Energy 84 (2015) 714–721

Contents lists available at ScienceDirect

Energy

journal homepage: www.elsevier.com/locate/energy

Investigation on the improved hydrolysis of aluminum–calcium hydride-salt mixture elaborated by ball milling

Yongan Liu [a], Xinhua Wang [a, b, *], Haizhen Liu [a], Zhaohui Dong [a], Shouquan Li [a], Hongwei Ge [a], Mi Yan [a, *]

[a] State Key Laboratory of Silicon Materials, Department of Materials Science and Engineering, Zhejiang University, Hangzhou 31007, China
[b] Key Laboratory of Advanced Materials and Applications for Batteries of Zhejiang Province, Zhejiang University, Hangzhou 310027, China

ARTICLE INFO

Article history:
Received 10 November 2014
Received in revised form
9 March 2015
Accepted 11 March 2015
Available online 31 March 2015

Keywords:
Hydrogen generation
Aluminum
Calcium hydride
Salts
Ball milling

ABSTRACT

A novel Al based hydrogen production material is prepared by high energy ball milling using Al, CaH_2 and different salts as the starting materials. The parameters affecting the Al–H_2O reaction are investigated and discussed. Among the salts added, $NiCl_2$ shows the best activation capability. The addition amount of both CaH_2 and $NiCl_2$ is found to be an important factor affecting the hydrolysis process during which a kind of hydrocalumite, $Ca_2Al(OH)_6Cl(H_2O)_2$, is generated and facilitates the removal of the by-product layer. Milling time can also generate significant impacts on the hydrogen generation performances of the mixture and 3 h proves to be the optimum choice in this work. The 3 h milled Al-10 mol% CaH_2-10 mol% $NiCl_2$ sample shows a hydrogen yield of 92.1% and mHGR (maximum hydrogen generation rate) of 1566.3 ml min^{-1} g^{-1}. A preliminary study is carried out to understand the optimization mechanisms.

1. Introduction

Hydrogen is a clean energy carrier and has been considered to be a promising candidate to replace traditional fossil fuels in the future [1,2]. With its high energy density and eco-friendly by-product, hydrogen can serve as a perfect energy source for proton exchange membrane fuel cells which could then be used in vehicles, portable devices and so on [3–5]. And before the wide application of hydrogen energy, finding a proper technique to produce hydrogen becomes a key issue. Contemporary hydrogen production methods mainly involve water electrolysis [6] and steam reforming [7]. However, the low conversion efficiency, high cost, as well as the non-clean preparation process render these methods unsuitable for onboard hydrogen production [8]. The generation of hydrogen from $NaBH_4$ hydrolysis once attracts scientists' attention and many works have been published [9–12]. However, $NaBH_4$ has recently been banned for hydrogen generation for its high cost, limited solubility, necessity of expensive catalysts, etc. [13].

Nowadays, hydrogen production from the hydrolysis of the light weight metal Al is believed to be promising [1]. Al is the most abundant metal in the earth's crust [5], and is of low cost (approximate US$3 kg^{-1}). The reaction between Al and water is expressed as below:

$$2Al + 6H_2O \rightarrow 2Al(OH)_3 + 3H_2 \quad \Delta H = -444.1\ kJ/mol \tag{1}$$

According to Eq. (1), 1 g of Al will generate 0.11 g of hydrogen, showing a high theoretical hydrogen capacity. What's more, the by-product is environmental friendly and can be fully recovered through Hall–Héroult process. Nonetheless, the main problem existing in the hydrolysis of Al is that the by-product $Al(OH)_3$ will cover the surface of Al and block the Al–H_2O reaction. In order to overcome this problem, many different methods have been proposed. A common way is to place aluminum into caustic solutions [14–16]. Belitsku [17] studied the reaction of Al with NaOH almost forty years ago and believed that the hydrolysis of Al provided an inexpensive, compact source of hydrogen. However, the required amount of alkaline was said to be 1.5 g NaOH/g Al, and the highly caustic environment could do harm to the fuel cell equipment. Amalgamation is also an effective method to promote the Al–H_2O reaction [18,19]. Parmuzina et al. [20] activated Al with eutectic Ga–In (70:30) and Ga-In-Sn-Zn (60:25:10:5). The mixture reacted

