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Enhancement of hydrogen generation using waste aluminum cans hydrolysis in low alkaline de-ionized water

*Ching-Yuan Ho**, *Chi-Hang Huang*

Dept. of Mechanical Engineering, Chung Yuan Christian University, Chung-Li, Taiwan

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ABSTRACT

In this study, hydrogen generation using hydrolyzed waste aluminum can in low alkaline aqueous solution is evaluated and the result is efficient in comparison with Al powders. Waste Al can was pretreated using a series of methods, such as paint removal in concentrated sulfuric acid and fragmented Al pieces in planetary ball milling, and then characterized with BET, XRD and SEM techniques. During hydrogen generation, low alkaline solution combined with elevating temperature and Ni or Ni/Bi additives in waste Al can-water hydrolysis system could achieve rapid hydrogen generation rate to 150 ml s^{-1} g^{-1} and total volume 1350 ml g^{-1}. Moreover, planetary ball-milling of waste Al scraps could increase effective reactive area to improve generated hydrogen. The optimized results, which are attributed from micro-galvanic cell formation between Al/Ni closely contact, and accelerating reaction activity, are comparable with Al powders. In this report we successfully optimize the generated hydrogen efficiency of waste Al can base without high alkaline concentration which could cause environmental pollution and instrument damage problems.

Introduction

Aluminum is the most abundant metal in the earth and inherently provides light and better electrical conductivity property which has been widely used for drinking can and transmission line in IC device. Therefore, to recycle these waste Al materials, on the other hand, is emerged as interesting topic for both economic efficiency and environmental pollution consideration. Recently, eco-friendly green energy product, hydrogen gas used for fuel cell has been proven to be cleanest and appropriate for portable products. Different methods for hydrogen extraction, including biological [1], water electrolysis [2] and chemical methods [3], have been proposed but each of them has its own disadvantages such as high cost, low efficiency [4] and the production of carbon dioxide [5]. Because Al inherently provides light and is economic properties, 1 g of Al can theoretically produce 1360 ml of H_2 in ambient conditions, according to the reaction:

$$2Al + H_2O \rightarrow 2Al(OH)_3 + 3H_2$$

These by-products of aluminum hydroxide produced from a hydrolysis process do not create carbon dioxide and environmental pollution. Besides, the reacted by-product of

* *Corresponding author*. 200, Chung Pei Rd., Chung-Li, 32023, Taiwan. Tel.: +886 3 2654321; fax: +886 3 2654399.
E-mail address: cyho@cycu.edu.tw (C.-Y. Ho).

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aluminum hydroxide after the Al-water reaction is eco-friendly and can be widely used in water treatment, fire inhibition and paper making. Therefore, it has been proven to be the best candidate for hydrogen generation [6]. Although there are many benefits for hydrogen generation in an Al-water reaction, however, a critical issue to limit the efficiency of hydrogen generation is the formation of a dense oxide film which further protects the aluminum surface against the continuation of Al corrosion and limits hydrogen production. Therefore, the major challenge is to remove the passive oxide on the Al surface for the enhancement of Al's continuing reaction with water. It is well-known that the function of alkaline aqueous solution usually acted as catalyst role to dissolve the oxide film by the chemical reaction. Alkali aqueous (e.g. NaOH) usually acts as the catalyst to eliminate the oxide film by the chemical reaction between OH^- and Al_2O_3 or $Al(OH)_3$. The formed $Al(OH)_4^-$ dissolved in alkaline aqueous solution and then the fresh Al surface allows the aluminum–water reaction to continuously proceed [7]. However, the use of the strong alkali solution causes the corrosion and environmental pollution.

