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A Dehydrogenation Mechanism of Metal Hydrides Based on Interactions between $H^{\delta+}$ and H^{-}

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This paper describes a reaction mechanism that explains the dehydrogenation reactions of alkali and alkaline-earth metal hydrides. These light metal hydrides, e.g., lithium-based compounds such as LiH, $LiAlH_4$, and $LiNH_2$, are the focus of intense research recently as the most promising candidate materials for on-board hydrogen storage applications. Although several interesting and promising reactions and materials have been reported, most of these reported reactions and materials have been discovered by empirical means because of a general lack of understanding of any underlying principles. This paper describes an understanding of the dehydrogenation reactions on the basis of the interaction between negatively charged hydrogen (H^{-}, electron donor) and positively charged hydrogen ($H^{\delta+}$, electron acceptor) and experimental evidence that captures and explains many observations that have been reported to date. This reaction mechanism can be used as a guidance for screening new material systems for hydrogen storage.

Introduction

Because of the growing demand for efficient and clean fuel alternatives, the development of hydrogen storage materials, including research on solid reversible hydrogen storage materials, has gained and is continuously gaining momentum in recent years. Although substantial progress has been made in the past few years in the discovery of new materials, none of these materials have demonstrated sufficient reversible hydrogen storage capacity in terms of the gravimetric or volumetric density of hydrogen that is required for them to become practically usable hydrogen storage materials.

Among many different candidate materials for hydrogen storage, simple metal hydrides including alkali- and alkaline-earth metal hydrides such as LiH and MgH_2 have a high hydrogen weight capacity. However, these compounds are typically very stable and the dehydrogenation of these materials can be achieved only at high temperatures that are impractical for real applications. For example, the dehydrogenation temperature of LiH is higher than 720 °C at atmospheric pressure. Even at such a high temperature, the rate of hydrogen absorption/desorption is very slow.[1] These poor decomposition kinetic properties of simple metal hydrides render the material not viable for practical purposes. Therefore, the challenge for developing simple metal hydrides for on-board hydrogen storage applications is to find means of destabilizing these materials to lower their dehydrogenation temperatures and increase their dehydrogenation rates. A fundamental understanding of the process and the mechanism of dehydrogenation reactions is required.

In an effort to develop lithium-based materials, Chen[2,3] et al. and Hu[4−7] et al. reported that the dehydrogenation temperature of LiH could be decreased dramatically when it is combined with $LiNH_2$, as follows

$$LiNH_2 + LiH \rightarrow Li_2NH + H_2 \tag{1}$$

$$Li_2NH + LiH \rightarrow Li_3N + H_2 \tag{2}$$

To understand these reactions, researchers have proposed two possible mechanisms. Chen[3] et al. claimed that the dehydrogenation process between LiH and $LiNH_2$ proceeds by a

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Table 1. Dehydrogenation Temperatures of M−N−H Systems and Dissociation Temperatures of the Corresponding Simple Metal Hydrides

metal hydride	decomposition temperature (°C)	reaction with metal amide	dehydrogenation temperature (°C)
LiH	720[1]	$LiH + LiNH_2$	150−430 under a vacuum[2] 200−500 in an Ar atmosphere[20]
		$LiH + NaNH_2$	200 (present work)[a]
		$8LiH + 3Mg(NH_2)_2$	140[10]
		$LiH + C^{nano}H$	350[28]
MgH_2	327[1]	$MgH_2 + 2LiNH_2$	100[13]
		$MgH_2 + 2NaNH_2$	160 (present work)
		$MgH_2 + Mg(NH_2)_2$	near room temperature in ball milling[29]
NaH	425[1]	$NaH + NaNH_2$	240 (present work)
		$NaH + LiNH_2$	180−270 (present work)
		$2NaH + Mg(NH_2)_2$	120[17]
CaH_2	600[1]	$CaH_2 + 2LiNH_2$	140[18]
		$CaH_2 + Ca_3N_2$	350[19]
$LiAlH_4$	150−230[20,30]	$LiAlH_4 + LiNH_2$	85−320[20]
		$LiAlH_4 + NaNH_2$	100−350 (present work)
Li_3AlH_6	200[30]	$Li_3AlH_6 + 3LiNH_2$	150−300[21]
		$Li_3AlH_6 + 2LiNH_2$	100−400[22]
$NaAlH_4$	160−220[31]	$NaAlH_4 + LiNH_2$	140−300 (present work)
		$NaAlH_4 + NaNH_2$	130−320 (present work)
$LiNH_2$	350 (present work)	forming NH_3 only when they decompose	
$NaNH_2$	400 (present work)		
$Mg(NH_2)_2$	367[17]		

