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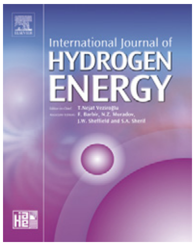

Comparisons between MgH_2- and LiH-containing systems for hydrogen storage applications

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ABSTRACT

The present study compares the dehydrogenation kinetics of ($2LiNH_2 + MgH_2$) and ($LiNH_2 +$ LiH) systems and their vulnerabilities to the NH_3 emission problem. The ($2LiNH_2 + MgH_2$) and ($LiNH_2 + LiH$) mixtures with different degrees of mechanical activation are investigated in order to evaluate the effect of mechanical activation on the dehydrogenation kinetics and NH_3 emission rate. The activation energy for dehydrogenation, the phase changes at different stages of dehydrogenation, and the level of NH_3 emission during the dehydrogenation process are studied. It is found that the ($2LiNH_2 + MgH_2$) mixture has a higher rate for hydrogen release, slower rate for approaching a certain percentage of its equilibrium pressure, higher activation energy, and more NH_3 emission than the ($LiNH_2 +$ LiH) mixture. On the basis of the phenomena observed, the reaction mechanism for the dehydrogenation of the ($2LiNH_2 + MgH_2$) system has been proposed for the first time. Approaches for further improving the hydrogen storage behavior of the ($2LiNH_2 + MgH_2$) system are discussed in light of the newly proposed reaction mechanism.

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1. Introduction

In searching for renewable energy sources and cleaner emissions for automobiles, hydrogen systems have attracted tremendous interests over the recent years. Among these systems, hydrogen storage materials, especially light metal hydrides, amides, and imides have been investigated extensively because light metal hydrides, amides, and imides have the potential of being reversible for hydrogen refueling as well as being compact due to the presence of light elements. Following the first report by Chen et al. [1] in 2002, studies on hydrogen sorption and desorption behavior and mechanisms of the lithium amide ($LiNH_2$) and lithium hydride (LiH) mixture have been very intensive [2–15]. It is generally agreed that the dehydriding reaction of this system can be expressed as [1]

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

This reaction can theoretically absorb and desorb 6.5 wt% hydrogen with a reaction enthalpy of 66 kJ/mol H_2. It has been proposed that reaction (1) proceeds with two elementary reactions [4,5]. First, $LiNH_2$ decomposes by releasing ammonia (NH_3), as shown in

$$LiNH_2 = \tfrac{1}{2}Li_2NH + \tfrac{1}{2}NH_3. \qquad (2)$$

Then, LiH reacts with NH_3 to form $LiNH_2$ again and liberate H_2, as shown in

$$\tfrac{1}{2}NH_3 + \tfrac{1}{2}LiH \rightarrow \tfrac{1}{2}LiNH_2 + \tfrac{1}{2}H_2. \qquad (3)$$

For a mixture of $LiNH_2 + LiH$ (with a molar ratio of 1:1), the reaction would continue to repeat the cycle of reactions (2) and (3) until all $LiNH_2$ and LiH transform to lithium imide (Li_2NH) and H_2 completely. It has been shown that reaction (3) is ultrafast and can take place in the order of microseconds [4], whereas reaction (2) is slow and proceeds in minutes [16].

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In spite of the high storage capacity, the lithium imide/amide/hydride system currently requires relatively high operating temperatures (~280 °C) to obtain 1 atm of hydrogen sorption and desorption pressure [1–15]. In order to increase the equilibrium pressure and lower the sorption and desorption temperatures, many studies have focused on destabilization of lithium amide through partial substitution of lithium by magnesium [7,8,12,17–25]. Promising results have been obtained from this approach. For example, the ($2LiNH_2 + MgH_2$) system has been demonstrated to absorb and desorb 5.2 wt% of hydrogen with a hydrogen pressure of 30 atm at 200 °C [18,19], showing superior hydrogen storage properties in comparison to the lithium imide/amide/hydride system. The suggested dehydriding reaction for this Li–Mg–N–H system is [17,22]

$$2LiNH_2 + MgH_2 \rightarrow Li_2Mg(NH)_2 + 2H_2. \quad (4)$$

The hydriding process of reaction (4), however, produces magnesium amide ($Mg(NH_2)_2$) and LiH, as shown in

$$Li_2Mg(NH)_2 + 2H_2 = Mg(NH_2)_2 + 2LiH \quad (5)$$

and the subsequent reversible reactions appear to take place according to reaction (5) rather than reaction (4) [17–19,21,22], suggesting that ($Mg(NH_2)_2 + 2LiH$) is either thermodynamically or kinetically more favorable than ($2LiNH_2 + MgH_2$). Recent work by Luo and Sickafoose [19], however, unequivocally indicates that ($2LiNH_2 + MgH_2$) is thermodynamically less stable than ($Mg(NH_2)_2 + 2LiH$) because the former changes to the latter gradually during holding at 220 °C.

