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A Potential Method of Hydrogen Generation from Milled Al-LiH Mixture in Water

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Hydrogen generation by hydrolysis of Al-LiH mixture was investigated in pure water. The results showed that the hydrolysis rate of Al-LiH mixture obtained by high-energy ball milling was significantly improved, comparing to lower reactivity of milled pure aluminum in water. The 20 h-milled Al-LiH ($\geq$ 15 wt %) mixture displayed a high conversion yield of 87-100 %, comparing with unhydrolyzed milled Al at 25 ºC. Its high reactivity was attributed to the hydrolysis of LiH and numerous defects and fresh surfaces after milled, which was helpful to accelerate the hydrolysis of aluminum in water. In addition, the presence of tin could improve hydrolysis kinetic of Al-LiH mixture. A maximum yield of 93 %, that was, a hydrogen gravimetric yield of 10 % (including tin mass and excluding water mass) had been obtained. The positive effect of tin addition on yield and kinetics of the mixture was explained from the creation micro-galvanic cells between Al and Sn components, which was simulated by hydrolysis byproduct of LiH.

Key Words: Aluminum, LiH, High-energy ball milling, Hydrolysis reaction.

INTRODUCTION

With the decrease of the fossil fuel and the appeal of environment protecting, a new sustainable energy economy will appear at the 21st century. Hydrogen with many attractive advantages such as high power density, non-polluted reaction products, *etc.*, has been attractively payed attention in the world. Hydrogen is mostly oxidized efficiently in fuel cells where the energy obtained in the reaction is converted to electric energy. And a safe, low cost and light hydrogen gas generator is a key problem to fuel cells which are alternative power sources for providing clean energy for transportation and personal electronic applications.

Generally, hydrogen application as a fuel is largely used by conventional physical storage devices (tanks containing gas under pressure or liquefied) or stored in many material such as metal hydrides, carbon nanostructures, metallic alloys and chemical compounds. However, their fatal shortcomings limit hydrogen commercializes. For example, the inter-metallic hydrides contain transition or rare earth metal, so their hydrogen storage capability in terms of specific energy density is too low to meet the requirements of various applications. For the wide range of potential applications, it is important to select combustible alloys that exhibit high hydrogen yields. It is well known that aluminum holds a promise as hydrogen-generating materials because aluminum has high hydrogen yield up to 11.1 % (excluding water mass). Moreover, this reaction has the advantage that its byproduct $Al(OH)_3$ is environmental friendly. The problem of using aluminum metal as expendable hydrogen sources is that it is highly inert to water. Several methods have been developed to accelerate the aluminum hydrolysis. For example, Nanoscale aluminum combusts with gelled water to generate hydrogen at gentle temperature. The use of nanopowder decreases the ignition temperature of Al, while gelling inhibits water evaporation during combustion. The addition of $NaBH_4$[1] into the mixture is promising to obtain high hydrogen yield. Unfortunately, high cost of the nanoscale Al and $NaBH_4$ is a drawback of this method. Kunio Uehara[2] had found that the fresh surface of aluminum or aluminum alloys reacted with water and hydrogen gas bubbles was formed when these materials were cut or grounded in water. The reaction occurred at room temperature and performed as long as cutting continued. Finely dispersed aluminum by the mechanical and chemical activation reacts rapidly and completely with water to evolve hydrogen, when aluminum was melted with particular metals[3-10], such as gallium, tin, indium, mercury, lead, bismuth, magnesium or zinc, the alloy posses higher activities than aluminum metal. The quantitative compositions of the solid aluminum alloys reacting with water to produce hydrogen were first reported in the literature[9]. Here, water acted as an oxidizer for Al and simultaneously produced the humid hydrogen.

However, Al/H_2O system has low hydrogen yield (theoretical limit 11.1 % (excluding water mass)), compared with most ionic hydrides[11], such as LiH, MgH_2, *etc.* To simultaneously reach high hydrogen yield and combustion efficiency, we select LiH as an addition into aluminum metal because LiH has theoretical hydrogen yield amount as 25 % (excluding water mass). Water acts as an oxidizer for the hydrolysis of both aluminum and LiH. LiH is not only an additional hydrogen source, but also a catalyst to improve aluminum activation. Therefore, AI-LiH mixture can react with water to generate hydrogen at normal temperature.