[a] More details about the dehydrogenation process of various combinations measured by the TGA in the present study are shown Figure 3.

direct molecule−molecule reaction attributable to the strong affinity between $H^{\delta+}$ in $LiNH_2$ and H^- in LiH. On the other hand, Hu[7] et al. and Ichikawa[8,9] et al. showed experimentally that the hydrogen desorption reaction between LiH and $LiNH_2$ is based on the intermediate reaction that involves the formation of ammonia gas, as follows

$$2LiNH_2 \rightarrow Li_2NH + NH_3 \qquad (3)$$

$$LiH + NH_3 \rightarrow LiNH_2 + H_2 \qquad (4)$$

It is noted that the ammonia-mediated reaction model was further demonstrated in a $Mg(NH_2)_2$ and LiH system.[10−12]

Following this groundbreaking work, several new systems were reported as potential candidate materials for high-capacity hydrogen storage applications, including Li−Mg−N−H,[10−16] Na−Mg−N−H,[17] Li−Ca−N−H,[18] Ca−N−H,[19] and Li−Al−N−H[20−22] systems. These systems generally consist of mixtures of simple metal hydrides and metal amides. A generalized reaction equation is as follows

$$\frac{y}{x}M^1H_x + M^2(NH_2)_y \rightarrow \frac{y}{x}M^1(NH)_{x/2} + M^2(NH)_{y/2} + yH_2 \qquad (5)$$

where M^1, M^2 = Li, Na, K, Mg, Ca, etc. For example, when $M^1 = M^2 =$ Li, reaction 5 becomes reaction 1, whereas when M^1 = Mg and M^2 = Li, reaction 5 becomes reaction 6. It was reported that the two imides formed in this reaction may combine and form a new ternary imide phase, $Li_2Mg(NH)_2$.[12]

$$MgH_2 + 2LiNH_2 \rightarrow MgNH + Li_2NH + 2H_2 \qquad (6)$$

The dehydrogenation temperatures of some of these systems and the dissociation temperatures of their corresponding simple metal hydrides are listed in Table 1, showing that the temperatures of hydrogen desorption from these systems are greatly reduced compared to those of the direct dissociation of the corresponding simple metal hydrides. Therefore, it can be said that simple metal hydrides are destabilized by combining with metal amides.

As additional effects of metal amides, it has been found that the kinetics of dehydrogenation of complex metal hydrides can also be enhanced by reacting with metal amides. For example, the authors' own research that was published recently found that the dehydrogenation temperature of lithium alanates, $LiAlH_4$, is reduced and that the rate of dehydrogenation reaction is increased when $LiAlH_4$ is combined with lithium amide, $LiNH_2$.[20] The overall reaction is given as follows

$$LiAlH_4 + LiNH_2 \rightarrow Al + Li_2NH + \frac{5}{2}H_2 \qquad (7)$$

Furthermore, all hydrogen contained in $LiAlH_4$ can be released on the basis of reaction 7, which raises the effective hydrogen storage capacity of $LiAlH_4$.

Reactions 5 and 7 suggest that there are many opportunities for discovering new material systems by combining metal amides with simple or complex metal hydrides. However,

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continued development of these materials and discovery of new materials face challenges because much of the advances made to-date have been achieved through empirical means. There is generally a lack of understanding of fundamental principles governing these reactions. It is not clear if there are rules or guidelines that could be followed, despite the fact that the reaction paths of specific reactions have been proposed for many of these systems.

In this paper, we propose a reaction mechanism that explains the dehydrogenation reactions of destabilized metal hydrides. The proposed reaction mechanisms can be used to predict whether a metal hydride will be destabilized or not when it reacts with another compound, such as metal amide. Additional experimental verifications of the proposed mechanism are also presented.