Other efforts in searching for viable hydrogen storage materials based on the Li–Mg–N–H system focus on compositions different from ($2LiNH_2 + MgH_2$) and ($Mg(NH_2)_2 + 2LiH$). These studies include the mixtures of ($2LiNH_2 + CaH_2$) [22], ($3Mg(NH_2)_2 + 8LiH$) [12,26,27], ($Mg(NH_2)_2 + 4LiH$) [20,28–31], ($Mg(NH_2)_2 + 3LiH$ or LiH) [24], ($Mg(NH_2)_2 + MgH_2$) [29,32,33], and ($Mg(NH_2)_2 + 2MgH_2$) [29]. However, all of these Li–Mg–N–H systems either exhibit higher hydrogen sorption and desorption temperatures or possess lower hydrogen storage capacities than ($Mg(NH_2)_2 + 2LiH$) and ($2LiNH_2 + MgH_2$) systems. In spite of many favorable properties of ($Mg(NH_2)_2 + 2LiH$) and ($2LiNH_2 + MgH_2$) systems, systematic comparisons in the reaction kinetics between ($2LiNH_2 + MgH_2$) and ($LiNH_2 + LiH$) systems have not been conducted yet. The potential problem of NH_3 emission from the ($Mg(NH_2)_2 + 2LiH$) and ($2LiNH_2 + MgH_2$) systems has not received due investigation either. Furthermore, the reaction mechanism for the dehydrogenation of the ($2LiNH_2 + MgH_2$) system has not been identified yet.

The present study compares the dehydrogenation kinetics of ($2LiNH_2 + MgH_2$) and ($LiNH_2 + LiH$) systems and their vulnerabilities to the NH_3 emission problem. The ($2LiNH_2 + MgH_2$) and ($LiNH_2 + LiH$) mixtures with different degrees of mechanical activation obtained via high-energy ball milling are investigated in order to evaluate the effect of mechanical activation on the dehydrogenation kinetics and NH_3 emission rate. A wide range of analytical instruments have been utilized to characterize the activation energy for dehydrogenation, the phase changes at different stages of dehydrogenation, and the level of NH_3 emission during the dehydrogenation process. Based on the phenomena observed, the reaction mechanism for the dehydrogenation of the ($2LiNH_2 + MgH_2$) system has been proposed for the first time. Approaches for further improving the hydrogen storage behavior of the ($2LiNH_2 + MgH_2$) system are discussed in the light of the newly proposed reaction mechanism.

2. Experimental

$LiNH_2$ with 95% purity and LiH with 99.4% purity were purchased from Fisher Scientific and Alfa Aesar, respectively. MgH_2 with 95% purity was kindly provided by Sandia National Lab. Mixture of $LiNH_2$–LiH and $LiNH_2$–MgH_2 samples were prepared with a molar ratio of 1 to 1.1 and 2 to 1.1 according to reactions (1) and (4), respectively. A 10% excess of LiH and MgH_2 was added to minimize the loss of NH_3 during the dehydriding process. High-energy ball milling was conducted using a modified Szegvari attritor that has been shown to be effective in preventing the formation of the dead zone and producing uniform milling products within the powder charge [34]. Furthermore, a previous study has demonstrated that the seal of the canister of the attritor is air-tight and there is no oxidation during ball milling [35]. The canister of the attritor and balls 6.4 mm in diameter were both made of stainless steel. The loading of balls and the powder mixtures to the canister was performed in a glove-box filled with ultrahigh-purity argon that contains Ar 99.999%, $H_2O < 1$ ppm, $O_2 < 1$ ppm, $H_2 < 3$ ppm, $N_2 < 5$ ppm, and THC < 0.5 ppm (to be referred as an Ar of 99.999% purity hereafter). The ball-to-powder weight ratio was 60:1, the milling speed was 600 rpm, and the milling temperature was maintained at 20 °C, achieved by water cooling at a flowing rate of 770 ml/min. The milling was performed under an Ar atmosphere of 99.999% purity, and the milling time varied from 45 to 180 min, depending on the requirements.

All the samples before and after high-energy ball milling were subjected to various characterizations and handled in a glove-box filled with Ar of 99.999% purity. The thermogravimetric analysis (TGA) was conducted using a TA instrument (TGA Q500). The mixture samples of 20–30 mg were loaded into a Pt-microbalance pan with a short exposure to air (less than 30 s). The system was then flushed immediately with Ar of 99.999% purity for 90 min before heating from 20 to 500 or 550 °C with a heating rate of 5 °C/min. The flow rate of argon was maintained at 60 ml/min in the entire holding and heating processes. The outlet gas from TGA was constantly monitored using a quadrupole residual gas analyzer (GRA) equipped with a mass spectrometer (Model ppt-c300-F2Y). The gases monitored included H_2, NH_3, N_2, O_2, and H_2O. The RGA unit was calibrated using two gas mixtures calibrations, with one containing 21.71 vol% H_2 and 78.29 vol% Ar and the other 301 ppm N_2, 1210 ppm O_2, 1990 ppm NH_3, and Ar balance.

The desorption pressure and kinetics at 210 °C were determined using a commercial Sieverts'-type pressure–composition-isotherm (PCI) unit (Advanced Materials Corporation, PA). The sample mixture of approximately 500 mg was loaded into the pressure cell in a glove-box filled with Ar of 99.999% purity. The loaded pressure cell was evacuated to 10^{-3} bar at room temperature before being inserted into the

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