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Hydrogen storage properties of Na–Li–Mg–Al–H complex hydrides

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Abstract

Lightweight complex hydrides have attracted attention for their high storage hydrogen capacity. $NaAlH_4$ has been widely studied as a hydrogen storage material for its favorable reversible operating temperature and pressure range for automotive fuel cell applications. The increased understanding of $NaAlH_4$ has led to an expanded search for high capacity materials in mixed alkali and akali/alkaline earth alanates. In this study, promising candidates in the Na–Li–Mg–Al–H system were evaluated using a combination of experimental chemistry, atomic modeling, and thermodynamic modeling. New materials were synthesized using solid state and solution based processing methods. Their hydrogen storage properties were measured experimentally, and the test results were compared with theoretical modeling assessments.

Keywords: Metal hydrides; Chemical synthesis; Solid state reactions; X-ray diffraction

1. Introduction

Automotive hydrogen fuel cells require hydrogen storage materials with high volumetric and gravimetric capacity. The discovery of the reversible Ti-doped sodium aluminum hydride, $NaAlH_4$, system by Bogdanovic [1] inspired extensive investigations of this light metal complex hydride for hydrogen storage applications [2–3]. Although $NaAlH_4$ has a 5.5 wt% theoretical hydrogen storage capacity with reasonable desorption kinetics at intermediate temperatures, it cannot meet the capacity requirements for on-board hydrogen storage. A new material with higher capacity and more rapid desorption kinetics is needed. Mixed alkali and alkaline earth alanates have theoretical hydrogen contents as high as 10.4 wt%. These compounds have the potential to achieve the required reversible storage capacity. In this paper, our results within the Na–Li–Mg–Al–H system are reported.

2. Experimental

The starting materials, NaH (95%, with NaOH and $NaNO_3$ as the major impurities by X-ray diffraction (XRD)), LiH (95%, with Li_2O as the major impurity), MgH_2 (90%, with Mg and MgO as major impurities), $MgCl_2$ (99.9%) and $LiAlH_4$ (95%, with Al and Li_3AlH_6 as the major impurities), were purchased from the Aldrich Co. AlH_3 was obtained using a proprietary method. Detailed characterization of this aluminum hydride will be described in a future publication [4]. The XRD pattern of this material shows solely α-AlH_3, with no detectable impurities. Purified $NaAlH_4$ (98.7% by ICP analysis), was obtained from Albemarle Co. All solid materials were used in the as-received condition without further purification. Anhydrous toluene and diethyl ether were purchased from Aldrich and dried over aluminum and Na/K, respectively. The chemicals were stored, measured, and transferred under high purity N_2 inside a glove box with oxygen content less than 25 ppm. High pressure hydrogen gas (240 bar, 99.95% purity), was used for hydriding reactions.

The Na–Li–Mg–Al–H system materials were prepared by mixing a 1:1:1:1 mole ratio of NaH, LiH, MgH_2, and AlH_3 in a mortar and pestle for 15 min. Approximately 10 g of the mixture were ball milled in a high energy SPEX mill in N_2 for 3 h. Immediately after ball milling, approximately 1 g samples were hydrided under 190–195 bar hydrogen for 20 h each at 60, 80, 100, and 120 °C, respectively, in a modified Sievert's apparatus (Advanced Materials Co.). The Li–Mg–Al–H complex materials were prepared by a similar method using LiH, MgH_2, and AlH_3 at a 1:1:1 mole ratio. $LiMg(AlH_4)_3$ was prepared by the solution method developed by Bulychev, et al. [5], using 30–50% of the solvent volume used in the original method. Approximately 0.6 g of sample was tested

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in a modified Sievert's apparatus for desorption under ca. 1 bar and absorption under ca. 190 bar of hydrogen pressure.

XRD analyses were performed on a Rigaku D/Max-b diffractometer, Model RU-200B, equipped with a rotating Cu anode, or a Scintag X1 Advanced Diffraction System equipped with a Cu anode housed in a glove box. Samples for the Rigaku were mounted on a glass sample holder and covered with a layer of DuraSeal^{TM}, sealed with a ring of silicone grease in a glove box. DSC measurements were conducted on TA Instruments 2910 or 2920. The sample pans were made of gold plated stainless steel, and the sample-heating rate was 10 °C/min.

The ground state atomic structures of known and hypothetical phases in the Na–Li–Mg–Al–H system were predicted with the density functional theory Vienna *Ab-initio* Simulation Package (VASP) code [6–7] using projector augmented wave potentials [8] with generalized gradient PW91 exchange-correlation corrections [9]. The thermodynamic properties of the most stable phase structures were predicted with direct method lattice dynamics using the Materials Design MedeA Phonon module [10–11].

