



# Improved hydrogen generation from the hydrolysis of aluminum ball milled with hydride



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## ABSTRACT

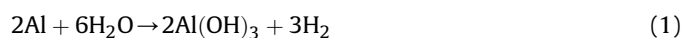
The hydrolysis of aluminum powder can be efficiently improved by milling with hydrides, among which LiH performs the best. Both sample composition and milling time affect the hydrolysis of Al–LiH mixture. Reaction temperature has a great impact on improving the hydrolysis properties. The reactions taken place in the solution are studied and the formation of the  $\text{LiAl}_2(\text{OH})_7$  hydrate is found to be important in enhancing the corrosion of Al. The Al-30 mol% LiH milled for 3 h sample reaches a yield of 96.3%, *i.e.* 1442.4 ml  $\text{H}_2$   $\text{g}^{-1}$  (composite) within 1 h at 75 °C.

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## 1. Introduction

The combustion of traditional fossil fuels is causing severe environmental pollution and energy crisis [1,2], and there is an urgent need to find new forms of energy with environmental friendliness. Hydrogen stands out as an ideal alternative to fossil fuels in the future, especially for on-board fuel cell applications [3–8], because it is regenerative, has a high caloric value and does not emit  $\text{CO}_2$ . The application of hydrogen energy begins with a proper hydrogen generation technique.

Traditionally, hydrogen is produced from natural gas or methanol, during which more energy is consumed [9] and the monoxides existing in the production could cause the catalyst poisoning in proton exchange membrane fuel cells [10]. Recently hydrogen generation from metal aluminum or aluminum alloys has attracted much attention because of its low cost, light atomic weight, high electron density and abundance in the earth's crust [11]. 1 g of Al will produce 1.36 L of  $\text{H}_2$  in ambient conditions assuming the hydrolysis goes on completely, according to reaction (1) [12].



This hydrolysis process doesn't generate  $\text{CO}_2$  and the by-product  $\text{Al}(\text{OH})_3$  has minimal environmental impact. What's more, aluminum can be fully recovered from the by-product through the Hall–Héroult process. However, the major challenge is that the passive  $\text{Al}(\text{OH})_3$  by-product covers the surface of Al and prevents its continuing reaction with water. Previous works show that the corrosion can be enhanced by adding alkali [13,14] or alkaline salts [15,16]. During the research of Al corrosion in alkaline solutions, Jorge et al. [17] found a AlHidrox process, which minimized Al passivation and allowed 100% yields and flow rates up to 2.9 L/min per gram of Al. But these alkaline additions could also corrode the reactor, which is not suitable for an energy source. Aluminum oxide or hydroxide modified Al composites are prepared through a ceramic process to improve the hydrolysis properties of Al [11,18]. However, the required addition amount is big which reduces the hydrogen generation per unit mass and the hydrolysis goes on very slowly, *e.g.*, 100% conversion in 20 h for 30 vol% Al + 70 vol% oxide [11]. Al based alloys formed by doping with other metals also obtain high hydrolysis reactivity in water. Parmuzina et al. studied the Al alloys containing Ga, In, Zn and Sn and obtained a conversion yield of 99.5% at RT (room temperature) [19]. Fan et al. [6] obtained a hydrogen yield of 1035 ml per gram of Al by applying the 10 h milled Al-5 wt%In-3 wt%Zn-2 wt%NaCl composite. Furthermore, when the hydrogen generation setup was connected to a micro fuel

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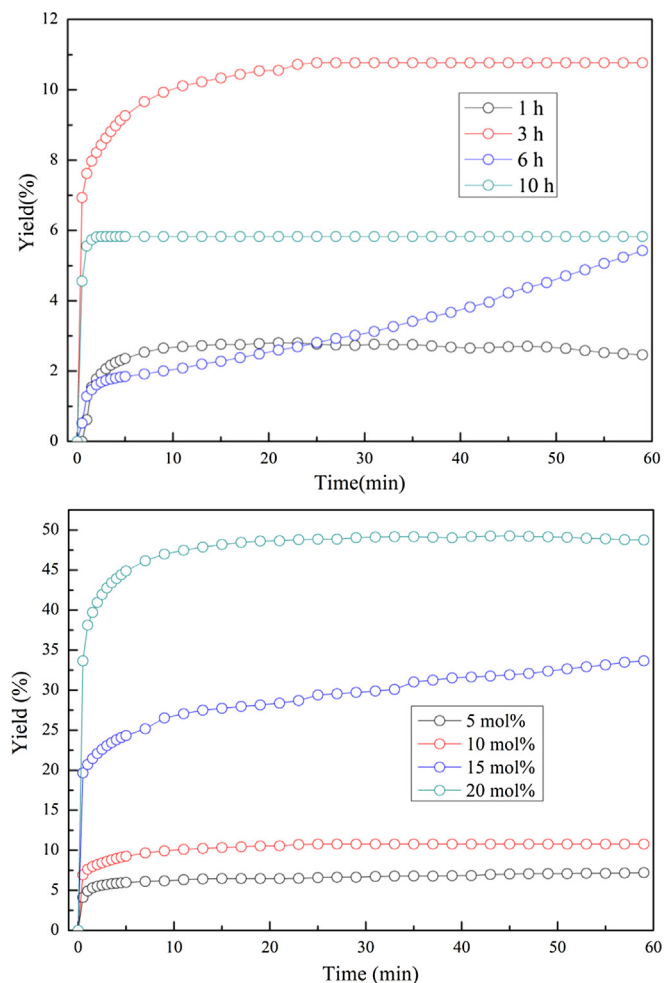


