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Hydrogen production by hydrolysis of aluminum

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ABSTRACT

Hydrogen production using the hydrolysis of aluminum is studied. The used aluminum cans are pretreated with different methods, such as mechanical rubbing, soaking in concentrated sulfuric acid and heat treatment, and characterized with XRD and SEM techniques. The results show that higher alkali concentration is benefit for the hydrolysis of aluminum, because the generated hydrogen bubbles on the aluminum materials prevent the precipitations from attaching on the reaction zones. Gibbsite and bayerite are present on the Al scraps surface. Pretreated Al scraps generate hydrogen much more quickly than sodium borohydride and un-pretreated Al scrap. The Al scrap pretreated with mechanical method releases hydrogen faster, while the Al scrap dealt with calcination method generates more hydrogen than other Al scraps. The area of exposed aluminum matrix and the sizes of aluminum particles are different with various pretreatment methods.

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1. Introduction

Hydrogen is considered as an effective and zero-emission alternative fuel for the internal combustion engine and fuel cells. Until now, there have been no effective, safe and economic hydrogen storage methods once considering the problems of the safety, capacity and refueling. Thus the onboard hydrogen generation has received considerable attentions recently.

Hydrogen can be produced from many resources, such as water, fossil fuels, and biomass. Currently about 95% hydrogen is generated from fossil-based raw materials and the most economical option to produce hydrogen is the steam reforming of natural gas [1]. But the reforming process has some drawbacks, such as the catalyst degradation and sensitivity, reformer start-up, and greenhouse emissions. It is reported that approximately 2.5 tonnes of carbon is released as CO₂ for each tonne of hydrogen generated through the reforming method [2]. Large-scale hydrogen generation not base on fossil fuels is water electrolysis, but this method demands large amounts of power and the energy efficiency is very low too. The hydrolysis of sodium borohydride can generate about 10.6% mass hydrogen at moderate temperatures, but the disadvantages of this method are the high cost of sodium borohydride, the re-use of BaBO₂ byproduct and the synthesis of effective catalysts. In 2007, the U.S. Department of Energy (DOE) has made a no-go recommendation for sodium borohydride for on-board vehicular hydrogen storage [3]. Active metals, e.g. Mg and Al, can release hydrogen via the hydrolysis with water under mild conditions [4,5], which makes a real-time hydrogen generation possible. Aluminum has

been identified as a promising and ideal substance for the on-site hydrogen production. Aluminum can produce hydrogen directly in water with the following reaction.

$$2AI + 6H_2O \rightarrow 2AI(OH)_3 + 3H_2 \tag{1}$$

In the air or water, a dense protective oxide film is formed easily on the aluminum surface. This film is passive in the neutral aqueous solution, but it can dissolve in the alkaline aqueous solution. Then the bare aluminum matrix can react with alkaline and evolve large amounts of hydrogen at room temperature.

Aluminum can produce hydrogen approximately 1244 mL g⁻¹, which is more than magnesium (950 mL g⁻¹) and exceeds U.S. DOE targets of transportation fuels for 2010. Being a solid, aluminum is much safer and easier to be stored than chemical hydrides and other hydrogen carriers. The by-product of hydrolysis, namely sodium aluminate, can be directly used in water treatment, paper making, and so on. It can also be fully converted to aluminum hydroxide and then be used to produce aluminum through the Hall–Héroult process. The recycled aluminum, with the cost of about 1.8 g^{-1} [6], can be reused to the hydrolysis reaction without any loss in quality.

Shkolnikov et al. have assembled the 2 W power sources based on air–hydrogen fuel cells with water–aluminum micro hydrogen generator. The highest power density of the fuel cell was 101 mW cm⁻² and the electrical energy was about 1.2–1.8 W h per gram of Al in micro-generator [7]. Shi et al. have designed a mini-type hydrogen generator, which can stably operate a single cell under 500 mA for nearly 5 h with about 77% hydrogen utilization ratio [8]. Kundu et al. have developed two different types of micro flow reactors of aluminum hydrolysis. The maximum conversion of 78.6% and 74.4% with respect to aluminum were



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achieved when water entering in the reactor was vaporized partially and liquid water, respectively [9].