EXPERIMENTAL

The starting materials were powders of pure aluminum and LiH. Then milling was performed by QM-1SP3 planetary ball miller under 0.2-0.3 MPa argon atmosphere. In most case, 2 g of powder mixture was processed with 16:1 ball-to powder ratio. The powders were handled inside an argon-filled glove box in high purity argon. Besides preventing contamination, isolation from air is also important for the safety point of view. Mechanically activated aluminum reacted with moisture to form alumina. Finely ground LiH may self-ignite if it contacted with water. Therefore, cleaning and rinsing the milling container had to be performed with caution. The hydrolysis of the Al-LiH mixture was referred to the experiments in the literature[10] . A weighed sample of the alloy (0.3 g pressed under 5 ton pressure in the mold with 10 mm diameter) was treated with 100 mL of distilled water in a temperature-measured stainless steel chamber attached to a gas burette graduated in 0.1 mL increments. The produced gas was flown through a condenser to remove water vapour before it enters into the burette. The experiments were processed at an initial pressure of 1 atm and initial temperature of 25 ºC.

Powder X-ray diffraction studies were carried out on an X-ray diffractometer (RIGAKU, Japan, model, D/MAX2550V/PC), using nickel filtered CuK$_\alpha$ Radiation. Differential thermal analysis of alloys samples was carried out on an Q2000 (TA Company, American) at the temperature range from 30 to 800 ºC .

RESULTS AND DISCUSSION

Effect of LiH addition: The common aluminum reacted with water steam[12] beyond the melting point of Al_2O_3 (2054 ºC) or reacted with alkali[13] solution to generate hydrogen gas. This paper introduces the 20 h-milled Al-LiH mixture in water to produce hydrogen. Note that Al hydrolysis was done at stable temperature, excess of water and the hydrogen gas without vapors of un-reacted water after condensation, the evolved gas is essentially hydrogen (--99 %). Table-1 compares hydrogen yield of different mixtures with the theoretical values. Al content values from 100 % to 0, correspond to reactions (1), (3) and (4), respectively. It appears that the hydrolysis of the Al-LiH mixture may provide relatively high hydrogen generation, higher than theoretically achievable for reaction (3) alone. The obtained efficiency, 87-100 %, is significantly higher than that reported for nano-Al/gelled water systems[14] at same conditions.

TABLE-1
THEORETICAL AND EXPERIMENT HYDROGEN YIELD FOR Al + LiH/H_2O REACTION AT 25 ºC

Al + LiH	H_2 yield (%) (including the mass of Al-LiH and excluding water)		Efficiency (%)
	Theoretical	Experimental	
100	11.10	0.00	0.00
90	12.49	9.22	73.86
85	13.19	11.51	87.28
80	13.88	13.88	100.0
70	15.27	15.27	100.0
0	25.00	25.00	100.0

The hydrogen generation rate of 20 h-milled Al-LiH mixture is shown in Fig. 1. For comparison, milled Al without LiH addition is also shown. Aluminum can not react with water at normal temperature, but milled Al-LiH mixture shows a fast reaction, which stops after several minutes. The Al-LiH mixtures (LiH content value exceeds 20 wt. %) has a hydrogen yield up to 100 %. And its yield exceeds 90 % of theoretic value in 1 min hydrolysis. From Fig. 1, we could distinctly see that hydrogen evolution curves include three regimes *i.e.*, a fast initial step, the second slope and the third flat. The most hydrogen evolution is obtained in the fast initial step which is followed by the second slope. In this regime, the LiH addition simulates a sustained reaction of aluminum, thus giving a faster kinetics and higher yield. In the second slope, the hydrogen rate keeps a constant value and the reacted fraction continues to increase along with time. The second slope is inversely proportional to the LiH content. The slope is shorter with higher LiH content. At the higher LiH content (above 20 wt. %), a third regime (the third flat) can appear where the hydrogen evolution rate seems to be unproportional to the LiH content and the hydrolysis reaction seems to level off. Moreover, the inflexion point, where the hydrogen evolution curves switches from the second to the third regime, is appearing sooner for higher LiH content. For LiH content above 20 wt. %, the inflexion point is estimated to be *ca.* 5 min, but the curve of Al-10 wt. % LiH mixture shows that the inflexion point need more time.

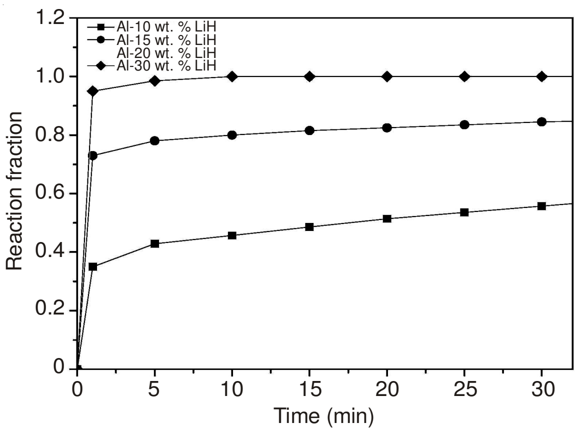

Fig. 1. Hydrogen evolution of the hydrolysis of Al-LiH mixture in water

Reaction of Al-LiH mixture with water steam during the temperature of 30-800 ºC are shown in Fig. 2. With LiH addition, the alloys have the same large exothermic peak at 390 ºC, which show that alloys react with water steam drastically.

