2$ by $Mg(NH_2)_2$ gave rise to $Mg(NH_2)_2$–2LiH (denoted as Li–Mg–N–H) composite system [45–48] (see Eq. (3)). Volumetric release and soak measurements revealed that more than 5 wt% hydrogen could be reversibly stored in this system within the temperature range of 100–300 °C [49] (as shown in Fig. 4).

$$2LiNH_2 + MgH_2 \rightarrow Mg(NH_2)_2 + 2LiH = Li_2Mg(NH)_2 + 2\,H_2 \qquad (3)$$

In comparison with the Li–N–H system, the Li–Mg–N–H system exhibits much lower absorption and desorption temperatures and higher plateau pressure [50,51]. The desorption enthalpy ΔH_{des} and entropy ΔS_{des} of the $Mg(NH_2)_2$–2LiH system were calculated to be ~38.9 kJ/mol H_2 and 112 J/mol H_2, respectively, which allow hydrogen desorption at 1 bar H_2 equilibrium pressure at a temperature lower than 90 °C [49], which enables the Li–Mg–N–H as an attractive candidate for fuel cell application. According to the results derived from in-situ XRD measurements, the hydrogenation and dehydrogenation consist of two steps [52] (see Eqs. (4) and (5)). This observation agrees well with the pressure–composition–isotherm (P–C–I) results, of which both the soak and release possess a plateau and a slop pressure regions. As shown in Fig. 5, the plateau at ~46 bars accounts for about 2/3 hydrogenation capacity, which corresponds to the reaction (4). The other 1/3 capacity, however, belongs to the slop region and likely result from the reaction (5) [45,49,50,52].

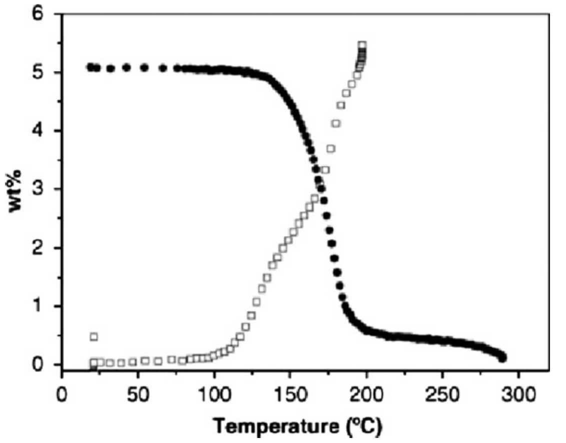

Fig. 4 Hydrogen absorption in a $Li_2MgN_2H_2$ sample and desorption from $Mg(NH_2)_2$–2LiH sample [49]. Reproduced by permission of Elsevier.

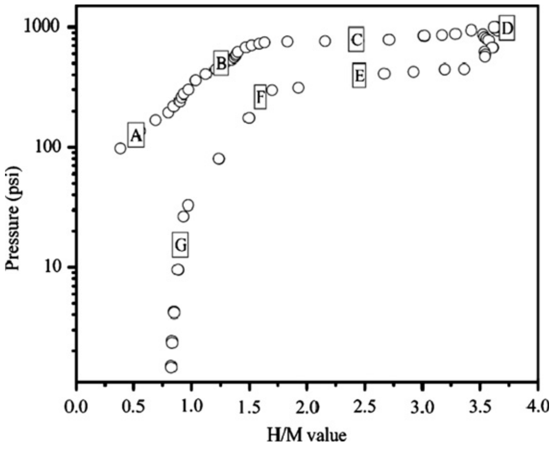

Fig. 5 PCI curves of the Li–Mg–N–H system [52]. Copyright 2007, American Chemical Society.

