

# RE-oxide doped alkaline hydrogen storage materials prepared by mechanical activation

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In the hydrogen energy system, hydrogen storage materials are considered to play an important role, such as H<sub>2</sub> storage and transportation media. In case of fuel-cell powered vehicles, storage material with large capacity and light weight are required.

Alanates e.g., NaAlH<sub>4</sub>, Na<sub>3</sub>AlH<sub>6</sub> or Na<sub>2</sub>LiAlH<sub>6</sub> have many advantages as hydrogen storage materials, because of their large hydrogen capacity, abundant in the earth crust and lower costs, etc. Alanates are, therefore, promising candidates for practical hydrogen transportation media, while investigations on their reaction kinetics with hydrogen are still insufficient.

In this study, we prepared Na<sub>2</sub>LiAlH<sub>6</sub> samples with different kinds of RE-oxides doped in the course of ball-milling. RE-oxides were used for improving hydrogen reactivity. Drastically improved hydrogen absorption kinetics obtained were discussed using thermodynamic consideration. © 2004 Kluwer Academic Publishers

## 1. Introduction

In the hydrogen energy system, hydrogen storage materials are considered to play an important role. Alkaline aluminum complex hydrides e.g., NaAlH<sub>4</sub>, Na<sub>3</sub>AlH<sub>6</sub> or Na<sub>2</sub>LiAlH<sub>6</sub> are promising candidates for hydrogen storage because of their higher hydrogen capacity. In previous studies [1], the samples have been prepared by the reactions with the use of solvents. Their reversible hydrogen reactivity is only obtained by doping small amount of Ti [1] or Zr [2] as a catalyst. On the other hand, (Na-Li)<sub>3</sub>AlH<sub>6</sub> can also be prepared by Mechanical Alloying (MA) [3]. In this case, the products obtained by MA exhibit reversible hydrogen reactivity without any additives.

Recently we have investigated the reaction kinetics of Na-Li-Al-H based hydrogen storage material prepared by ball-milling and confirmed its reversible sorption reaction. Additionally, we have found drastically improved reaction kinetics with enhanced sorption kinetics for the sample with the addition of La<sub>2</sub>O<sub>3</sub> powder [4]. The effect of the La<sub>2</sub>O<sub>3</sub> addition on the enhanced hydrogen sorption kinetics of these materials is attributed to the following factors; (1) La<sub>2</sub>O<sub>3</sub> surface has relatively higher reactivity for dissociation of H<sub>2</sub> molecules [5, 6], and (2) La<sub>2</sub>O<sub>3</sub> is more stable than any other oxides of Na, Li and Al, providing diffusion paths for dissociation of H<sub>2</sub> on atomic H in the bulk of powder particle.

In the present study, we prepared Na<sub>2</sub>LiAlH<sub>6</sub> samples doped with different kinds of RE-oxide powders. The aim of this work is to investigate the effect of the mechanical addition of La<sub>2</sub>O<sub>3</sub> and CeO<sub>2</sub> on improving hydrogen reactivity of the materials.

## 2. Experimental

The mixture (1.5 g) of NaH, LiAlH<sub>4</sub> and RE-oxides powders, mixed in 2:1:0.1 molar ratio, was mechanically milled in a rotary mill (Irie Syokai Co. Ltd.). NaH, LiAlH<sub>4</sub> and RE-oxides powders were obtained from Wako Pure Chemical Co. Ltd. and from High Purity Chemicals Co. Ltd., respectively. NaH was washed by hexane dehydrated with filtration (Wako Pure Chemical Co. Ltd., 96%) to clear off the preservation mineral oil [4]. The conditions of the ball-milling process are shown in Table I.

