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Hydrogen generation by the hydrolysis reaction of ball-milled aluminium–lithium alloys

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HIGHLIGHTS

- The hydrogen generation rate of Al–Li alloys (Li < 10%) is enhanced significantly.
- The hydrogen yields of Al–Li alloys (Li < 10%) can reach 100%.
- Al–Li alloys (Li < 10%) can react with water at different temperature to produce H_2.
- The cost of hydrogen generation for Al–Li alloys is reduced.

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ABSTRACT

The addition of Li can prevent an inert alumina film from forming on the surface of Al alloy particles, allowing the rapid hydrogen generation of Al alloys to be achieved. However, because the Li content is less than 10%, the hydrogen generation rate and hydrogen yield of Al–Li alloys are significantly decreased. In this work, NaCl is introduced to prepare Al–Li alloys with low Li contents by ball milling. The research results show that by increasing the amount of NaCl added, the ball milling time and Li content can effectively improve the hydrogen generation of the alloys. Under optimal preparation conditions, the ultimate hydrogen yield of Al–Li alloys can reach 100%. The initial water temperature has almost no effect on the generation of hydrogen, even at 0 °C. Ca^{2+} and Mg^{2+} can combine with OH^- to form the insoluble compounds $Ca(OH)_2$ and $Mg(OH)_2$, which can prevent hydrogen generation. NO_3^- reacts with Al to form ammonia and reduce the hydrogen yield of the alloys. Therefore, Al–Li alloys should be prevented from reacting with water containing Ca^{2+}, Mg^{2+} and NO_3^-. Al–Li alloys must be stored in isolation from air to maintain good hydrogen-generation performances.

1. Introduction

Automobiles offer a fast and convenient mode of travel to suit modern lifestyles. However, at the same time, individuals are concerned about the exhaust that automobiles produce. To reduce the emissions of greenhouse and polluting gases, it is urgent that we find a renewable and clean fuel to meet energy demand. Hydrogen possesses a high mass energy density that is three times that of gasoline. More importantly, when used as a fuel, hydrogen does not emit any pollution gas. Therefore, hydrogen may be a promising alternative fuel for automobiles in the future [1]. However, hydrogen must first be prepared by a traditional method and then delivered to the user in the form of a liquid or compressed gas. Some potential hazards arise in the process of storing and delivering hydrogen due to its flammable and explosive properties. Therefore, the rapid production, safe storage and delivery of hydrogen have become the main problems hindering the development of hydrogen-based automobiles [2]. If liquid or compressed hydrogen can be replaced by hydrogen-producing materials to provide hydrogen for automobiles, the safety of mobile hydrogen systems will be significantly improved.

Some metals and their alloys, such as Mg-based, Al-based, Zn-based and Fe-based materials, exhibit good activity and can react with water rapidly to produce hydrogen [3–6]. Among these materials, aluminium is inexpensive due to its abundance in the earth and has a low atomic weight (27 g mol^{-1}), 3 valence electrons and high activity [7]. As 1 mol or 27 g of aluminium reacts with water, it

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can produce 1.5 mol of hydrogen. The hydrogen density of aluminium (the hydrogen production of unit mass materials) can reach 11.1% and is only below that of Li (14.5 wt.%), among all other metals. Additionally, the products of the reaction between Al and water, Al_2O_3 or $Al(OH)_3$ are easily recycled by mature metallurgical processes [8]. Therefore, aluminium is the most promising material for future hydrogen generation.

Although aluminium exhibits a strong thermodynamic reaction with water when producing hydrogen, an inert oxide film easily forms on the Al surface, preventing further water from contacting the Al metal surface in near-neutral-pH water solutions and hindering the continued production of hydrogen [9]. This self-protection property, i.e., the formation of an inert oxide film, offers an advantage against continued corrosion when aluminium is used as a structural material [10]. However, this property significantly affects hydrogen generation by the hydrolysis reaction of aluminium. Therefore, the development of a method for destroying the inert oxide film or preventing it from forming on the Al surface has become the key to achieving the rapid generation of hydrogen.

Many methods have been adopted by researchers to destroy this inert oxide film. For example, either a NaOH or $NaAlO_2$ solution can be used to dissolve the alumina film [11,12]. Although hydrogen can be produced rapidly, such a method is difficult to apply in mobile hydrogen systems due to the highly corrosive nature of the reaction solution. As a result, some researchers have begun to study the activation and modification of aluminium. Either NaCl or Al_2O_3 is used to activate aluminium by ball milling [13,14]. However, only as the amount of added NaCl or Al_2O_3 addition reaches 76 wt.% or 90 wt.%, respectively, can a hydrogen yield of 100% or 70% be obtained with Al-based materials. Furthermore, these additions cannot produce hydrogen by themselves, thus significantly reducing the hydrogen produced per unit mass. Hence, the materials are also unsuitable for use in mobile hydrogen production. Research results have shown that the preparation of Al alloys, such as Al–Sn alloy, Al–In alloy and Al–Bi alloy, can alter the existing form of Al and prevent the formation of an inert oxide film [15–17]. In particular, Woodall, a professor at Yale University, observed that Al easily dissolves in Ga metal, forming Al–Ga alloy. Al is dispersed in the alloy at an atomic level, preventing the inert alumina film from forming [18]. As a result, Al–Ga alloy can react with water to produce hydrogen rapidly. However, only when the Ga content is sufficiently high (72 wt.%) can the hydrogen yield of Al reach 100%. Because Ga metal is not only very expensive but also cannot produce hydrogen by itself, the hydrogen density per unit mass of Al–Ga alloy is very low, and the cost of hydrogen generation is high. Ilyukhina et al. [19] and Parmuzina and Kravchenko [20] added low-melting-point metals such as In and Sn to improve the activity and decrease the Ga content of an alloy prepared by the ball-milling method. The research results showed that the Ga content of the alloy was significantly reduced to 10 wt.% and that the prepared Al–10 wt.%Ga–4.3 wt.%In and Al–10 wt.%Ga–4.2 wt.%In–1.7 wt.%Sn–0.8 wt.%Zn powder could react with water to generate hydrogen with 90% hydrogen yield. However, the addition of expensive rare metals not only increases the cost of hydrogen generation but also makes the byproducts complex, causing them to be more difficult to recycle. Therefore, it is necessary to develop new Al-based materials for hydrogen generation.