$$3LiH + 2Mg(NH_2)_2 = LiNH_2 + Li_2Mg_2(NH)_3 + 3H_2 \qquad (4)$$

$$LiH + LiNH_2 + Li_2Mg_2(NH)_3 = 2Li_2MgN_2H_2 + H_2 \qquad (5)$$

$Mg(NH_2)_2$–LiH composites with different molar ratios have been studied by several independent groups. Leng et al. [53] achieved a novel $Mg(NH_2)_2$–LiH system composed of $Mg(NH_2)_2$ and LiH in a molar ratio of 3:8, which can reversibly store about 6.9 wt% hydrogen. Nakamori et al. [47,54] increased the amount of LiH to form the $Mg(NH_2)_2$–4LiH composite, which improved the hydrogen storage capacity to ~9.1 wt%. Xiong et al. [55] developed the $Mg(NH_2)_2$–nLiH ($n = 1, 2, 3$) systems and revealed that lowering the LiH amount led to the increasing release of ammonia from the system. On the other hand, increasing the LiH amount in the composite may lift the hydrogen desorption temperature. Hu and Fichtner [56] altered the molar ratio range from 1:1.5 to 1:2.7 for $Mg(NH_2)_2$–LiH and observed both dynamic and quasi-equilibrium dehydrogenation pathways. However in any way, ternary imide $Li_2Mg(NH)_2$ always presents in the dehydrogenated products. Investigation reveals that such imide is a thermodynamically stable phase which indicates that the optimized composition for $Mg(NH_2)_2$–LiH that possesses the highest hydrogen capacity and the lowest operating temperature should be 1:2. Similar dehydrogenation plateau pressures can be observed in the $Mg(NH_2)_2$–LiH samples (1:2, 3:8 and 1:4 in M ratios), suggesting that they possess nearly the same thermodynamic nature in that part of dehydrogenation state [57]. It demonstrates that tuning the molar ratio hardly modifies the major dehydrogenation reaction (within lower temperature range) in these samples. The $Li_2Mg(NH)_2$ and LiH phases are always produced in these LiH-rich samples after dehydrogenation at ca. 200 °C [57–59].

Thermodynamic calculations showed that the dehydrogenation temperature for the $Mg(NH_2)_2$–2LiH system is ca. 90 °C at the equilibrium hydrogen pressure above 1 bar. However, the majority of hydrogen release can only be achieved at temperatures above 180 °C, which should be attributed to the severe kinetic barrier where the activation energy for hydrogen desorption is higher than most of metal hydrides [49,60]. Doping additives effectively improved the hydrogenation/dehydrogenation kinetics. Sudik et al. [61] proposed that seeding 10 wt% excessive $Li_2Mg(NH)_2$ can decrease the peak temperature of hydrogen desorption by 40 °C in comparison with the unseeded sample. Nevertheless, the peak temperature of dehydrogenation was lifted by 10 °C due to the complete conversion of $Li_2Mg(NH)_2$ to $Mg(NH_2)_2$–2LiH after one cycle of dehydrogenation–hydrogenation. Seeding the product in a reversible reaction was employed by Yang et al. [62], who proposed a self-catalyzing mechanism in $LiNH_2$–MgH_2–$LiBH_4$ system later. In that system, $LiNH_2$ combines with $LiBH_4$ to form $Li_4BN_3H_{10}$ first which interacts with MgH_2 to yield $Li_2Mg(NH)_2$ nuclei. These $Li_2Mg(NH)_2$ nuclei facilitate the interaction between $Mg(NH_2)_2$ and LiH, and results in an enhancement of the overall kinetic properties (see Eqs. (6) and (7)).

$$3LiNH_2 + LiBH_4 \rightarrow Li_4BN_3H_{10} \qquad (6)$$

$$2Li_4BN_3H_{10} + 3MgH_2 \rightarrow 3Li_2Mg(NH)_2 + LiBH_4 + 6H_2 \qquad (7)$$

Hu et al. [63–65] intensively studied the effect of $LiBH_4$ on the $Mg(NH_2)_2$–2LiH system. It was revealed that several molar percentage of $LiBH_4$ can significantly improve the dehydrogenation/hydrogenation properties of the $Mg(NH_2)_2$–2LiH system. For example, 5 wt% H_2 can be desorbed at 140 °C and fully reabsorbed at 100 °C. The rates of hydrogen desorption/absorption are 3 times as fast as those of the pristine system. They concluded that addition of $LiBH_4$ not only improved the kinetics but also changed the thermodynamics of Li–Mg–N–H system, because the $LiBH_4$ can react with $LiNH_2$ to form $Li_4(BH_4)(NH_2)_3$, which weakens the N–H bonds of $LiNH_2$ and changes the reaction path of Li–Mg–N–H [65].