Experimental Section

The experimental detail is as follows: The starting materials, lithium aluminum hydride ($LiAlH_4$, 95%), lithium amide ($LiNH_2$, 95%), lithium hydride (LiH, 95%), sodium hydride (NaH, 95%), sodium amide ($NaNH_2$, 95%), and magnesium hydride (MgH_2, 98%), were purchased from Aldrich Chemical. Sodium aluminum hydride (sodium alanate $NaAlH_4$, 98%) was supplied by Albemarle Co. All the starting materials were used as received without any further purification. They were stored and handled in an argon-filled glovebox to prevent samples and raw materials from undergoing oxidation and/or hydroxide formation.

All the mixtures in the present paper were mechanically milled in a SPEX 8000 high-energy mill using 50 WC−Co milling balls with a 3 mm diameter under an argon atmosphere for 30 min. After ball milling, the samples were transferred to a glovebox. Sample mixing is described elsewhere in detail.[23]

The thermal gas desorption properties of the mixtures were determined by a thermogravimetric analyzer (TGA; Shimadzu TGA50) by heating to 400 °C at a heating rate of 2 or 5 °C/min. This equipment was placed inside an argon-filled glovebox equipped with a recirculation system to avoid any exposure of the sample to air.

The identification of reactants and reaction products in the mixture before and after thermogravimetric analysis was carried out using a Siemens D5000 model X-ray diffractometer with Ni-filtered Cu Kα radiation ($\lambda = 1.5406$ Å). A scanning rate of 0.02 °/s was applied to record the patterns in the 2θ range of 10−90°. In addition, it is noted that the amorphous-like background in the XRD patterns is attributed to the thin plastic films that were used to cover the powders.

Results and Discussion

I. Negatively Charged Hydrogen (H^-) and Positively Charged Hydrogen ($H^{\delta+}$) Reaction Mechanism. First of all, metal hydrides can be grouped in three basic types on the basis of the nature of their metal−hydrogen bond. The first group consists of ionic or saline hydrides, which are formed by alkali and alkaline earth metals, such as LiH, CaH_2, and NaH. In these compounds, hydrogen exists as a negatively charged ion (H^-) or an electron donor, whereas hydrogen is partially negatively charged ($H^{\delta-}$) in complex ionic hydrides such as $LiAlH_4$ and $NaAlH_4$. The second group is covalent hydrides or the hydrides containing a covalent bond, for example, NH_3, H_2S, and $LiNH_2$. In these hydrides, hydrogen is partially positively charged ($H^{\delta+}$), which can act as an electron acceptor. The third group consists of metallic hydrides, such as TiH_2 and ThH_2, in which hydrogen acts as a metal and forms a metallic bond.[24]

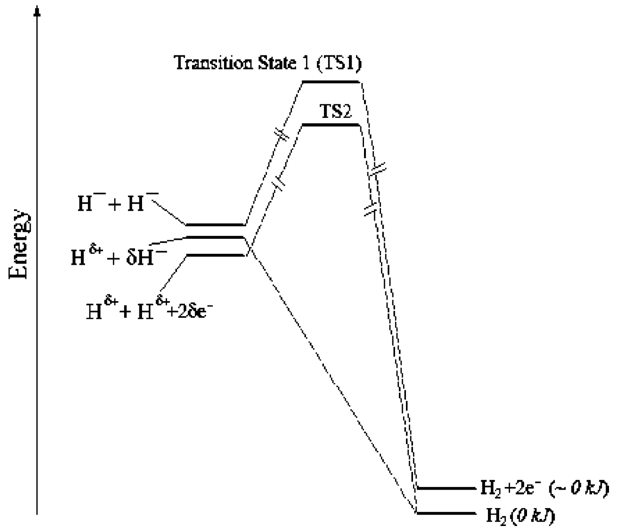

Figure 1. Schematic reaction coordinates for $H^- + H^-$, $H^{\delta+} + H^{\delta+}$, and $H^- + H^{\delta+}$. The curves connecting reactants and products are just to guide the eyes.