Li is an active metal that can react with water to produce hydrogen by itself and has a very high hydrogen density (14.5%). Therefore, Li can be added to preparations of Al–Li alloy to improve the activity of Al. In our previous research [21], an Al–Li alloy was prepared using a melting method. Because the Li contents ranged from 10 wt.% to 20 wt.%, the hydrogen yield of the alloy was almost able to reach 100%. In addition, Fan [22] prepared an Al–Li alloy by ball milling. Only as the Li content of the alloy reached 30 wt.% could the hydrogen yield of the alloy reach 92%. If the Li content is decreased to 20 wt.%, the hydrogen yield of the alloy will be significantly reduced To improve the hydrogen yield of Al–Li alloy with a low Li content (<20 wt.%), rare metals such as Bi, Sn and In or compounds such as $NaBH_4$ and $CoCl_2$ are incorporated into the alloy by ball milling [23]. Although the hydrogen yield is improved, the composition of the alloy becomes more complex, which causes some difficulties when recycling the metal. Generally, Li can improve the activity of Al. However, the Li content of the aforementioned Al–Li alloy is still high, which causes the cost of hydrogen generation to increase due to the high cost of Li. Only by decreasing the Li content of the alloy can the cost of hydrogen generation be effectively reduced.

However, as indicated by our work and that of Fan, the effect of the Li content on the hydrogen yield of the alloy is significant, and the hydrogen generation rate and hydrogen yield of Al–Li alloys can be reduced with decreasing Li content. To achieve the rapid generation of hydrogen using an Al–Li alloy with a low Li content, the alloy preparation method is critical. In this study, an Al–Li alloy with a low Li content was prepared by the ball-milling method. The effects of the preparation conditions and reaction conditions on the hydrogen generation of the resulting Al–Li alloy were investigated.

2. Experimental

Al–20 wt.%Li (99.5 wt.%, 250 μm), Al (99.9 wt.%, analytical grade, 150 μm) and NaCl (99.8 wt.%, analytical grade, 140 mm) are used as the starting materials for the preparation of an Al–Li alloy by the ball-milling method. Ball milling was performed in a planetary ball miller (Qm-1SP-2, Nanjing University Instrument Plant, China) equipped with 500-ml stainless steel milling jars and steel balls measuring 4–5 mm in diameter. In each experiment, 20-g mixtures of Al–20 wt.%Li, Al and NaCl combined in different ratios and approximately 200 g steel balls were charged into the jars. During the process of ball milling, the rotational milling speed was maintained at 40 Hz, and the milling time was varied from 0.5 h to 4.0 h. Scanning electron microscopy (SEM, JSM-5600, JEOL, Japan) was used to observe the surface morphology of the samples.

The hydrogen generation reactions of the Al–Li alloy were carried out in a plastic reactor with a capacity of 50 ml. In each experiment, 0.2 g of Al–Li alloy powder was first placed in the reactor. Then, 20 ml of water was charged into the reactor. The generated H_2 was cooled in a water bath at room temperature and dried in a pipe filled with CaO. The volume of H_2 gas was measured by the water-displacement method, which was described in our previous study [24]. A drawing of the experimental apparatus was also presented in a previous study [25]. Under 1 atm of pressure and at 25 °C, the volume of 1 mol H_2 is 24.45 L. When 0.2 g Al–Li alloy containing a% of Al and b% of Li reacts with water to produce H_2, the hydrogen yield is calculated as follows:

$$\text{Hydrogen yield}/\% = \frac{\text{volume of generated } H_2}{[(a\%/27) \times 1.5 + (b\%/6.9) \times 0.5] \times 24.45 \times 0.2}\% \quad (1)$$

In the experimental process, water with different initial temperatures and different salt solutions reacted with Al–Li alloy to produce H_2. Additionally, the Al–Li alloy was also used to produce H_2 after being placed in the solution for different amounts of time.

3. Results and discussion

3.1. The hydrogen generation of Al–Li alloy with a low Li content

Fig. 1 presents the hydrogen-generation curves of Al–Li alloys with different Li contents, ball-milled for different times and