Partial substitution of Mg or Li by Na in the $Mg(NH_2)_2$–2LiH system shows kinetic improvements in the dehydrogenation/hydrogenation process [66–68], which may be attributed to the interaction of Na species with $LiNH_2$ to form $Li_3Na(NH_2)_4$ [67]. A few percentage (~3 mol%) of potassium compounds, such as KH, KOH, KF, KNH_2, K_2CO_3 and K_3PO_4, can significantly reduce the peak temperature of hydrogen desorption by approximately 50 °C in comparison with the potassium-free system (shown in Fig. 6). Whatever *K*-additive is, it will be eventually converted to KH and K-containing amide in the system due to the interaction between LiH or $Mg(NH_2)_2$ and the doped potassium salts [69]. Wang et al. found that the intermediates, such as $K_2Mg(NH_2)_4$, $Li_3K(NH_2)_4$ etc., are crucial for the improvement of the kinetics of hydrogen desorption/absorption of the KH-doped $Mg(NH_2)_2$–2LiH system [70]. Other materials such as single-walled carbon nanotubes, Li_3N, TaN, TiN, TiF_3, Si, Al, $MgCl_2$, various transition metal halides ($TiCl_3$, VCl_3, $ScCl_3$ and $NiCl_2$) etc. have also been tested as additives on the $Mg(NH_2)_2$–2LiH system [71–77]. Interestingly, TaN and TiN modified $Mg(NH_2)_2$–2LiH samples exhibit N-deficient patch of metal atoms on the surface and edges, which facilitates the dissociation of the N–H bond in $Mg(NH_2)_2$ of this system [72]. Reducing the particle size of reactant is another effective way to improve the dehydrogenation/hydrogenation kinetics of the $Mg(NH_2)_2$–2LiH system. Liu et al. [78] found that $Li_2Mg(NH)_2$ milled for 36 h started to re-hydrogenate at 80 °C, while the onset temperature for hydrogen absorption of the hand-grounded sample was about 150 °C. The decreasing of absorption temperature was caused by shortened diffusion distance and enlarged specific surface area. Similar conclusions were drawn by Xie et al. [79] who combined $Mg(NH_2)_2$ in different particle sizes (100, 500, and 2000 nm) with LiH, and found that the activation energy for desorption monotonously increased with the augmentation of the particle size. In fact, nano/micro-sized particles are liable to aggregate during heating process. It directly leads to the reduction in surface area, the extension of mass transport distance, and the degradation of the hydrogen ab/de-sorption performances. Wang et al. found that triphenyl phosphate [80] can prevent the sample from aggregation and improve the hydrogenation/dehydrogenation kinetics to some degree. Another issue concerned with the $Mg(NH_2)_2$–2LiH system is the co-production of minor NH_3, a gaseous by-product that not only poisons the membrane in the PEMFC, but also degrades the cycling stability of the material [81–83]. Increasing LiH can effectively depress the formation of NH_3 [57], but may tailor the de/re-hydrogenation capacity at low operating temperature.