The X-ray powder diffraction analysis of the milled mixtures was carried out using a Rigaku Miniflex with Co-K<sub>α</sub> radiation. For X-ray analysis, the powder sample was glued to a glass plate within a small amount of high vacuum grease. The micro structural observation was carried out using SEM (Hitachi S-3200N) and EDS (Horiba EMAX5771W). Reactivity of the materials with the ultra high purity hydrogen (H<sub>2</sub>, 99.99999%) was measured using a high pressure Sieverts' type apparatus with ultimate vacuum pressure of

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TABLE I Ball milling conditions

Mill type	Rotary mill
Material of vial/balls	SUS316
Outer diameter of vial	6.00 cm
Capacity of vial	70.33 cm <sup>3</sup>
Diameter and number of balls	0.95 cm, 35 pieces
Total weight of the sample to be milled	1.5 g
Ball-to-sample mass ratio	70:1
Dispersion medium	Hexane dehydrated (<0.3 ppm H <sub>2</sub> O)
Milling atmosphere	Ar (99.999%)
Rotating velocity	180 rpm
Milling time	50 h

$2.0 \times 10^{-4}$  Pa. Hydrogen pressure used was ranged from 3.0 to 6.0 MPa.

Because Na<sub>2</sub>LiAlH<sub>6</sub> was very sensitive to air oxidation and humidity, all steps of the sample preparation and transfer into the reactor vessel were carried out under a high purified Ar (99.999%) atmosphere.

### 3. Results and discussion

#### 3.1. Mechanical alloying of Na<sub>2</sub>LiAlH<sub>6</sub>

Fig. 1 shows SEM images of the NaH + LiAlH<sub>4</sub> + La<sub>2</sub>O<sub>3</sub> mixture after the ball-milling of 50 h. White

color pieces indicate La<sub>2</sub>O<sub>3</sub> both in secondary electron (SE) and back scattering electron (BSE) images. La<sub>2</sub>O<sub>3</sub> can be recognized as mixed finely in the powder after 50 h of ball milling.

The X-ray diffraction pattern of the mixture of NaH + LiAlH<sub>4</sub> + La<sub>2</sub>O<sub>3</sub> after ball milling is shown in Fig. 2a. Fig. 2b presents the X-ray diffraction pattern of the mixture of NaH + LiAlH<sub>4</sub> + CeO<sub>2</sub> after ball milling. The phases of Na<sub>2</sub>LiAlH<sub>6</sub> and Na<sub>3</sub>AlH<sub>6</sub> are clearly recognized in both milled mixtures. This result indicates that the alanates (Na<sub>2</sub>LiAlH<sub>6</sub> and Na<sub>3</sub>AlH<sub>6</sub>) can be synthesized from the NaH + LiAlH<sub>4</sub> powdered mixture only by ball milling. Because La<sub>2</sub>O<sub>3</sub> and CeO<sub>2</sub> (as doping oxides) are thermodynamically more stable than alkali metals and Al at room temperature (see Table II), they are not reduced during milling and kept in the initial phase, see Fig. 2a and b, respectively. As seen in the XRD patterns (Fig. 2a and b), small amount of Na<sub>3</sub>AlH<sub>6</sub> is also formed during milling.

#### 3.2. Hydrogen reactivity of Na<sub>2</sub>LiAlH<sub>6</sub>

Fig. 3 shows the hydrogen reactivity of the mechanochemically prepared samples. La<sub>2</sub>O<sub>3</sub> or CeO<sub>2</sub> doped Na<sub>2</sub>LiAlH<sub>6</sub> shows drastically improved hydrogen