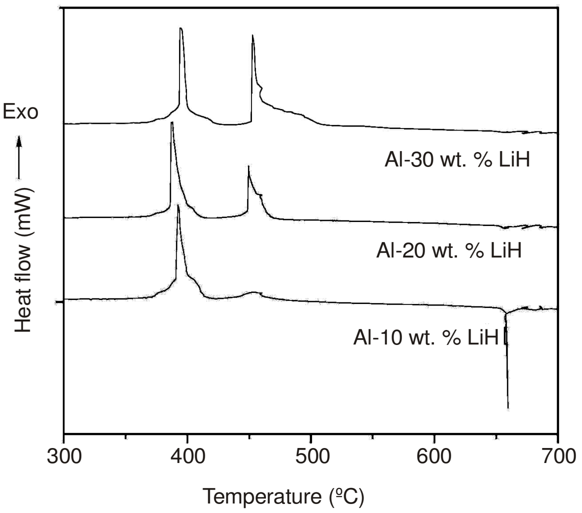

Fig. 2. Heat flow curves of hydrolysis of 20 h-milled Al-LiH mixture

However, there are also some differences between them. Al-10 wt. % LiH mixture has a small exothermic peak at 452 ºC, not easily found, and a large endothermic peak at 660 ºC that is phase-transformation peak, in which solid aluminum melt into liquid. But aluminum with 20 wt. % (or more) LiH mixtures have exothermic peak at 452 ºC, but no endothermic peak at 660 ºC. It is clear that the 20 h-milled aluminum with 10 wt. % LiH can not make aluminum completely react with water, but the mixture with 20 wt. % LiH (or more) has the ability to consume aluminum entirely. Fig. 3 presents XRD patterns of Al and Al-20 wt. % LiH mixture of 20 h milled. There is no great difference between them, except the appearance of peak broadening of Al-20 wt. % LiH mixture, reflecting the decrease of Al crystallite size. LiH is easily dispersed into many small fractions which can prevent the combination of Al-Al. The XRD results also show that there is no reaction of Al and LiH obtained but simple blend in the milling process. The overall hydrolysis reactions between LiH and aluminum with excess water proceed according to the following chemical equations:

$$LiH(s) + H_2O(l) \longrightarrow LiOH(aq) + H_2(g) + heat \qquad (1)$$

where 37 Kcal of heat are generated per mole of LiH reacted and an additional 5 kcal of heat is generated per mole of lithium hydroxide (LiOH) dissolved in water as an ionic solution. In general, the reaction proceeds in two steps. The first step (reaction 2) is the formation of hydrogen gas and a layer of solid LiOH.

$$LiH(s) + H_2O \longrightarrow LiOH(s) + H_2(g) \ \ (fast) \qquad (2)$$

$$LiH(s) + H_2O \xrightarrow{k=0.675} Li^+(aq) + OH^-(aq) \ \ (slow) \qquad (3)$$

$$Al(s) + H_2O \longrightarrow Al(OH)_3 + H_2 + heat \qquad (4)$$

$$OH^- + Al(OH)_3 \xrightarrow{k=6.3\times10^{-12}} AlO_2^- + H_2O \ (slower) \qquad (5)$$

The second step (reaction 3) is the dissolution in water of LiOH, which is beneficial to break down and reduce the passive layer on aluminum particle, favouring the extensive reaction between freshly exposed Al surface and water. Reaction 4 is the hydrolysis of aluminum, where 97.5 Kcal heat is generated per mole of aluminum reaction with water. Since the reaction 5 is significantly slower than others, seen from the kinetic coefficient, it is the rate.controlling step in the sequence. Meanwhile, the heat is attributed to quicken the reaction 5, from exothermal reaction of Al and LiH in water.