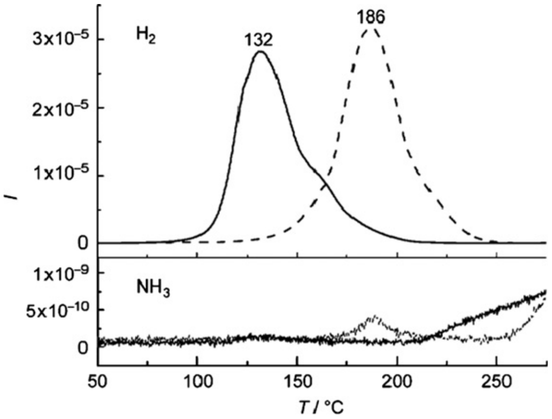

Fig. 6 Temperature dependencies of H_2 and NH_3 release from the potassium-modified (—) and the pristine samples(——) [69]. Copyright, Wiley–VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

In the past decades, people proposed several mechanisms to understand the reactions in the Li–Mg–N–H composite. The solid state reaction mechanism suggested by Chen et al. [84] believes that the positively charged hydrogen ($H^{\delta+}$) in $Mg(NH_2)_2$ combines easily to the negatively charged hydrogen ($H^{\delta-}$) in LiH to form molecular hydrogen. While, the ammonia mediated mechanism proposed by Ichikawa et al. [85,86] figures that amide initially decomposes into imide (or even into nitride) with increasing temperature, and simultaneously releases ammonia. Ammonia promptly reacts with hydride in the system and results in dehydrogenation.

Based on the $H^{\delta+}$ and $H^{\delta-}$ combination mechanism [27,84], several amide/hydride composites have been developed (Table 2). Examples include the combinations of $Mg(NH_2)_2$–MgH_2 (at either 1:1 or 1:2 M ratio) [87,88], $Mg(NH_2)_2$–xNaH ($x=1$, 1.5, 2) [89], $Mg(NH_2)_2$–$2CaH_2$ [90], $Mg(NH_2)_2$–CaH_2 [91], $Mg(NH_2)_2$–$Ca(NH_2)_2$–4LiH [92], $Ca(NH_2)_2$–NaH [93] and $x$$LiNH_2$–$CaH_2$ ($x=2$, 3, 4) [94], etc.

4. Amide–complex hydride systems

Complex hydrides such as $LiAlH_4$ and Li_3AlH_6 possess high hydrogen capacities (10.5 wt% and 11.1 wt%, respectively). The thermal dehydrogenation of $LiAlH_4$ studied by Block and Gray [95] in 1965 indicated that the initial release of hydrogen took place in the temperature range of 187–218 °C. The second-step dehydrogen occured at 228–282 °C. The final step of LiH dehydrogenation started from the temperatures of above 550 °C. Unfortunately, the dehydrogenation of $LiAlH_4$ is a one-way reaction. Li_3AlH_6 is difficult to absorb hydrogen to form $LiAlH_4$ under moderate condition. The hydrogenation of LiH/Al to Li_3AlH_6 is weakly exothermic and could be accomplished under extraordinarily high pressure in principle. Amides were chosen to modify the thermodynamics, kinetics and reversibility of alanates by Xiong et al. [96]. For the $LiAlH_4$–$2LiNH_2$ system [97], the whole dehydrogenation reaction can be expressed by the following equation:

$$2LiNH_2+LiAlH_4\rightarrow(Li_3AlN_2H_4)+2H_2\rightarrow Li_3AlN_2+4H_2 \tag{8}$$

More than 5 wt% of hydrogen can be reversibly stored by Li_3AlN_2 by means of heating to 500 °C under 80 bar of hydrogen pressure (see Fig. 7). Recently, Dolotko et al. systematically investigated the $LiAlH_4$/$LiNH_2$ system through thermochemical [98] and mechanochemical transformations [99]. They found that

Table 2 Summary of the chemical reactions between various amides and hydrides.