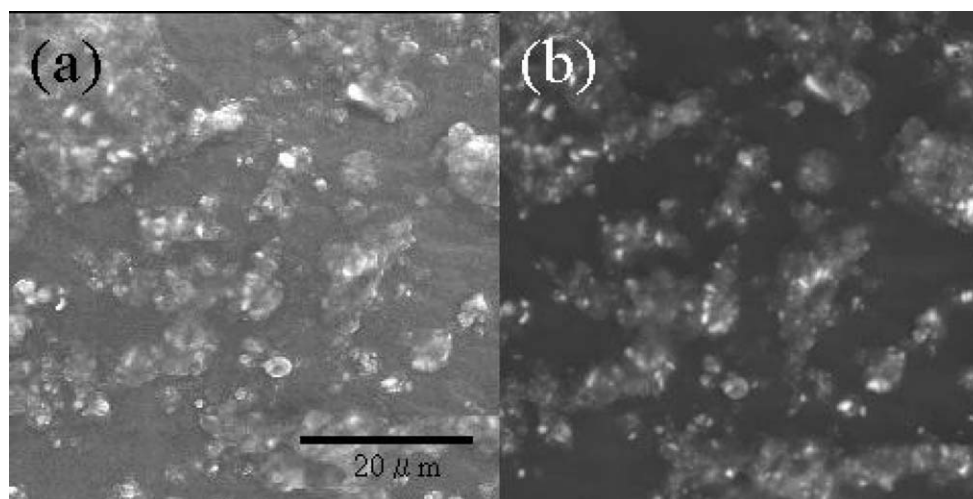


Figure 1 Mapping images of Na<sub>2</sub>LiAlH<sub>6</sub> doped with La-oxide: (a) secondary electron image and (b) back scattering electron image.

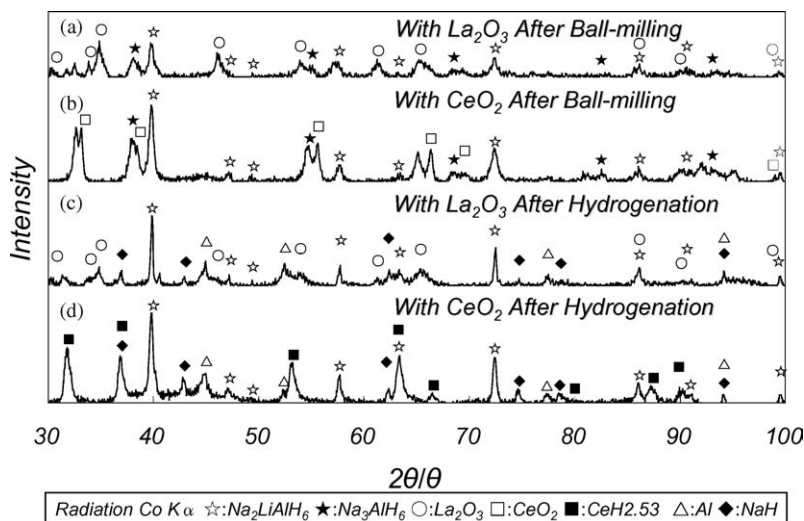
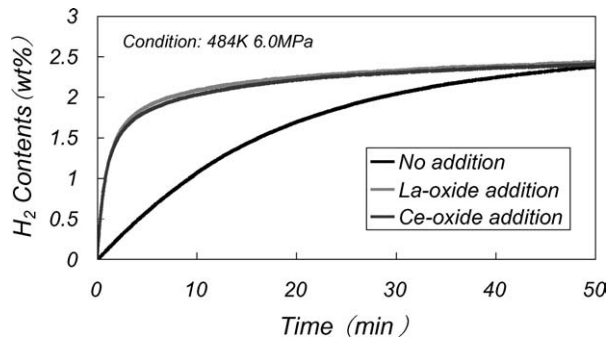


Figure 2 X-ray diffraction patterns of the samples doped with La<sub>2</sub>O<sub>3</sub> or CeO<sub>2</sub> after mechanical activation ((a) and (b)) followed by hydrogenation ((c) and (d)).