3. Results and discussion

3.1. Na–Li–Mg–Al–H

The syntheses of mixed alkali and alkaline earth salts of aluminum hydride from simple hydrides were attempted by the solid synthesis method described in the experimental section. XRD examination of the hand mixed sample of NaH, LiH, MgH_2, and AlH_3 at 1:1:1:1 molar ratio did not show evidence of chemical reactions, although the LiH signal was absent in mixture. It is suspected that the LiH signal, which should not be masked by any of the other constituents, is absorbed by one or more of the other compounds present. After SPEX milling, several reaction products were detected by XRD, including $NaAlH_4$, Na_2LiAlH_6, $NaMgH_3$, and Al (Fig. 1). This observation suggests that the following reactions occurred during milling process:

$$2AlH_3 \rightarrow 2Al + 3H_2 \quad (1)$$

$$NaH + AlH_3 \rightarrow NaAlH_4 \quad (2)$$

$$2NaH + LiH + AlH_3 \rightarrow Na_2LiAlH_6 \quad (3)$$

$$NaH + MgH_2 \rightarrow NaMgH_3 \quad (4)$$

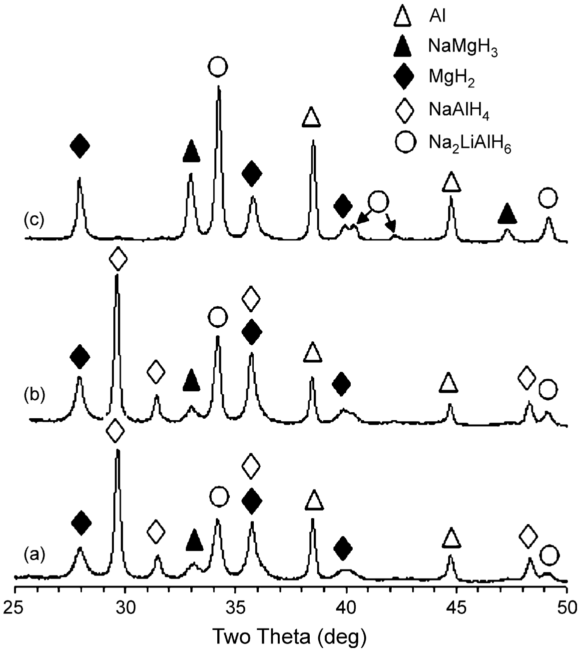

Fig. 1. XRD of the reaction mixture of LiH, NaH, MgH_2, and AlH_3 at 1:1:1:1 molar ratio: (a) SPEX milled for 3 h, (b) 80 °C hydriding at 195 bar hydrogen pressure for 20 h, and (c) 120 °C hydriding at 195 bar hydrogen pressure for 20 h.

Upon heat-treatment under 195 bar of hydrogen, the sample composition remained unchanged below 100 °C. At temperatures greater than 100 °C, the signal of $NaAlH_4$ decreased substantially. Signals from the Na_2LiAlH_6, $NaMgH_3$, and Al phases increased, indicating that Eqs. (5) and (6) may occur at this temperature.

$$2NaAlH_4 + LiH \rightarrow Na_2LiAlH_6 + Al + 3/2H_2 \quad (5)$$

$$NaAlH_4 + MgH_2 \rightarrow NaMgH_3 + Al + 3/2H_2 \quad (6)$$

In this system, NaH appears to be the most reactive among alkali and alkaline earth hydrides. It can form binary complex hydrides with AlH_3 and MgH_2, respectively, and ternary complex with LiH plus AlH_3. Among the complex hydrides formed, Na_2LiAlH_6 and $NaMgH_3$ are most stable. The existence of Na_2LiAlH_6 and $NaMgH_3$ [1,12–13] has been reported in the literature. No $LiAlH_4$, Li_3AlH_6, Na_3AlH_6 or mixed Li–Mg–Al hydride phases were observed, indicating they are less stable than the Na_2LiAlH_6 and $NaMgH_3$ under this reaction environment. It could also be due to the fact that their formation is kinetically impeded.

In order to further understand thermodynamic stability without the interference of the kinetic factors, first principles thermodynamic property predictions were utilized to generate data for equilibrium thermochemical calculations. Below 87 °C, the LiH destabilization of $NaAlH_4$ to form the Na_2LiAlH_6 intermediate phase (Eq. (5)), with the release of only 2.6 wt% H_2, is predicted to predominate. At higher temperatures, the $NaAlH_4$ decomposition to the intermediate phase, Na_3AlH_6, with the release of 3.7 wt% H_2 is predicted to predominate, even in the presence of LiH. In contrast, the MgH_2 destabilization of $NaAlH_4$ to form $NaMgH_3$ (Eq. (6)), is predicted to predominate above 52 °C, leading to the release of 4.8 wt% H_2. These predictions confirm the above experimental observations that Na_2LiAlH_6 and $NaMgH_3$ are the predominant phases at higher temperature.