Reactions	Theoretical (wt% H_2)	Experimental (wt% H_2)	ΔH_{des} (kJ/mol H_2)	References
$2LiH+LiNH_2=LiH+Li_2NH+H_2=Li_3N+2H_2$	6.5	6.3	66.1	[21]
	10.3	11.5	161[a]	
$MgH_2+Mg(NH_2)_2\rightarrow 2MgNH+2H_2$	4.9	4.8	–	[87]
$2MgH_2+Mg(NH_2)_2\rightarrow Mg_3N_2+4H_2$	7.4	7.4	3.5[a]	[88]
$CaH_2+CaNH=Ca_2NH+H_2$	2.1	1.9	88.7	[21]
$2LiH+Mg(NH_2)_2=Li_2Mg(NH)_2+2H_2$	5.6	5.2	38.9	[45,46]
$8LiH+3Mg(NH_2)_2=4Li_2NH+Mg_3N_2+8H_2$	6.9	6.9	–	[53]
$4LiH+Mg(NH_2)_2=Li_3N+LiMgN+4H_2$	9.1	9.1	–	[47]
$3KH+3Mg(NH_2)_2=K_2Mg(NH_2)_4+MgNH+KH+2H_2=3KMg(NH_2)(NH)+3\ H_2$	2.1	1.9	56.0	[70]
$4CaH_2+2Mg(NH_2)_2\rightarrow Mg_2CaN_2+Ca_2NH+CaNH+7H_2$	5	4.9	21.4	[90]
$Mg(NH_2)_2+4LiH+Ca(NH_2)_2=Li_4MgCaN_4H_4+H_2$	5	3.0	–	[92]
$2LiH+LiNH_2+AlN=Li_3AlN_2+2H_2$	5	5.1	50.5[a]	[97]
$2LiBH_4+MgH_2=LiH+MgB_2+4H_2$	11.5	8.3	–	[115,116]
$2LiNH_2+LiBH_4\rightarrow Li_3BN_2H_8\rightarrow Li_3BN_2+4H_2$	11.8	10.2	–	[120]
$2Li_4BN_3H_{10}+3MgH_2\rightarrow 2Li_3BN_2+MgN+LiH+12H_2$	9.2	8.2	–	[62]

[a]Obtained by simulation or calculation.

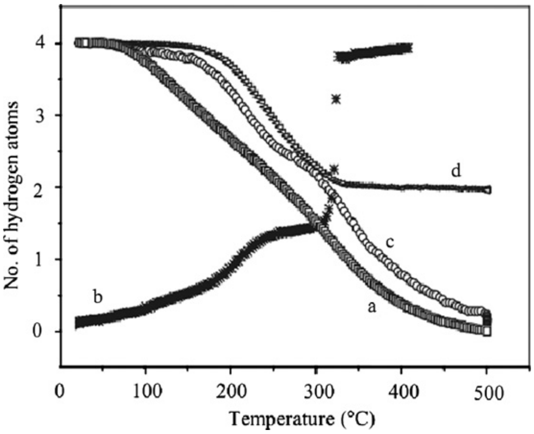

Fig. 7 Volumetric measurments of: (a) hydrogen release from post-12 h-milled $LiNH_2$–$LiAlH_4$ (2:1) sample; (b) hydrogen absorption over Li_3AlN_2; (c) hydrogen desorption from the fully hydrogenated Li_3AlN_2 sample and (d) hydrogen release from the $LiNH_2$–LiH(1:2) mixture [97]. Copyright, Wiley–VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

the thermochemical transformation of the $LiAlH_4/LiNH_2$ mixture produced Li_3AlN_2, metallic Al and LiH, and released 9 wt% hydrogen. The reaction mechanism of the thermal decomposition differs from that of the mechanical treatment [96,99]. Lu and Zang [100] and Naik et al. [101] observed that $2LiAlH_4/LiNH_2$ mixtures without any catalysts can liberate a large amount of hydrogen (~8.1 wt%) in the temperature range of 85–320 °C. The reaction temperatures of the three-step dehydrogenation are lower than that of Ti-doped $LiAlH_4$. Similar phenomenon can also be found in $2LiNH_2/Li_3AlH_6$ system [102]. For Li_3AlH_6–$3LiNH_2$–4 wt% $TiCl_3$–1/3 $AlCl_3$ composite, large amount of hydrogen (~7.1 wt%) can be released in two steps at the temperatures between 150 and 300 °C. Noticeably, the system is nearly 100% reversible under 2000 psi hydrogen pressure and 300 °C. The de/re-hydrogenation experiments showed that the reversible capacity is hardly reduced in several cycles [103]. Recently, Lu et al. investigated the effects of heating rate on the reversible hydrogen storage properties [104]. It was found that Li_3AlH_6 can be formed when faster heating rates (>5 °C/min) were employed, while the formation of nitride species occurs when heating is slower (<2 °C/min). Similar works are also found in other Li–Al–N–H systems such as Li_3AlH_6–$LiNH_2$ (1:2, 1:3) [105,106], $Mg(NH_2)_2$–$xLiAlH_4/Li_3AlH_6$ system [107–109], and $LiAl(NH_2)_4$–4LiH [110] etc.