TABLE II Standard free energy of formation of various oxides at 300 and 573 K

	$\Delta G^0$ (kJ/mol-O <sub>2</sub> )	
	300 K	573 K
2Na <sub>2</sub> O	-750	-700
CeO <sub>2</sub>	-1025	-975
2/3Al <sub>2</sub> O <sub>3</sub>	-1050	-1000
2Li <sub>2</sub> O	-1125	-1060
2/3La <sub>2</sub> O <sub>3</sub>	-1140	-1090
2/3Nd <sub>2</sub> O <sub>3</sub>	-1150	-1100
2/3Sm <sub>2</sub> O <sub>3</sub>	-1160	-1110
2/3Ce <sub>2</sub> O <sub>3</sub>	-1150	-1125

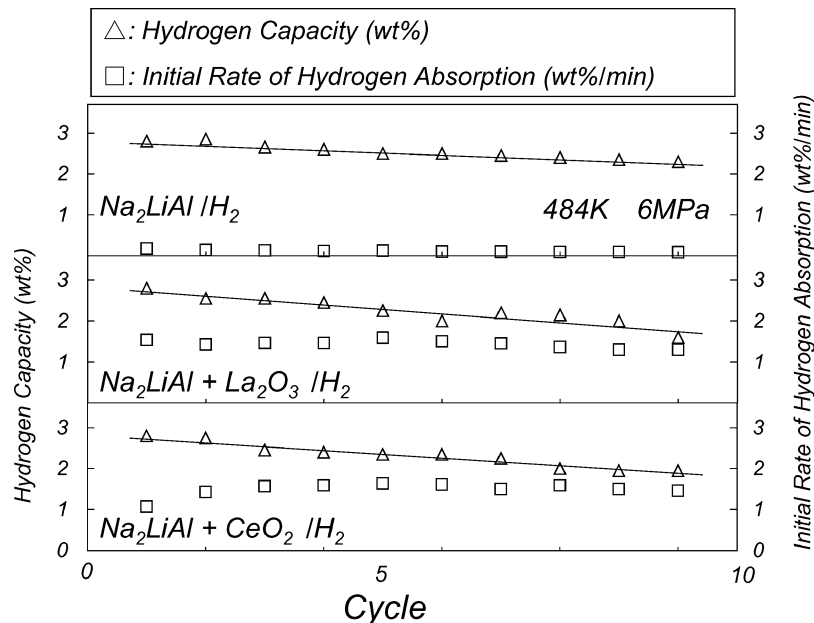
Figure 3 Hydrogen absorption curves for the samples with nominal composition of Na<sub>2</sub>LiAlH<sub>6</sub>, Na<sub>2</sub>LiAl(CeO<sub>2</sub>)<sub>0.1</sub>H<sub>6</sub> and Na<sub>2</sub>LiAl(La<sub>2</sub>O<sub>3</sub>)<sub>0.1</sub>H<sub>6</sub> in the course of 3 times sorption cycles.

absorption kinetics when compared to that of un-doped samples. At the same time, the cyclic characteristics of the initial rates of hydrogen absorption are improved by doping RE-oxides (Fig. 4). The accelerated initial reaction rates are almost kept in the cycling, while the hydrogen capacity is reduced. For explaining these effects, we considered the problem from thermodynamic points of view.

Fig. 2c and d show the X-ray diffraction patterns of the samples doped with La<sub>2</sub>O<sub>3</sub> or CeO<sub>2</sub> after mechanical activation and hydrogenation at 573 and 484 K, respectively. For the sample doped with La<sub>2</sub>O<sub>3</sub>, XRD pattern shows the following phases: Na<sub>2</sub>LiAlH<sub>6</sub>, NaH, Al and La<sub>2</sub>O<sub>3</sub> (see Fig. 2c), whereas CeO<sub>2</sub>-doped sample consists of Na<sub>2</sub>LiAlH<sub>6</sub>, NaH, Al and CeH<sub>2.53</sub> phases (Fig. 2d). The alkaline hydrides and metallic Al can be yielded according to the following reaction: Na<sub>2</sub>LiAlH<sub>6</sub> ⇌ 2NaH + LiH + Al + 3/2H<sub>2</sub>. Thus, Na<sub>2</sub>LiAlH<sub>6</sub> is decomposed into each element and/or their hydrides at the dehydrogenation and recombined at the hydrogenation.

