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Hydrogen generation by the hydrolysis of magnesium–aluminum–iron material in aqueous solutions

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ABSTRACT

Highly activated Mg–Al–Fe materials are prepared from powder by mechanical ball milling method for hydrogen generation. The hydrolysis characteristics of Mg–Al–Fe materials in aqueous solutions under different experimental conditions are carefully investigated. The results show that the hydrolysis reactivity of Mg–Al–Fe material can be significantly improved by increasing the ball milling time and Fe content. The increase of NaCl solution concentration and initial temperature is also found to promote the hydrogen generation reaction. At 25 °C, the Mg₆₀–Al₃₀–Fe₁₀ (wt%) material ball-milled for 4 h shows the best performance in 0.6 mol L⁻¹ NaCl solution, and the reaction can produce 1013.33 ml g⁻¹ hydrogen with a maximum hydrogen generation rate of 499.50 ml min⁻¹ g⁻¹. In comparison to NaCl solution, natural seawater is found to have an inhibiting effect on the hydrolysis of Mg–Al–Fe material. Especially, the presence of Mg²⁺ and Ca²⁺ in seawater can greatly reduce the hydrogen conversion yield, and the SO₄²⁻ can decrease the hydrogen generation rate.

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Introduction

Hydrogen is widely considered to be a promising alternative to traditional energy in the future because of its high calorific value and clean combustion. It is an ideal energy source for fuel cells, which can convert the chemical energy of hydrogen into electricity without pollution [1–3]. However, hydrogen, as a secondary energy, must be produced from other energy sources. Currently, most industrial hydrogen production

methods are based on fossil fuels, such as steam reforming of natural gas [4–6]. However, there are some limiting factors deter their applications, such as low conversion, high cost and environmental pollution. Additionally, the use of hydrogen energy is largely restricted by the safety and low efficient hydrogen storage. Therefore, the development of new methods for compact and convenient hydrogen sources is becoming increasingly important to the large-scale commercialization of fuel cells [7,8].

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Many studies have been focused on the hydrogen production from the hydrolysis reaction of light metals. In this regard, Mg and Al alloys are primarily considered for reasons of reactivity, economy and "greenness" [9,10]. Metals, such as Mg and Al, are so active thermodynamically that they readily corrode in water with hydrogen evolution. Furthermore, in this process, the hydrogen storage is no longer needed and the corresponding cost will be reduced. Thus, Mg and Al alloys have great potential to provide on-board hydrogen for fuel cells. The hydrolysis reactions of Mg and Al with water can be generally described as follows [11,12]:



However, under mild conditions, the reaction of Mg and Al with water is limited and the production of hydrogen is therefore only to a negligible extent. This is because that the passive layers (the metal oxide or hydroxide) formed on the metal surface can prevent the contact between metal and water. As a result, the hydrogen generation reaction is blocked. Therefore, in order to achieve a high hydrogen production, much effort has been devoted to overcome this problem for many years.

Ball milling process has been demonstrated to be an effective method to improve the reactivity of Mg and Al alloys. Mg–10 wt% Ni material after ball milling for 0.5 h were found to react completely in 1 M KCl aqueous within an hour reaction [12]. Mg-based powders ball-milled with chlorides (KCl, LiCl, NaCl, AlCl_3 , and MgCl_2) were investigated, and the 6 h milled Mg–3 mol% AlCl_3 showed the best performance with a hydrogen yield of 93.86% and an initial hydrogen generation rate of $455.9 \text{ ml min}^{-1} \text{ g}^{-1}$ [13]. Al-based powders mechanical alloyed with low melting point metals [14–16], active metals [17–19] and inorganic additives [20–23] have also been reported to display higher hydrolysis reactivity than un-milled Al powder. Furthermore, hydro-reactive material of Mg–Al–Co–Bi alloy was successfully prepared using high-energy ball milling [24]. The hydrolysis reaction is immediately noticeable in seawater that can generate $397 \text{ ml min}^{-1} \text{ g}^{-1}$ of hydrogen in the first two minutes with a hydrogen conversion yield of 97.1%. This type of Mg–Al-based alloy is believed to have great value in the production of hydrogen. However, alloying with high-priced metals Co and Bi in the preparation process not only increases the cost but also make the recycling more difficult for complex hydrolysis product. Moreover, reports on the hydrolysis characteristics of Mg–Al-based alloy are still insufficient. Therefore, a lot of work is still needed to be done for this material.

According to the research of Wang et al. [25], the 0.5 h milled Mg–10 wt% FeCl_3 material was found to have outstanding hydrolysis properties. This is attributed to the effective micro-galvanic cells formed between Mg and Fe elements. In the hydrolysis of Al–Fe alloy, Fe was also reported to accelerate the hydrogen generation by inducing both intergranular and galvanic corrosion simultaneously [26]. Therefore, Fe is expected to be an effective additive to promote the hydrogen generation of Mg–Al-based material in aqueous solution.

In the present work, Fe was selected as the catalyst to activate Mg–Al-based material, which has very cheap price and plentiful reserve on the earth. A new hydrogen generation material, Mg–Al–Fe material, was successfully prepared by a ball milling method. The main purpose of this study was to improve the reactivity of Mg–Al–Fe materials, and to study the reactive properties of these materials in aqueous solutions. Keeping in mind the salinity of seawater (35 g dm^{-3}), the 0.6 mol L^{-1} NaCl solution in a similar concentration of seawater was chosen as the starting solution for hydrogen production experiments.

Experimental

Materials

Mg powder (99.8 wt% purity), Al powder (99.9 wt% purity), and Fe powder (99.9 wt% purity) were used as the starting materials. Stearic acid (99.9 wt% purity) was used as the milling-assisted agent and 1 wt% of it was mixed with the metal powders in an argon-filled glove box prior to milling process. Ball milling was performed in a planetary ball mill (QM-1SP-2, Nanjing University Instrument Plant, China) under argon atmosphere, equipped with stainless steel jars 100 ml and steel balls 6 mm in diameter. Ball to powder mass ratio was kept 20:1 and milling speed was maintained at 450 rpm. Distilled water was used to prepare the aqueous solutions. Seawater was directly sampled in "Baicheng coast" of Xiamen and then kept at room temperature. The tested solutions were freshly prepared before performing the H_2 generation experiments.

Hydrogen measurement

The method used for the hydrogen measurement was described in previous study [22]. The hydrolysis reaction was performed in a 250 ml flask reactor that has two openings: a water inlet and a gas outlet. 0.3 g powders and 100 ml selected aqueous solution were used for each test. Hydrogen measurement started immediately when the powders came into contact with the solution. The conversion yield (%) was defined as the volume of generated hydrogen over the theoretical H_2 yield at 25 °C and 1 atm. The hydrogen generation rate was calculated by differentiating the measured hydrogen volume over reaction time. The theoretical hydrogen generation amount of 1 g Al (or Mg) is 1360 ml (or 1019 ml) at 298 K and 1 atm.

Analysis and characterization methods

X-ray diffraction (XRD) studies were carried out in an X-ray diffractometer (D/MAX-Ultima IV, RIGAKU Corporation, Japan). Microstructure studies were performed using the scanning electron microscopy (SEM, SU-70, HITACHI, Japan), equipped with AZTEC energy dispersive X-ray spectroscopy (EDS) measurements. The solid hydrolysis product in the reactor was collected by removing solution through a filter and then dried under vacuum at 50 °C for 24 h after being rinsed with distilled water for three times. The temperature of

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