Metal borohydrides also hold potentials for hydrogen storage owing to their high gravimetric and volumetric hydrogen capacities [18,111–113]. For examples, hydrogen content of $LiBH_4$ is 18.5 wt%, $NaBH_4$ is 10.8 wt%, $Mg(BH_4)_2$ is 14.9 wt%, and $Ca(BH_4)_2$ is 11.6 wt%. However, high temperature is necessary for the hydrogen release from these borohydrides due to their high thermal stability. Several strategies have been tried to destabilize these borohydrides, including the interaction of borohydrides with amides and hydride additives [114–119]. $LiBH_4$–$xLiNH_2$ ($x=1$, 2, 3) [120–124] composites were synthesized according to the chemical compositions of Li_2BNH_6, $Li_3BN_2H_8$, and $Li_4BN_3H_{10}$. They are able to release more than 11 wt% of H_2 within the temperature range of 250–350 °C. Pinkerton et al. [120] obtained the quaternary $Li_3BN_2H_8$ compound by combining $LiNH_2$ and $LiBH_4$ powders in a molar ratio of 2:1. It possesses a hydrogen capacity of 11.9 wt% and a melting point at ~190 °C, and releases more than 10 wt% hydrogen at temperatures above ~250 °C (shown in Fig. 8.). Yu et al. [125] investigated $Mg(BH_4)_2$–$LiNH_2$ with molar ratios of 1:1.5, 1:2, and 1:3, respectively. In the $Mg(BH_4)_2$–$LiNH_2$ (1:1) samples, the first-step dehydrogenation started at 160 °C and liberated totally 7.2 wt% H_2 at ~300 °C. By the Kissinger's method, the activation energies (Ea) for the first and second steps of dehydrogenation of the sample were estimated as ~121.7 and 236.6 kJ/mol, respectively. Recently, Chu et al. [126] prepared $Ca(BH_4)_2$–$2Ca(NH_2)_2$ and $Ca(BH_4)_2$–$2Mg(NH_2)_2$ composites. Those binary phase systems exhibited an onset dehydrogenation temperature of ~220 °C, which was lowered from that of pristine $Ca(BH_4)_2$ by ~100 °C. Zheng et al. [127] introduced LiH–Co co-catalysts to modify the $LiBH_4$–$3LiNH_2$ mixture. More than

9.6 wt% of H_2 can be release from that system at ~250 °C, while only 8.0 wt% hydrogen can be released from the pristine system under the same condition (shown in Fig. 9.). Similar amides–borohydrides systems have been developed in recent few years, such as $LiBH_4$–$NaNH_2$ [128], $LiBH_4$–$Mg(NH_2)_2$ [129], $Ca(BH_4)_2$–$LiNH_2$ [130], $NaBH_4$–$NaNH_2$ [131,132], $Mg(BH_4)_2$–LiH–$LiNH_2$ [133], $LiBH_4$–$LiNH_2$–MgH_2 [134–136] etc. Although amide–complex hydride system has broadened the material scopes for hydrogen storage and improved the dehydrogenation performances, its reversible hydrogen capacities degraded notably in comparison with amide–hydride system (e.g. $LiNH_2$–2LiH, $Mg(NH_2)_2$–2LiH), especially when temperatures are below 180 °C.