Recently, many approaches have been developed to improve the efficiency of hydrogen generation, which are used to disrupt the passive oxide film and continuously retain the Al-water split reaction. These methods include preparation of activated aluminum by the addition of a metal [8], metal oxide additives [9,10] and immersing the aluminum in an alkaline solution [11]. The Al-water system is essentially an exothermic reaction, so the temperature control has been reported to enhance the efficiency of hydrogen generation [12]. In particular, the ductile NaCl particles enable the fraction of micrometer-sized brittle Al particles to enlarge effective surface area. Therefore, activated aluminum particles milled with inorganic NaCl, which acts as a milling assistant agent, can increase the contact possibility of Al-water by the salt-gate effect [13,14]. Besides, the conductivity in the Al-water system, due to the dissolving of NaCl particles and the effect of the Al/metal micro-galvanic cell, have been explored to improve efficiency of hydrogen generation [15–17]. Besides, Al particles, milled with other metallic oxide additives using TiO_2, Co_3O_4, and Cr_2O_3 nanocrystals as effective modifiers for the production of hydrogen, are considered to be a pitting mechanism originating from point defects but additional cost has to be considered [10]. An Al-water reaction in an alkaline solution is another important method used to dissolve the passive oxide layer on the Al surface with a generation rate approaching 2.9 L/min per gram of Al with 100% yields. However, these alkaline additions could also accelerate the reactor's corrosion; thus, it is not a suitable method for hydrogen generation [18–20]. Although, improvements of these aforementioned features for the water split reaction, including temperature effect, change of pH value and the addition of an additive to the Al-water reaction system, have been individual reported [21,22] but the combination of all helpful parameters to enhance the efficiency of hydrogen generation in Al-water system is never reported. Therefore, it is of interest to understand not only the mechanism of Al/NaCl mixtures reacted with water but optimize the approach for the enhancement of hydrogen generation.

In this paper, the mechanical milling to create effective surface reactive area, temperature effect during hydrolyte reaction, micro-galvanic cell by Ni/Bi additives and lower alkaline solution are all considered to achieve the highest hydrogen generation rate and excellent efficiency of total hydrogen volume. The controlled factors during oxidation between Al-water interfaces are analyzed using the linear parabolic law [23]. The vibration function in a reaction period is added to enhance the hydrogen generation. Polarization curves are used to estimate the capability of corrosion capability and reliability for Al powders and waste Al can.

Experimental details

Both High purity of Al powders (99.5%, particle size <45 um, Alfa Aesar) and wastes Al can mixed with NaCl (99.5%, 0.5 mm, Taiyen Biotech) were used as ball milling materials and then reacted with DI water for hydrogen generation. The original thickness of Al can is 0.18 mm–0.20 mm and is fragmented after ball milling. There were three mechanically milling methods to fracture the Al powders including planetary type of ball milling (PM), roll type of ball milling (RM) and hand grind (HG). In planetary milling process, ball-to-powder weight ratio was 10:1 and salt to aluminum weight ratio was taken to be 1.0. All of the mixtures were taken out in a glove box filled with 0.4 MPa argon atmospheres and rotated at 300 rpm for 5 h by planetary type of stainless steel ball milling jar with inner radius of 4.5 cm and volume of 50 ml. Roll type of ball milled with rotated at 180 rpm for 24 h and grind by hand. After the milling process, an appropriate mass of mixtures containing 0.5 g Al was added in 100 ml flask with 50 ml distilled water at a different temperatures ranging from RT to 70 °C. The flask was placed in a water bath to keep it at constant temperature and add vibration function to enhance the reacting performance. The generated hydrogen was collected in an inverted burette full of water at room temperature and volume of produced hydrogen was recorded directly as a function of time. In order to evaluate the mechanism of surface oxidation rate, an Al ball with 0.5 mm diameter instead of Al powders was simulated in similar environment of hydrogen generation and observed the mechanism of oxidation limit affecting growing thickness.

The specific surface area of the powders was determined through nitrogen adsorption using Brunauer–Emmet–Teller method (BET). The nitrogen adsorption/desorption isotherm is used to quantify the surface area of the activated Al particles. The morphology of various mechanical fractures were characterized by scanning electron microscopy (FESEM, JEOL 7600 F) equipped with energy dispersive x-ray (EDS) measurement and the remaining compositions of reacted Al powders were identified by X-ray diffraction (XRD) using a Philips 3710W X-ray diffractometer with CuKa ($\lambda = 1.54184$ Å) at a scanning rate of 2°/min from $2\theta = 20°–80°$ radiation. For the evaluation of Al powders and wastes Al can corrosion capability, the polarization curves were measured on a CHI 600 with scanning rate of 0.01 V/sec using three electrodes; Aluminum as working electrode, Pt as the auxiliary electrode and Hg/Hg_2Cl_2 as the reference electrode.