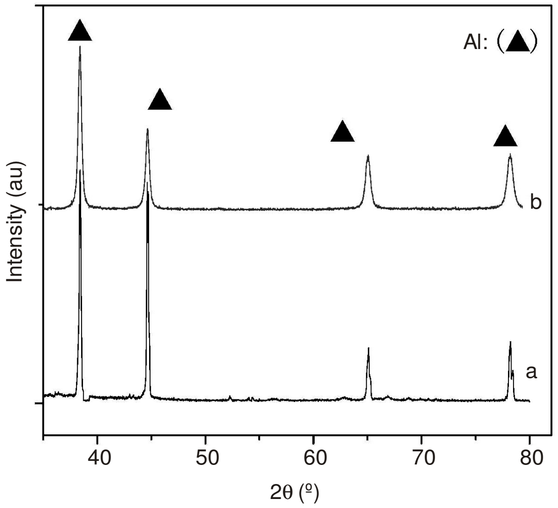

Fig. 3. X-ray diffraction patterns of (a) aluminum and (b) 20 h-milled Al-20 wt. % LiH mixture

Effecting of milling time: A study of hydrogen release as a function of milling time was performed for the milled Al-10 wt. % LiH mixture. As revealed by Fig. 4, the milling time has some effect on the hydrogen yield and hydrogen generation rate. The reaction fraction increases with milling time from 0 to 2 h and then decrease with milling time further increased up to 20 h. A hydrogen yield of 73 % of 2 h milled Al-10 wt. % LiH is obtained, compared to 40 % for unmilled mixture in the hydrolysis of 0.5 h. The hydrolysis reactivity decay of Al-10 wt. % LiH mixture with longer milling is explained by two possible reasons (the formation of Al_2O_3 and Li_2O with air entering in the longer milling process or the decrease of the powder surface area), which need further detailed research.

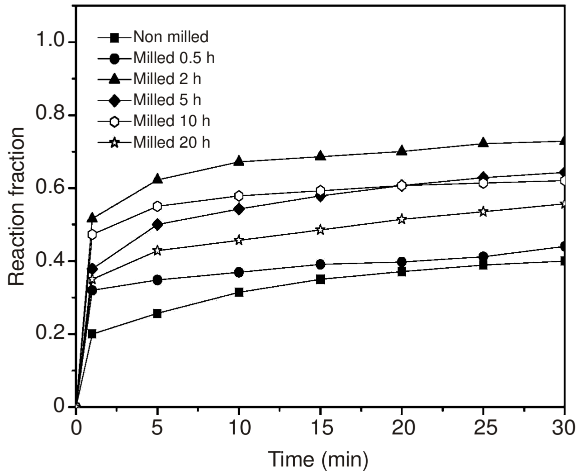

Fig. 4. Hydrogen evolution of the hydrolysis of Al-LiH mixture in water at different milling time

The hydrogen evolutions of Al-10 wt.% LiH mixture with different ball milling time are shown in Table-2. The total conversion yield enhances with milling time from 0 to 2 h, reaching

TABLE-2
CONVERSION YIELD (%), H_2 VOLUME [mL g^{-1}] AND AFTER 2 h OF HYDROLYSIS OF Al-10 wt. % LiH AND HYDROGEN GENERATION RATES [mL (min g)$^{-1}$] AT DIFFERENT STAGES OF HYDROLYSIS REACTION TESTED IN THE PRESENT WORK

Milling time (h)	Hydrogen evolution rate ($mL\ g^{-1}\ min^{-1}$)			H_2 volume	Total conversion
	0-1 min	1-15 min	15-30 min		
0.0	280	15.0	6.0	800	57
0.5	450	7.1	4.7	700	50
2.0	730	17.0	2.0	1160	83
5.0	530	12.9	60.0	1085	77
10.0	480	15.0	8.7	890	64
20.0	490	13.6	6.7	1035	74

the maximum hydrogen yield of 83 % for 2 h-milled mixture. There may be two reasons for the improved performance of the mixture. One is up to the creation of numerous defects and fresh surfaces through milling process which can accelerate the hydrolysis reactivity of the mixture. The other is the diffusion hesitancy. After milled, aluminum can mix uniformly with LiH. When contacted with water, LiH reacts quickly to produce LiOH (aq) and release a lot of heat. In a very shot time and small region, LiOH keeps high concentrations and high temperature, so LiOH reacts swiftly with aluminum before LiOH diffuses. Hydrogen generation comes from hydrolysis of LiH and hydrolysis of aluminum catalyzed by LiOH. The former is a constant value and the latter varies with milling time. The reaction of non-milling mixture and water can produces 80 mL (0.1 g H_2)$^{-1}$ (including 28 mL produced by hydrolysis of LiH and 56 mL produced by hydrolysis of aluminum), but the same mixture milled 20 h can react with water to produce 103.5 mL (0.1 g H_2)$^{-1}$ (including 28 mL produced by hydrolysis of LiH and 75.5 mL produced by hydrolysis of aluminum) and the mixture milled 2 h can react with water to produce 116 mL (0.1 g H_2)$^{-1}$ (including 28 mL produced by hydrolysis of LiH and 88 mL produced by hydrolysis of aluminum). The hydrogen evolution from aluminum hydrolysis has great difference with milling time, so we have the evidence that LiH can not only produce LiOH to catalyze the aluminum hydrolysis, but also improve aluminum reactivity through milling time.