* Corresponding authors. State Key Laboratory of Silicon Materials, Department of Materials Science and Engineering, Zhejiang University, Hangzhou 31007, China. Tel./fax: +86 571 8795 2716.
E-mail addresses: xinhwang@zju.edu.cn (X. Wang), mse_yanmi@zju.edu.cn (M. Yan).

http://dx.doi.org/10.1016/j.energy.2015.03.035
0360-5442/

with water intensively and almost completely. Besides, Al alloys formed by ball milling with other metals also proves to be effective [3,21]. Fan et al. [22] prepared Al–Bi alloys by ball milling and a conversion yield of 92.75% was achieved by Al-16 wt.% Bi composite in 1 M NaCl solution. The microgalvanic cells formed between the anode (Al) and cathode (Bi) was believed to be important in boosting the hydrolysis. Though the improvement is obvious, these Al based alloys require addition of expensive metals which could increase the cost.

However, hydride prove to be another useful additive, Soler et al. [23] found that a synergistic effect existed between Al and $NaBH_4$, suggesting a possibility that other hydrides might also promote the Al hydrolysis. Given that CaH_2 effectively improved the hydrolysis of $Mg_{17}Al_{12}$ hydride [24] and no literature has reported the hydrolysis of Al–CaH_2 system, CaH_2 was chosen to activate Al in this work. Considering the high cost and possible flammability of CaH_2, different salts are added into the mixture to maintain a relatively high hydrogen generation yield with less CaH_2 addition, as the hydrolysis of Al can be greatly optimized by milling with salts [25] as well. The mixture is prepared by high energy ball milling, and Al will act as the main fuel to generate hydrogen. However, the following comparative analysis will consider the overall performance of the mixture to choose the best one, not focus just on the hydrolysis properties of Al powder. The effects of preparation parameters on the hydrogen generation are investigated and preliminary mechanistic study is carried out for better understanding of the observations. The novel Al–CaH_2-salts mixture has not been reported elsewhere and proves to be an efficient hydrogen generation system which provides a new idea for the contemporary hydrogen production technology.

2. Experimental

Al (Sinopharm Chemical Reagent Co., Ltd, 99.0%, 100–200 mesh), CaH_2 (Sigma Aldrich, 95%), $NiCl_2$ (Alfa Aesar, 98%), and KCl, NaCl, LiCl and $MgCl_2$ salts (Sinopharm Chemical Reagent Co.,Ltd, AR, ≥99.5% purity) were used as received. Samples were weighed and mounted into special stainless pots in an Ar filled glove box with a recirculation system. Ball milling was performed with a planetary QM-3SP4 ball miller. There were 13 stainless steel balls in all with 4 big ones (dia. 1 cm) and 9 small ones (dia. 0.6 cm). The ball-to-powder weight ratio was 25:1 and the rotational speed was set at 400 rpm.

The hydrolysis equipment is similar to what was described in a previous work [26]. Briefly speaking, the experimental setup is composed of six apparatus: reaction flask, water bath, condenser, desiccator, flow meter and a computer. A transparent plastic pipe is used to connect the different facilities to makes sure that the whole setup is airtight during the hydrolysis process. The Al–H_2O reaction was carried out in the 250 ml flask which was dipped into a water bath to maintain a constant temperature (75 °C). The temperature of 75 °C was chosen because this value was close to the working temperature of a polymer electrolyte membrane fuel cell [9]. 50 mg of Al powder was reacted with 10 ml of water. Hydrogen generated was flown through a spiral condenser and a tube filled with CaO to remove water vapor. Then the hydrogen flow was tested by a flow meter (ADM 2000, Agilent Technologies) which was connected to a computer to record the data. The background flow that was measured without addition of samples was subtracted from the data, and values obtained were converted to those under the standard situation (273 K, 1 atm) using the ideal gas equation. Each test was repeated at least twice to make sure that the results has good reproducibility. The hydrogen production yield (%) was defined as the volume of generated hydrogen over the theoretical value, assuming that the hydrogen was completely released. The mHGR (maximum hydrogen generation rate) was the largest volume of hydrogen generated per minute per gram composite. The HG (hydrogen generation) curves within the first hour were presented and discussed in this work.