3.2. Li–Mg–Al–H

The initial attempted synthesis of Li–Mg–Al–H compounds focused on solid state methods. A reaction mixture containing LiH, MgH_2, and AlH_3 (1:1:1) was hand mixed and SPEX milled for 3 h. The SPEX milling resulted in the formation of $LiAlH_4$. Upon heat-treatment to 60 °C under 190–195 bar hydrogen, $LiAlH_4$ dissociated to Al and Li_3AlH_6. Further heating above 100 °C in hydrogen dissociated the Li_3AlH_6 to LiH and Al. The MgH_2 did not react. No mixed Li–Mg–Al hydride phase formed using the solid-state method with simple hydride precursors.

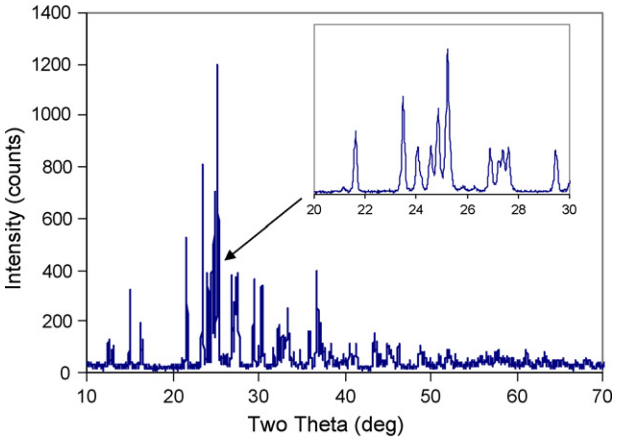

Fig. 2. XRD of $LiMg(AlH_4)_3$ synthesized by a solution based chemical synthesis method.

3.3. $LiMg(AlH_4)_3$

It has been reported by Bulychev, et al. [5] that $LiMg(AlH_4)_3$ can be synthesized from $MgCl_2$, $LiAlH_4$, and $NaAlH_4$ in ether. Recent work by Mamatha, et al. [14] have shown the formation of $LiMg(AlH_4)_3$ by ball milling of $LiAlH_4$ and $MgCl_2$. This compound has a theoretical hydrogen capacity of 7.8–8.2 wt%, depending on the decomposition products formed. In this study, $LiMg(AlH_4)_3$ was prepared using the solution method based on the procedures provided in Ref. [5]. XRD analysis (Fig. 2) shows that the synthesized compound is reasonably pure based on the XRD data reported in ICDD PDF #00-034-0926 with a small amount of LiCl present as impurity. Preliminary indexing of the XRD data yielded a monoclinic structure with the preliminary lattice parameters of: $a = 8.40$, $b = 8.83$, $c = 14.59$ (in Å). Numerous VASP–minimized $LiMg(AlH_4)_3$ candidate models were very similar in energy, but the most favorable had monoclinic symmetries. The refinement of this compound structure has been conducted in collaboration with the Institute for Energy in Norway [15]. Elemental analysis by ICP determined the compound composition to be: Li, 5.5 wt%; Mg, 19.1 wt%, and Al, 63.9 wt% (theoretical: Li, 5.6 wt%; Mg, 19.6 wt%, and Al, 65.1 wt%).

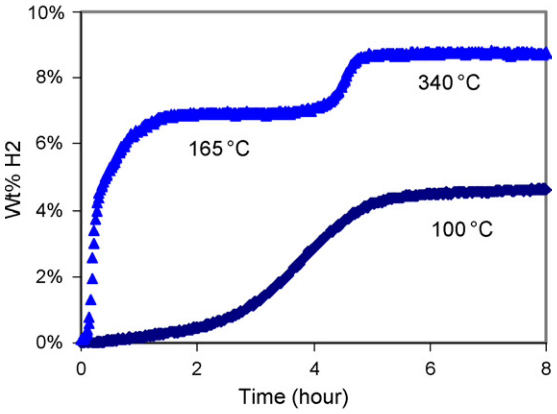

Fig. 3. Hydrogen desorption of $LiMg(AlH_4)_3$ at 100, 165, and 340 °C, respectively.