Fig. 1. Yield of Al-10 mol% LiH ball milled for different hours (top) and Al milled with different amounts of LiH for 3 h (bottom) at RT.

cell, 0.96 W was produced with stable hydrogen supply rate. Although the hydrolysis properties are improved, the metal added cannot produce hydrogen and reduces its theoretical hydrogen generation volume per unit mass.

In this work, Al is doped with LiH and ball milled to improve its hydrolysis property. As a hydride, LiH has a high hydrogen capacity of about 12.6%. By doping with LiH, Al can be activated and the overall theoretical hydrogen generation volume can be increased. Several other hydrides are also added to carry out comparisons.

## 2. Experimental

### 2.1. Al (Sinopharm chemical Reagent co., Ltd, 99.0%, 100–200 mesh), LiBH<sub>4</sub>

(Acros Organics, 95%), LiH, NaBH<sub>4</sub> (Alfa Aesar, 98%) were used as received. In order to avoid oxidation, all sample handling was performed in an Ar filled glove box (MIKROUNA Universal) with a recirculation system. The samples were mounted into stainless pots with a ball-to-powder ratio of 25:1 and milled using a planetary QM-3SP4 ball miller.

The experiment setup used to measure the hydrogen generation was similar to Zhao's [4]. The reaction was carried out in a 250 ml flask with three openings, one for water addition, one for hydrogen exhaust and the last one sealed with a clog. The flask was dipped

into a water bath to keep a constant temperature. The mass of sample was fixed at 50 mg and the volume of water was fixed at 10 ml for each experiment. Hydrogen production started when the milled powder came into contact with water. Then the hydrogen flowed through a spiral condenser and entered into a glass tube containing drierite to remove water vapor. After that the generated hydrogen was measured by a flow meter (ADM 2000, Agilent Technologies) which was connected to a computer to record the HG rate (hydrogen generation rate) and volume as a function of time. Each test was repeated at least twice to confirm its reproducibility ( $\pm 5\%$ ). The background flow that was measured under the same condition without solid samples was measured and subtracted from the original data. The volume of hydrogen is converted to those under the standard conditions (273 K and 1 atm) using the ideal gas equation. The hydrogen yield (%) is defined as the experimental hydrogen generation amount over the theoretical hydrogen generation amount. The hydrogen generation curves within the first hour and the HG rate curves in the first 5 min were presented and discussed in this work.

X-Ray diffraction (XRD) analysis was carried out using an X'Pert PRO diffractometer with Cu K $\alpha$  radiation. The microstructure studies were performed on a SEM (scanning electron microscopy) system (SIRON) equipped with INCA EDS measurements (energy dispersive X-ray spectroscopy).

## 3. Results and discussion

### 3.1. Hydrogen generation at RT

High-energy ball milling is known to be an effective method to activate materials through the repeated welding and fracturing process. In this period, the samples' microstructure is changed and many defects are generated which are considered to benefit the hydrolysis of Al particles [20,21]. During the milling process, time and sample composition are believed to be important factors that affect the chemical properties of the final composites. Fig. 1 shows the hydrogen yield of Al-10 mol% LiH milled for different hours (top) and Al milled with different amounts of LiH for 3 h (bottom) at RT. Different from what has been reported before [22,23], there is no discernable induction period at the beginning parts of these hydrogen generation curves. The milled Al–LiH composites quickly react with water to generate hydrogen, then the reaction ceases because the passive by-product layer covers the surface of Al, blocking its reaction with water.

As stated above, milling time and sample composition apparently affect the hydrogen generation performances of Al–LiH composites. With increased milling time, the yield increases initially, reaches the maximum value of 10.8% at 3 h and then decreases. The increase in hydrolysis performances is due to the fact that aluminum is activated during the high energy milling process. The grain size can be reduced and many defects can be generated, which work together to promote the reactivity of Al powder. The decrease of the yield can be ascribed to the partial oxidation and agglomeration of Al powder during the prolonged ball milling, which has also been found in previous works [22,24]. The SEM images of Al-10 mol% LiH milled for different hours are shown in Fig. 2 (a, c, f). Apparently, the microstructure of Al grains is changed from platelet (1 h) to fractured smaller particles (3 h) and finally again to big platelets (10 h). This change of the microstructure is consistent with the inferences stated above.

In the case of sample composition, more LiH addition leads to higher hydrogen yield. The Al-20 mol% LiH milled for 3 h sample reaches a yield of 48.8% with the highest mHGR (maximum hydrogen generation rate) of about 970 ml min<sup>-1</sup> g<sup>-1</sup> among all these samples, which can be seen in Fig. S1 showing the HG

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