Upon examining the common characteristics of the reactions according to reaction 5, it was found that all reactions that demonstrate significantly improved dehydrogenation kinetics involve partially positively charged hydrogen ($H^{\delta+}$) and negatively charged hydrogen (H^-). A hypothesis is thus developed that states that a fundamental factor positively affecting the dehydrogenation of these materials is the following reaction

$$\delta H^- + H^{\delta+} \rightarrow (1 + \delta)H_2 \tag{8}$$

where H^- is a donor and $H^{\delta+}$ is an acceptor of electrons. Reaction 8 can also be generalized as the interaction between Lewis base and Lewis acid. As was pointed out earlier, Chen et al. has proposed to explain the reaction between LiH and $LiNH_2$ on the basis of the strong affinity between positively charged hydrogen ($H^{\delta+}$) and negatively charged hydrogen (H^-).[3,14,25]

Theoretically, the formation of hydrogen (H_2) from the metal hydrides can be achieved by either reaction 8 or the following reactions 9 and 10

$$H^- + H^- \rightarrow H_2 + 2e^- \tag{9}$$

$$H^{\delta+} + H^{\delta+} + 2\delta e^- \rightarrow H_2 \tag{10}$$

Reaction 9 describes the H_2 forming reaction during decomposition of simple metal hydrides such as LiH and MgH_2,

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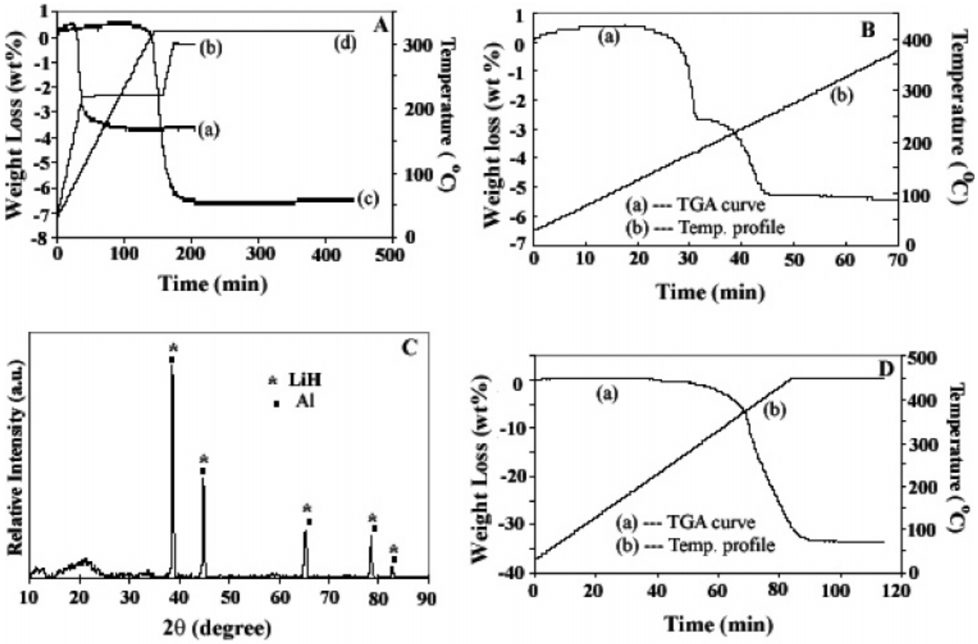

Figure 2. (A) TGA results of pure MgH_2 and $MgH_2/2LiNH_2$. Curves a and c show the hydrogen generation from pure $MgH_2/2LiNH_2$ and MgH_2, respectively. Curves b and d show the corresponding temperature profiles. (B) TGA results of $LiH/LiAlH_4$. (C) XRD pattern of the mixture of $LiH/LiAlH_4$ after being heated to 400 °C. (D) TGA results of pure $LiNH_2$. Curve a shows the ammonia generation from pure $LiNH_2$; curve b shows the corresponding temperature profiles.