Aluminum cans are one of the most common package items and more than 80% of Al in the municipal solid waste is Al cans [10]. Producing hydrogen with used aluminum cans will save natural resources and reduce greenhouse gas emissions. Hiraki et al. have proposed that the energy requirement of waste aluminum-based hydrogen generation is only 2% and the amount of CO_2 emission is 4% of the conventional method [11]. But the used aluminum cans are usually coated with a colorful and thick paint film, which inhibits the contact between the reactants and delays hydrogen evolution.

In this study, the concentrations of sodium hydroxide solutions and the pretreated methods of the used cans, such as mechanical rubbing, dissolution extraction and heat treatment, are investigated.

2. Experimental

2.1. Materials

Aluminum powder (99.0% purity), aluminum foil (99.9% purity) and sodium borohydride (98.0% purity) were supplied by Tianjin kermel chemical reagent Co. Ltd. Sodium hydroxide solutions with different concentrations were prepared with distilled water. Al scraps were obtained from used beverage cans of Sprite, a beverage brand of the Coca-Cola Company. The used aluminum can was first cut off both ends and the rest was then cut into small slices. The un-pretreated Al slice was denoted as Al scrap-1. To remove the lacquer and coated plastics, the Al scraps were treated with different methods and denoted as Al scrap-2 to Al scrap-4. The Al scrap-2 was calcined at 500 °C for 20 min and the Al scrap-3 was mechanically polished with abrasive papers. The Al scrap-4 was dipped into the concentrated sulfuric acid for two minutes to eliminate the coating layer. The used aluminum cans of other popular soft drink brands, such as Fanta, 7-up and pineapple beer, were investigated too, but all these Al scraps were pretreated with the same pretreatment method as the Al scrap-4 mentioned above.

2.2. Apparatus and measurements

The given weighted Al foil or Al scrap is placed into a 250 mL round-bottomed flask and 100 mL NaOH aqueous solution is fed into the flask quickly. The produced hydrogen is collected by an upside down burette cylinder filled with water. The cumulative hydrogen amounts are measured by the volumes of water displaced from the cylinder. The absolute measurement error of the hydrogen volume is 0.5 mL. The hydrogen generation rate refers to the volume of hydrogen generated in unit minute per unit mass of the reactant.

X-ray diffraction analysis was performed on the XD-3 diffractometer with Cu K α radiation, operating at 30 kV and 20 mA. SEM analysis was carried out on the ISM-6360LA scanning electron microscope at the voltage of 10 kV.

3. Results and discussions

3.1. Hydrolysis of waste aluminum

Fig. 1 shows a comparison of hydrogen generation in different NaOH solutions. It is seen that the hydrolysis reaction rates of un-pretreated Al scraps are very slow. The total volumes of hydrogen evolved in different NaOH solutions are much lower than the theoretical values due to the presence of coating layer. Higher hydrogen evolution rates and yields are obtained at higher NaOH solution concentrations. With increasing the concentration of NaOH solution from 1.0 M to 5.0 M, the amount of hydrogen generated increases from 117.1 mL $g^{-1}\,$ to 360.8 mL $g^{-1}\,$ after 1 h hydrolysis, corresponding to the hydrogen generation rates of 1.9 mL min⁻¹ g⁻¹ and 6.0 mL min⁻¹ g⁻¹, respectively. It is noticed that there are some effervescence regions on the surface of aluminum scraps during the course of hydrolysis. As Andersen said [12], sodium hydroxide, acting as the catalyst for the hydrolysis of aluminum, promotes the evolution of hydrogen and the generated bubbles prevent the precipitation from attaching on the reaction zone. Thus higher NaOH concentration causes an increase of the effervescence regions on the aluminum matrix.