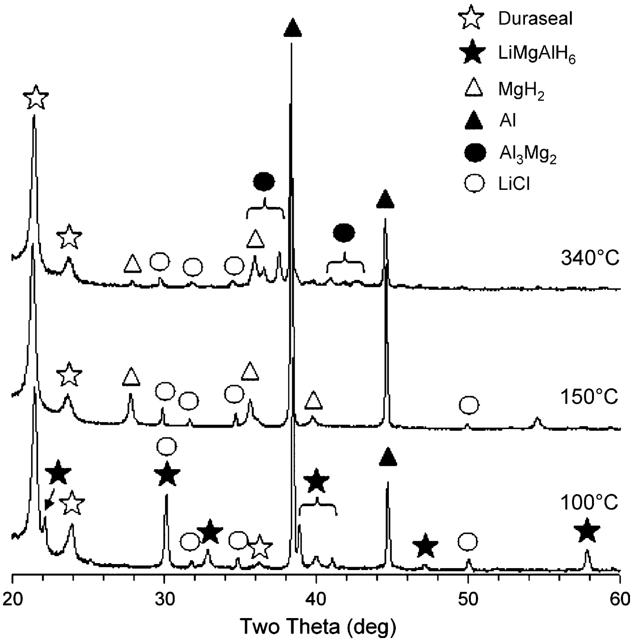

Fig. 4. XRD of decomposition products of $LiMg(AlH_4)_3$ at 100, 150, and 340 °C, respectively.

The as-synthesized compound was tested for isothermal hydrogen desorption at 100 and 165 °C (Fig. 3). At 100 °C, 4.0 wt% H_2 was released at a slow rate. The desorption rate increased significantly at 165 °C, with 6.9–7.0 wt% H_2 released. An additional 1.8 wt% H_2 was released at 340 °C, yielding a total capacity of 8.7–8.8 wt% H_2.

The XRD characterization of the dehydrogenated $LiMg(AlH_4)_3$ indicated that the phase composition varied with desorption temperature (Fig. 4) and desorption time. After 5 h of desorption at 100 °C, XRD showed the presence of Al and an unknown compound, proposed to be an intermediate $LiMgAlH_6$ phase based on the H_2 wt% released (Eq. (7)). This hypothesis was corroborated by the identification of a VASP-minimized $LiMgAlH_6$ trigonal P321 candidate structure [16] whose simulated powder pattern very closely matched the unknown XRD peaks [17]. Desorption at 150 °C for 24 h resulted in the formation of MgH_2 and additional Al (Eq. (8)). Note that a small amount of LiH cannot be determined by XRD in the presence of Al. Increasing the temperature to 340 °C caused the appearance of Al_3Mg_2 via Eq. (9).

$$100\,^{\circ}\mathrm{C}: LiMg(AlH_4)_3 \rightarrow LiMgAlH_6 + 2Al + 3H_2 \tag{7}$$

$$150\,^{\circ}\mathrm{C}: LiMgAlH_6 \rightarrow LiH + MgH_2 + Al + 3/2H_2 \tag{8}$$

$$340\,^{\circ}\mathrm{C}: 2MgH_2 + 3Al \rightarrow Al_3Mg_2 + 2H_2 \tag{9}$$

Thermal analyses and first principle thermodynamic predictions confirmed the likelihood of these reactions. When $LiMg(AlH_4)_3$ was heated at 10 °C/min in a DSC, an exothermic reaction began at 140 °C with a latent heat of −5.5 kJ/mol-H_2 (Eq. (7)), immediately followed by an endothermic reaction with a latent heat of 13.1 kJ/mol-H_2 (Eq. (8)). Results from the first principle thermodynamic modeling confirm their exothermic (Eq. (7)), and endothermic (Eq. (8)), nature. The heat of reaction for Eq. (8) agrees with the value reported by Mamatha [14].

The reverse hydrogen absorption of Eq. (8) was experimentally tested using both undoped and 2% $TiCl_3$ doped $LiMg(AlH_4)_3$. The doping was achieved by 15 min of SPEX milling. After discharging at 150 °C for more than 5 h, the samples were charged under 190 bar of hydrogen at 80 and 100 °C for a total of 24 h. No absorption was observed. The material is not rechargeable under these conditions.

4. Conclusion

In this study, complex hydrides of the Na–Li–Mg–Al–H system were synthesized by a solid-state method. Under the testing conditions, $NaAlH_4$ and Na_2LiAlH_6 are the most stable compounds at temperatures below 100 °C, and $NaMgH_3$ and Na_2LiAlH_6 are the most stable compounds at 120 °C.

Reasonably pure $LiMg(AlH_4)_3$ was synthesized by a solution based method. Below 150 °C, this compound thermally dissociated in two steps (Eqs. (7) and (8)), via $LiMgAlH_6$ as an intermediate, releasing ca. 6.9–7.0 wt% hydrogen. Both undoped and 2% $TiCl_3$ doped $LiMg(AlH_4)_3$ were not rechargeable at 80–100 °C under 190 bar hydrogen pressure after being discharged at 150 °C.

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