and reaction 10 describes the possible H_2 forming reaction of complex metal hydrides that contain only partially positively charged hydrogen ($H^{\delta+}$), such as the decomposition reactions of $LiNH_2$ or NH_3. Reaction 8 describes the H_2 forming reaction of simple metal hydrides when they are combined with covalent hydrides, such as $LiNH_2$, $NaNH_2$, and NH_3. With respect to the formation of H_2 gas, the model stipulates that only when alkali and alkali-earth metal hydrides are reacted with a covalent hydride that contains partially positively charged hydrogen ($H^{\delta+}$) could the simple metal hydride be destabilized. This is because reaction 8 is energetically more favored than either reaction 9 or 10. To illustrate why reaction 8 is favored, we plotted Figure 1 to schematically show the reaction coordinates of these three reactions. It shows that reactions 9 and 10 have very high energy barriers due to the transition states of these reactions. The transition states are the results of the repulsive potential between two positively charged ($H^{\delta+}/H^{\delta+}$) or negatively charged (H^-/H^-) species. This explains why the dehydrogenation of simple metal hydrides needs a very high temperature and the dehydrogenation rate is very slow. On the other hand, reaction 8, which is the deprotonation process, does not have any energy barrier, because there is no repulsive potential between H^- and $H^{\delta+}$. Therefore, from the energy point of view, reaction 8 is much more favorable for the dehydrogenation process than reaction 9 or 10. According to reaction 8, we can deduce that if negatively charged hydrogen (H^-) in a metal hydride is combined with partially positively charged hydrogen ($H^{\delta+}$) in another metal hydride, the dehydrogenation would be favored and the metal hydride thus destabilized.

The favorability or unfavorability of reactions 8−10 can also be understood qualitatively on the basis of the need for electron transfers. Reactions 9 and 10 need accompanying reactions that either release or take up the electrons, whereas for reaction 8, such reactions are not required. Therefore, the thermodynamics and kinetics of reactions 9 and 10 will depend on the likely unfavorability of these accompanying reactions.

It must be pointed out that the feasibility of any reaction is first determined by the change of the free energy, ΔG, which of course must be negative. For the reactions studied in the present work, all the raw materials were in solid state. Thus, the formation of H_2 is entropically favored, which should lead to more favorable ΔG values at a higher temperature. For example, the ΔG of the dehydrogenation reaction of Li_3AlH_6 ($Li_3AlH_6 = 3LiH + Al + 1.5H_2$) is -4.4 kJ/mol H_2 at room temperature, whereas ΔG changes to a more negative value of -40.7 kJ/mol H_2 at 300 °C because of the entropy variation of H_2 at different temperature.

It must be stressed, however, that even when the ΔG of a reaction is negative, the rate of dehydrogenation for many materials systems could still be too slow. The kinetics of dehydrogenation is very important for considering the potential of a system for practical applications. For example, it is well-known that the decomposition of MgH_2, which involves H^-/H^- interaction, can take place between 300 and 400 °C. However, the rate of the dehydrogenation is very slow and the equilibrium pressure of hydrogen within this temperature range is also too low.

It should also be noted that this reaction mechanism described above does not explain the reactions of borohydrides. For example, the reaction of $LiBH_4$ with MgH_2 can be used to release hydrogen.[26] In this system, both hydrogen in $LiBH_4$ and MgH_2 are negatively charged. This is probably because the electron pair in the covalent bonds between boron