Fig. 1. The curves of hydrogen generation of Al scrap-1 in different NaOH solutions.



Fig. 2. Effects of pretreatment of used Al cans on the hydrogen generation.

The effects of different pretreatment methods on the hydrolysis of Al scraps are shown in Fig. 2. It is found that the hydrogen volume of un-pretreated Al scrap-1 at 5 min is only 20 mL g^{-1} in 1.0 M NaOH solution, while the amounts of Al scrap-2, Al scrap-3 and Al scrap-4 can reach 302, 344, 354 mL g⁻¹, respectively. The hydrogen evolution rates of pretreated Al scraps are much higher than those of un-pretreated Al scrap. The Al scrap treated with mechanical method (Al scrap-3) releases hydrogen more quickly than those pretreated with other two methods. The Al scrap immersed into the concentrated H₂SO₄ (Al scrap-4) has a higher initial hydrolysis rate than the calcined Al scrap (Al scrap-2) in the first eight minutes. The total volume of hydrogen generated of Al scrap-2 is more than those of other Al scraps. It was cited that annealing of the aluminum-based metal composites at 450 °C led to the redistribution of the components in the solid phase [13], which may be promote the complete hydrolysis of Al scrap-2. Increasing the concentration of NaOH solution enhances the hydrogen generation of pretreated Al scraps, too. The tendency of hydrogen evolution for the Al scraps pretreated with various methods in 1.0 M NaOH solution is same as that in 1.5 M NaOH solution.

Chemical hydride, such as MgH₂, NaBH₄, can be used as a storage medium for hydrogen, recently. NaBH₄ and different aluminum materials, i.e. Al powder, Al foil and Al scraps, are applied into the hydrolysis and the results are present in Fig. 3. It shows that Al powder releases hydrogen most quickly, followed by Al foil. The hydrogen volume and the hydrolysis reaction rate of NaBH₄ are



Fig. 3. Comparison of hydrogen evolution curves obtained for different materials at 45 °C. -■-Al scrap-1; -▲-Al Scrap-2; -●-Al Scrap-3; -△-Al Scrap-4; -○-Al foil; -★-Al powder; -□-NaBH₄



Fig. 4. Hydrogen evolution curves obtained for different used cans in 1.5 M NaOH solution.

lower than those of pretreated Al scraps. The rates of hydrogen generation diminished in the following sequence: Al powder > Al foil > pretreated Al scraps > NaBH₄ > un-pretreated Al scrap. It may be because various aluminum materials have different surface areas, which are related to the contact interface between aluminum and alkali solution. The painting layers of the pretreated Al scraps may not be removed completely, so the yields of hydrogen are smaller than those of Al powder and Al foil.

Other waste Al cans with the brands of Fanta, 7-up and pineapple beer are used to produce hydrogen and the obtained hydrogen evolution curves are compared in Fig. 4. It is found that the hydrogen generation curves of various Al used cans have the same tendency. The volumes of hydrogen produced increase rapidly at the initial reaction stage and then become slow with further reaction. The rates and total volumes of hydrogen obtained from the four Al scraps are not much difference, which shows the universality of hydrogen production with various Al used cans.

3.2. Characterization of different aluminum materials

The Al scraps after hydrolysis for 15 min are characterized with XRD technique and the spectra are shown in Fig. 5. For comparison, the XRD patterns of Al foil and its precipitation after hydrolysis



Fig. 5. XRD spectrum of different Al materials after hydrolysis.

reaction are displayed in Fig. 5, too. The patterns of the Al scraps exhibits the diffraction peaks of aluminum crystal at 38.5° , 44.7° , 65.1° and 78.2° . The main peaks of gibbsite at 18.3° , 20.3° , 20.5° and 37.7° , and the peaks of bayerite at 18.8° , 20.4° , 40.6° and 53.1° are present, too. It shows that the coexistence of Al(OH)₃ and aluminum on the Al scraps after hydrolysis for 15 min. The passive Al(OH)₃ layer reduces the hydrogen yields and the rates of hydrolysis reaction, which can be confirmed by the hydrogen evolution curves in Fig. 3.