XRD (X-ray diffraction) analysis of the mixture and hydrolysis by-product was carried out using an X'Pert PRO diffractometer with Cu Kα radiation. The microstructure of powders and distribution of different elements were characterized using a SIRON SEM (scanning electron microscope) equipped with INCA EDS (energy dispersive X-ray spectroscopy) measurements.

3. Results and discussion

3.1. Effects of different salts addition

Fig. 1 shows the hydrogen generation curves of Al-10 mol% CaH_2 milled with 10 mol% salts for 1 h. As can be seen from the picture that hydrogen generation starts immediately when the mixtures contacts with water. The hydrolysis enters an induction period after the initial quick reaction, which is different from the usual 3-stage reaction mechanism proposed by Dupiano et al. [27]. This difference probably results from the high energy ball milling process adopted in this work, which is known to be able to activate materials by changing the sample's microstructure, redistributing the constituents and inducing severe plastic deformation and defects [28]. In a word, Al powder is well activated after the milling process and can react with water directly. Meanwhile, CaH_2 is easier to hydrolyze than Al and additional hydrogen will be generated, which actually cannot be quantified exactly. To simplify this situation, the discussion will uniformly focus on the hydrogen generated per gram of mixture. Different salts seem to affect the hydrolysis differently. $NiCl_2$ shows the best performance with the hydrogen yield to be 88.8% and mHGR of 1900 ml min^{-1} g^{-1}, while LiCl has the minimum effect with the yield to be 74.6%. It has been reported [25] that NaCl can greatly promote the hydrolysis of Al by creating salt gates. These salt gates are claimed to be formed by the dissolution of NaCl that was embedded into Al grains during the milling process, leaving many holes or gates for water to penetrate through. However, the required salt to aluminum ratio is 1.5 which is much higher than that of this work. This could be one of the reasons why the sample with NaCl addition shows a lower yield of 79.4%. Besides, the activation mechanism could also be different, which will be discussed below. Although $NiCl_2$ (approx. US$1.46 g^{-1}) is more expensive compared with other salts, it is still cheaper than CaH_2 (approx. US$2.13 g^{-1}) and the mixture will be

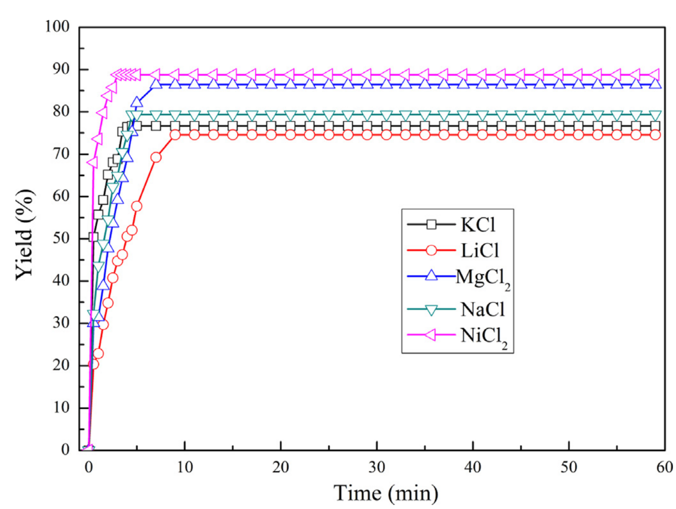

Fig. 1. Hydrogen yield of Al-10 mol% CaH_2 milled with 10 mol% different salts for 1 h.