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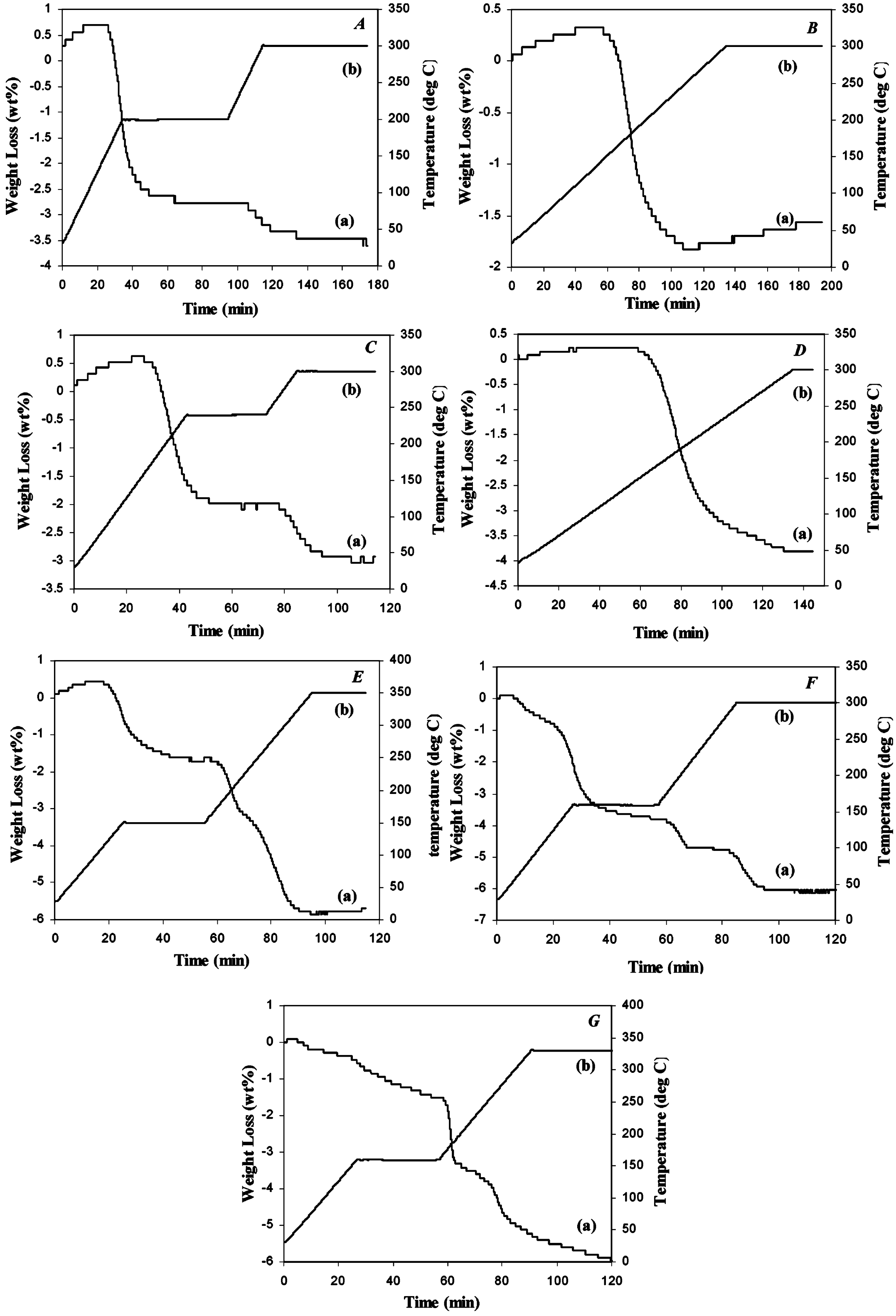

Figure 3. TGA results of the dehydrogenation process of various combinations in the present study. Curves a and b in each figure show the hydrogen generation and the corresponding temperature profiles, respectively. (A) LiH + $NaNH_2$; (B) MgH_2 + $2NaNH_2$; (C) NaH + $NaNH_2$; (D) NaH + $LiNH_2$; (E) $LiAlH_4$ + $NaNH_2$; (F) $NaAlH_4$ + $LiNH_2$; and (G) $NaAlH_4$ + $NaNH_2$.

and hydrogen are closer to boron rather than hydrogen, which makes the hydrogen lean toward the positively charged state.

The understanding of the reaction mechanism on the basis of the interaction between $H^{\delta+}$ and H^- can be used to analyze many known reactions as well as provide a guidance with respect to kinetics of the reaction for screening and discovery of potential new hydrogen storage materials.

II. Analysis of Known Reactions Using the Current Reaction Mechanism. The first group of reactions that obey the proposed model is described by reaction 5, in which a simple metal hydride that contains a negatively charged hydrogen (H^-) is reacted with a metal amide that contains a partially positively charged hydrogen ($H^{\delta+}$).[2−19,] As an example, Figure 2A shows the TGA curves for pure MgH_2 and MgH_2/$LiNH_2$. It clearly shows that the dehydrogenation temperature of MgH_2 decreases significantly when it is combined with $LiNH_2$. Table 1 compares the decomposition temperatures of MgH_2 and other similar metal hydrides via decomposition or via reactions with metal amide. References for these data are given where applicable. As we can see, all the results in Table 1 are consistent with the proposed reaction mechanism.