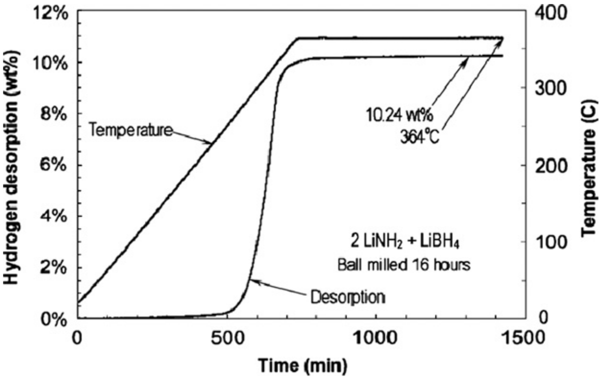

Fig. 8 Volumetric measurement of thermal desorption from $Li_3BN_2H_8$, heated at 0.5 °C/min to 364 °C, and soaked for 680 min, calculated by assuming that all of the desorbed gas is H_2 [120]. Copyright 2005, American Chemical Society.

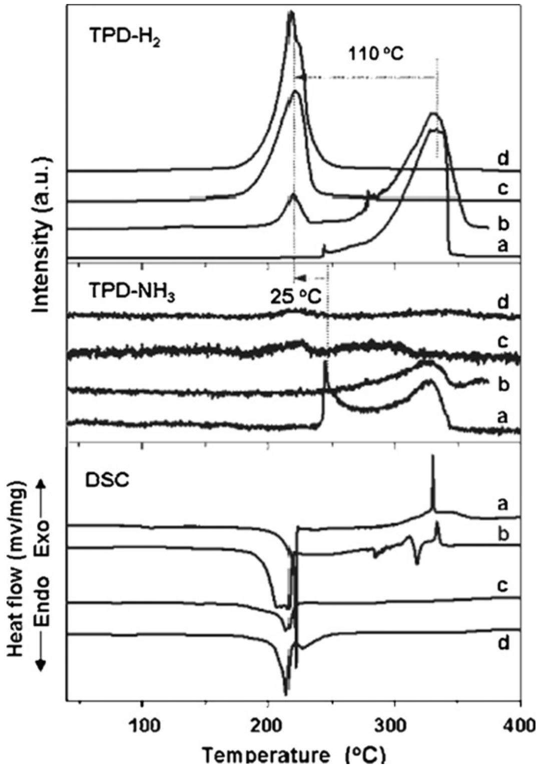

Fig. 9 TPD and DSC traces of: (a) pristine $Li_4BN_3H_{10}$; (b) LiH–$Li_4BN_3H_{10}$; (c) Co–$Li_4BN_3H_{10}$ and (d) LiH–Co–$Li_4BN_3H_{10}$ samples [127]. Copyright 2011, American Chemical Society.

5. Summary

The emerging amide–hydride composite systems during the past decades expanded the material scopes for hydrogen storage considerably. However, development of an amide-based material with high hydrogen capacities, favorable thermodynamics and suitable kinetics is still a challenging mission. The first challenge is to achieve a favorable thermal stability and to realize hydrogen storage at moderate temperature. Secondly, NH_3 is the unwanted by-product and will poison the membrane of PEMFC even in the concentration of ppm level. Preventing NH_3 release from these systems is also a tough challenge. Thirdly, amide–hydride composite systems suffer from sluggish kinetics in the hydrogenation and dehydrogenation. The kinetic barriers are mainly resulted from the mass transport and reactions occurring at the surface and interface. Reducing particle size of reactants, e.g., by mechanical ball milling and nano-confinement, and introducing additives into the hydrogen storage materials are effective ways to improve kinetics. However, the current achievements are still far from the practical applications. Varieties of material optimization and modification are bringing the amide-based systems into the most promising candidates for hydrogen storage.

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