Fig. 6 presents the morphologies of Al scraps pretreated with different methods. It can be seen that the surface of Al scrap without pretreatment is covered by a layer of dense paint, which hinders the contact between sodium hydroxide and aluminum (see Fig. 6a). After calcination, the coating on the Al scrap wrinkles and peels from the surface (see Fig. 6b), thus some Al particles covered with painting previously are exposed and alkali solution can penetrate into the gap between the coating and Al matrix. Most of the paint layer on the polished Al scrap is removed and Al matrix as well some Al grains is exposed (see Fig. 6c). The coating of the Al scrap pretreated with concentrated sulfuric acid is extracted effectively. A small part of Al matrix is present and a new dense layer appears on the rest surface of Al scrap-4 (see Fig. 6d), which is because that aluminum reacts with concentrated sulfuric and then produces a new protective layer. The exposed Al matrix is the effervescence region and the initial contact area of the reactants. The area of the exposed Al matrix decreases in the following order of Al scrap-3 > Al scrap-4 > Al scrap-2 > Al scrap-1 and this order is consistent with the sequence of the initial hydrolysis rates in Fig. 2.

The photographs of Al scraps after hydrolysis for 15 min are displayed in Fig. 7. It is shown that most of the paint on the un-pretreated Al scrap is still present even after hydrolysis for 15 min (see Fig. 7a), thus the hydrolysis rate is very slow in the whole period. Non-uniform Al grains and the surface cracks are present on the surface of calcined Al scrap (see Fig. 7b). It is reported that the surface cracks and interfaces are the regions for hydrolysis reaction because that the cracks may propagate much easier than the surroundings [14]. On the other hand, NaOH solution can flow through the cracks and react with the underlying aluminum matrix, too. In Fig. 7c, many fine spherical grains with about 0.5 μm diameters and flake agglomerates are observed for the polished Al scrap. For Al scrap-4, many agglomerations of small particles with an irregular geometry are showed in Fig. 7d. The naked Al particles of Al scrap-3 are smallest, followed by Al scrap-2 and then Al scrap-4. Compared with their hydrogen generation rates in Fig. 1, it is illustrated that the activities of the Al scraps in the later hydrolysis stage are related to the particle sizes of Al grains.



Fig. 6. SEM images of Al scraps pretreated with different methods. (a) Al scrap without pretreatment; (b) Al scrap calcined at 500 °C for 20 min; (c) Al scrap polished with abrasive papers; (d) Al scrap pretreated with concentrated sulfuric acid.



Fig. 7. SEM images of Al scraps after hydrolysis for 15 min. (a) Al scrap without pretreatment; (b) Al scrap calcined at 500 °C for 20 min; (c) Al scrap polished with abrasive papers; (d) Al scrap pretreated with concentrated sulfuric acid.

4. Conclusions

Higher alkali concentration facilitates the hydrolysis reaction, but the effect is not very significant. For un-pretreated Al scrap, the hydrogen generation rates are very slow. Pretreated Al scraps evolve hydrogen much more quickly than un-pretreated Al scrap and sodium borohydride. There are more naked aluminum matrix and fine spherical aluminum grains on the Al scrap treated with mechanical method, so this Al scrap releases hydrogen most quickly in the whole reaction stage. The amount of hydrogen generated for the Al scrap calcined with high temperature is more than that of other Al scraps. The used cans with different brands, e.g. Sprite, Fanta, 7-up, pineapple beer, exhibit the same performance of hydrogen generation. The particle sizes of Al grains and the area of bare Al matrix affect the rate of hydrolysis.

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