The second group involves the destabilization of complex metal hydrides by reaction with metal amides. For example, our previous work[20] on a $LiAlH_4$/$LiNH_2$ system showed that the dehydrogenation temperature of $LiAlH_4$ is reduced and the rate of dehydrogenation reaction is increased when $LiAlH_4$ is combined with $LiNH_2$. The dehydrogenation reactions of $LiAlH_4$ involve several reaction steps including the formation of Li_3AlH_6 during the first step and that of LiH during the second step. The overall improvement of the dehydrogenation kinetics of $LiAlH_4$ can at least be partially attributed to the destabilization of LiH by its reaction with $LiNH_2$. Although the reason the temperature for the first decomposition step of $LiAlH_4$ is also reduced when it is combined with $LiNH_2$ is still debatable, it is probably also attributable to the interaction between the positively charged hydrogen ($H^{\delta+}$), partially negatively charged hydrogen ($H^{\delta-}$) reaction, which is energetically favored.

III. Experimental Verifications. To further verify the effect of the interaction between $H^{\delta+}$ and H^- during dehydrogenation reactions, reactions of several metal hydrides, including NaH, LiH, MgH_2, $NaAlH_4$, and $LiAlH_4$, with metal amides that are not available in the literature were tested in this study. The results are also listed in Table 1 and Figure 3. The results once again demonstrate that the dehydrogenation temperature can be reduced dramatically when metal hydrides containing a negatively charged hydrogen (H^-) are combined with metal amides containing a positively charged hydrogen ($H^{\delta+}$).

One of the concerns for using TGA to analyze amide-containing material systems is the possibility of the coproduction of ammonia gas during the dehydrogenation process. We believe that the effect of NH_3 is minimum for the material systems that were included in this study for the following reasons. First, the weight-loss percentages of the gas that were recorded by TGA match with the stoichiometry balance of the equation for hydrogen. Therefore, the effect of the weight loss due to NH_3, if any, is negligible. Second, the equilibrium pressure of NH_3, for example, are 0.3 and 1.9 psi at 300 and 400 °C, respectively, during the decomposition of $LiNH_2$ to Li_2NH and NH_3,[27] which implies that even a very small amount of NH_3 could suppress the further decomposition of $LiNH_2$. Recently, Ichikawa[8] et al. quantitatively studied the NH_3 partial pressure of $LiNH_2$−LiH system in a closed system. They found that only 0.1 psi (0.1%) of NH_3 was detected by Raman spectroscopy. Thus, the NH_3 content was at a trace level. Because the reaction between NH_3 and metal hydrides, such as LiH, has proven to be ultrafast,[7] the trace NH_3 gas is likely to be captured by metal hydrides, which produces H_2.

In contrast, the model prediction of the H_2 forming reaction when a metal hydride containing a negatively charged hydrogen (H^-) is reacted with another metal hydride containing a negatively charged hydrogen (H^-) was tested as follows: LiH was mixed with $LiAlH_4$, which, unlike $LiNH_2$, also contains partially negatively charged hydrogen ($H^{\delta-}$) and heated. Hydrogen evolution occurred between 170 and 200 °C, in agreement with the decomposition temperature range of $LiAlH_4 \rightarrow Li_3AlH_6 \rightarrow LiH$. On further heating to higher temperatures, there was no indication of the decomposition of LiH (Figure 2B), which proves that the H_2 forming reaction is unfavorable when a protide-containing compound LiH is combined with another negatively charged hydrogen compound ($LiAlH_4$). Figure 2C shows the XRD pattern of the mixture of LiH/$LiAlH_4$ after being heated to 400 °C, from which it is clearly seen that the final products are LiH and Al.

The dehydrogenation process is also unfavorable when the system contains only positively charged hydrogen ($H^{\delta+}$). To demonstrate this, Figure 2D shows the TGA result of pure $LiNH_2$. It shows that only NH_3 rather than H_2 gas was detected at temperatures above 240 °C and that the majority of weight loss is around 370 °C. This is because the formation of H_2 gas must rely on reaction 10 when $LiNH_2$ is heated, which will be very difficult on the basis of the present model. Similarly, one can understand that the formation of H_2 by dissociation of ammonia NH_3 is also very difficult. It requires catalysts and significant external energy input.

Conclusion

In conclusion, the proposed reaction mechanism between positively charged hydrogen ($H^{\delta+}$) and negatively charged hydrogen (H^-) provides a reasonable explanation for the destabilization mechanism of metal hydrides. It can therefore be applied as a theoretical guidance for the screening and discovery of potential new hydrogen storage materials.

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