The change of the pH of the solution, during the hydrolysis reaction of 20 h-milled Al-10 wt. % LiH mixture is shown in Table-3. The pH value increases quickly and stabilizes to above 11 after several minutes of hydrolysis. In the same condition, the end values of pH for hydrolysis of pure Al (no reaction at 25 °C) and pure LiH are 7.20 and 12.76, respectively.

TABLE-3
pH OF SOLUTION AS A FUNCTION OF HYDROLYSIS TIME OF 20-h MILLED Al-10 wt. % LiH MIXTURE

Hydrolysis time (min)	pH
0	7.20
1	11.09
5	11.15
12	11.67
20	11.67
40	11.46

Influence of Sn addition to Al-LiH mixture: Fig. 5 compares the hydrogen evolution curves for Al-10 wt. % LiH mixture and Al-10 wt. % LiH-5 wt. % Sn mixture milled 20 h. The aluminum powder reactivity is significantly improved with Sn addition. Indeed, a maximum conversion yield of 93 % is obtained in presence of Sn, corresponding to a hydrogen yield of 10 % (including Sn mass and excluding water mass). More importantly, the hydrogen generation rate increase remarkably. The positive effects of the Sn addition on the yield and kinetics of hydrolysis reaction can be explained by the creation of micro-galvanic cell between Al and Sn components. The Sn addition causes aluminum behaving hyperactively at high negative potential values, which leads to crevice formation and conditions favourable for dissolution. In other words, assuming that the corrosion of aluminum in water is largely cathodically controlled, the presence of Sn may stimulate the aluminum reaction with water by decreasing the cathodic overpotential[15,16] and lower cathodic over potential favours the reduction of water to hydrogen and the oxidation of Al to alumina. Furthermore, the hydrolysis of LiH produce a lot of LiOH, which increases the ionic conductivity of the media. The solubility of LiOH in water[17] at room temperature exceeds 32 g L^{-1}. Therefore, the presence of soluble and dissociared Li^+ and OH^- is sufficient amount to ensure the ionic conduction between the anode (Al) and cathode (Sn) components and lead to induce the galvanic corrosion process.

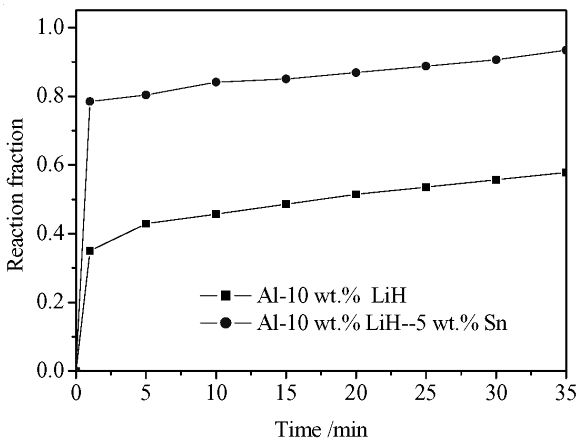

Fig. 5. Hydrogen evolution of the hydrolysis of Al-LiH mixture and Al-LiH-Sn mixture in water

Conclusion

We have elaborated an effective and cheap H_2 source material from milled Al-LiH mixture in water. The hydrolysis reaction rate increases very quickly with augment of LiH content and the hydrogen production is much higher than theoretical hydrogen yield of aluminum. LiH can produce LiOH to catalyze the aluminum hydrolysis and improve aluminum reactivity *via* milling method. Milling has great effect on the aluminum reactivity in pure water while numerous defects, fresh surfaces and uniform mixing of Al and LiH obtained in the milling process are helpful to improve Al reactivity and accelerate Al hydrolysis in water. The additive metal Sn can also accelerate hydrolysis of Al-LiH mixture. The performance for hydrogen production has been obtained with the composite

Al-10 wt. % Li-5 wt. % Sn mixture, with a maximum conversion yield of 93 %, corresponding to a hydrogen gravimetric yield of 10 % (including Sn mass and excluding water mass). However, the hydrogen generation *via* hydrolysis of Al-LiH mixture presents a serious limitation due to a violent, uncontrollable reaction and large amounts of heat, making them hardly suitable for fuel cell applications.

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