The reduction of CeO<sub>2</sub> into CeH<sub>2.53</sub> can be understood also when taking into account the thermodynamic values listed in Table II, where the standard free energies of formation (at 300 and 573 K) for oxides related with this study are given. La<sub>2</sub>O<sub>3</sub> is thermodynamically more stable than both Al<sub>2</sub>O<sub>3</sub> and alkaline metal oxides even at 573 K, whereas CeO<sub>2</sub> is more unstable than La<sub>2</sub>O<sub>3</sub>. The experimental result, that CeO<sub>2</sub> in Na<sub>2</sub>LiAlH<sub>6</sub> is reduced to CeH<sub>2.53</sub> when hydrogenated (Fig. 2d), is explained only by this difference in thermodynamic stability, i.e., the CeO<sub>2</sub> is reduced by alkaline metal hydrides and/or metallic Al in the course of hydrogen sorption cycles under the experimental condition at 484 K and 6.0 MPa of hydrogen pressure. Because the phase of CeH<sub>x</sub> is highly reactive for the H<sub>2</sub> dissociation, the reduction may result in the drastically improved sorption kinetics.

If the dissociation of H<sub>2</sub> on the sample surface is rate determining, the pressure dependence of the initial reaction rate should be observed in the reaction kinetics. In the experiments, however, there was no difference in pressure dependence of the initial absorption rates for both samples with and without RE-oxide. Furthermore, La<sub>2</sub>O<sub>3</sub> cannot be reduced by Al at temperatures lower than 573 K, however, La<sub>2</sub>O<sub>3</sub> exhibits also similar modified reaction kinetics to that of CeO<sub>2</sub>. It

Figure 4 Cyclic characteristics for hydrogen absorption capacity and initial reaction rates of hydrogen absorption for the samples with nominal composition Na<sub>2</sub>LiAlH<sub>6</sub>, Na<sub>2</sub>LiAl(CeO<sub>2</sub>)<sub>0.1</sub>H<sub>6</sub> and Na<sub>2</sub>LiAl(La<sub>2</sub>O<sub>3</sub>)<sub>0.1</sub>H<sub>6</sub>.

can be concluded that RE-oxides added to the mixtures provide the reactive points for H<sub>2</sub> dissociation. Other different reaction mechanism should be predominant, such as increased diffusion pass through hydride layer of the particle by mechanically buried RE-oxide particles. The mechanism of increasing sorption rate, however, results in the decrease of the hydrogen capacity.

#### 4. Conclusion

It is shown that Na<sub>2</sub>LiAlH<sub>6</sub> can easily be produced by rotary ball milling of NaH and LiAlH<sub>4</sub> powders in stoichiometric composition without any heating, any pressurizing or purification steps.

The hydrogen absorption capacity for samples without RE-oxide kept almost as same as the initial capacity in the cycling, while the samples with RE-oxide exhibited the decreasing capacity. Na<sub>2</sub>LiAlH<sub>6</sub> doped with RE-oxide exhibits, however, drastically improved initial hydrogen absorption rate. Moreover, the cyclic characteristics of absorption rate dose do not change in the course of 10 times absorption cycling.

During the mechanochemical preparation of the doped samples, La<sub>2</sub>O<sub>3</sub> in alanate is not reduced by Al metal, while CeO<sub>2</sub> is reduced into CeH<sub>x</sub> by alkaline

metal hydrides and/or Al according to the manner of thermodynamic properties.

The improved initial hydrogen absorption rate seems to be related with the increased hydrogen diffusion path by finely dispersed RE-oxides mechanically buried, because there was no pressure dependence in the initial absorption rates of any samples with and without RE-oxide, and also with RE-oxide or RE-hydride.

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