Journal of Electroanalytical Chemistry 799 (2017) 424–430

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

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

High-capacity silicon electrodes obtained from the hydrogen production process by aluminum alloy hydrolysis

Juan Yang[a], Yang Nie[a], Haochen Zhou[b], Jingjing Tang[c], Jiaming Zhang[a], Xiangyang Zhou[a,*]

[a] School of Metallurgy and Environment, Central South University, Changsha 410083, China
[b] School of Aerospace Engineering, Tsinghua University, Beijing 100084, China
[c] Department of Mechanical and Engineering, The Hong Kong Polytechnic University, Hong Kong, China

ARTICLE INFO

Keywords:
Al alloys
Hydrogen production
Silicon anode
Lithium-ion batteries

ABSTRACT

Silicon has been considered as one of the most promising anode materials for the next generation of lithium-ion batteries (LIBs) because of its ultrahigh theoretical capacity. However, not only its poor cycle stability and low coulombic efficiency, but also the high-cost, complex preparation methods present significant challenges for its commercialization. Hydrogen, an environmentally friendly and sustainable resource, can be used as fuel or reductant. In this study, we propose an effective strategy for the generation of hydrogen subsequent with the recovery of Si products (R-Si). The addition of Si in the initial Al alloy was demonstrated to be critical for the high-yield production of hydrogen via hydrolysis process. Si product was obtained subsequently by acid washing procedure. When the recovered Si was evaluated as anode material in LIBs, a high initial charge capacity of 3073 mAh/g at a rate of 150 mA/g was obtained. And it also showed excellent initial coulombic efficiency of 86% without any other modification. Furthermore, the R-Si could deliver a reversible capacity of 1735 mAh/g at 1.5 A/g after 100 cycles and have a reversible capacity of 521 mAh/g at 6 A/g. This work will provide referential significance for the research of hydrogen production with Al alloy and facile synthesis of Si anodes.

1. Introduction

High performance lithium-ion batteries (LIBs) have drawn much attention nowadays with the highlight of the energy depletion and environment issues [1,2]. It can be used in many fields like portable devices, electric vehicles and large energy storage systems [3–5]. With the increasing demand of LIBs, it is more important to develop new types of electrode materials with high energy density, long life and low cost. Compared with currently commercialized graphite anode materials with low theoretical capacity (372 mAh/g), silicon (Si) has attracted tremendous attention because of the ultrahigh theoretical specific capacity (3579 mAh/g) and low delithiation potential (< 0.5 V versus Li/Li^+),and has been regarded as one of the most promising anode materials for next-generation of LIBs [6–8]. However, the widespread application of Si anodes is hindered by its inherent issues, such as the huge volume changes during the lithiation/delithiation processes and low electric conductivity [8–12]. In order to overcome these problems, many researches have been done such as decreasing the dimension of Si into nanometers [13,14], designing reserved pores [15], compositing Si into carbon matrix [16–18], alloying with other metals [19] and so on. Candace K. Chan et al. [10] synthesized Si nanowires using the vapour–liquid–solid (VLS) template-free growth methods on stainless steel substrates, which demonstrated that the facile strain relaxation in Si nanowires could prevent structural failure, and the Si nanowires electrodes reached the theoretical charge capacity with little fading. Dae Soo Jung et al. [20] proposed a spray drying method to composite nano-Si into porous carbon, which can accommodate the volume changes of Si, and achieve 91% (1243 mAh/g) capacity retention after 150 cycles. Nian Liu et al. [21] used a magnesiothermic reduction to synthesize nano-Si from rice husks, an abundant agricultural byproduct, which delivered a high reversible capacity of 2790 mAh/g and remained 86% capacity after 300 cycles. However, most of the research results are difficult to be industrialized due to the expensive Si sources, high-cost and complex procedure or inability of large scale production.

From another point of view, hydrogen has been regarded as a clean, environment-friendly and alternatively energy source to substitute the non-sustainable fossil fuel [22]. Traditionally, hydrogen energy is come from reforming of nature gas, coal and oil and electrolysis of water. Biomass resources can also be used to produce hydrogen by thermochemical and biological processes. But these methods usually need large equipments or consume a lot of energy and cannot produce

* Corresponding author.
E-mail address: j-yang@csu.edu.cn (X. Zhou).

http://dx.doi.org/10.1016/j.jelechem.2017.06.049
Received 6 March 2017; Received in revised form 14 June 2017; Accepted 27 June 2017
Available online 28 June 2017
1572-6657/

hydrogen portably [23,24]. One of the most promising ways to produce hydrogen is to use aluminum or its alloys to reduce water or hydrocarbons to hydrogen [25]. Compared with the traditional approaches, the use of aluminum and its alloys is much safe, effective, and convenient for both hydrogen production and storage. Usually the dense Al_2O_3 layer coated on the surface of Al would prevent Al from further reaction with water [26]. For the continuous Al-water reaction under mild condition, metals such as Ga, In, Sn, Ca, Mg, Zn, Bi are introduced to Al to form alloy, which can destroy the oxide layer and can be recycled by further treatment [27–30].

In previous work, researchers used the Al-Si alloy, which has been widely applied in casting and powder metallurgy industries, to produce porous Si by simple acid-etching method [31–34]. However, to the best of our knowledge, there is no concern about hydrogen production combined with recovery of anode materials. During the typical acid-etching process of Al-Si alloy, the reaction rate of aluminum and acid is so high and uncontrollable that the resulting hydrogen can not be utilized, therefore the large amount of aluminum component in the alloy is dissolved in the solution without any economic value. Herein, we propose Al-Si alloy as the raw material to produce hydrogen due to its high specific surface area and favorable hydrolysis characteristics. The hydrolysis of the Al-Si alloy could not only produce the high-performance Si anode, but also collect hydrogen as a useful product, which can be deemed as an economic process for obtaining a diversity of high value-added products. The as-prepared Al alloy with Si showed better performance in the terms of hydrogen production efficiency and quantity compared with that without Si. Furthermore, the recovered Si (R-Si) after the hydrogen production exhibits high reversible capacity of about 1700 mAh/g at a rate of 1.5 A/g with an excellent initial coulombic efficiency (86%) without any modification when evaluated as anode material in LIBs. A remarkable reversible capacity of 521 mAh/g is maintained even at a high rate of 6 A/g.

2. Experimental

2.1. Synthesis of Al alloy, collection of hydrogen and recovery of Si

For a typical synthesis of Al alloy to produce hydrogen, Al-Si alloy powders (20% Si, $3000/ton, Changsha Tianjiu metal material company) were used as raw materials. As shown in Fig. 1a, Al-Si alloy powders, metal Ga, In and Sn with a mass ratio of 90:7:2:1 were cold pressed to alloy ingot precursor with 87 MPa of pressure after mixing and then sealed in an graphite crucible. The graphite crucible was place into a vacuum graphitizing furnace and heated to 800 °C for 3 h under the vacuum condition of $< 6.62 * 10^{-2}$ Pa. After cooling down to room temperature, the resulting product (Al alloy) was dissolved in deionized (DI) water to produce hydrogen. The yield of hydrogen generation by Al alloy was measured by a typical drainage gas-collecting method with a device shown in Fig. 1b. When the Al alloy samples in the spoon were dropped into water, reaction took place immediately and the water in gas burette would be drain away. The temperature, yield of hydrogen and reaction time were recorded immediately after adjusting the water in calibrated bottle and gas burette at the same level. The deposition was collected by filtration, washed by DI water and dried in oven.

For the recovery of Si, the deposition was immersed in 2 M HCl for 10 h to remove residual Al, Ga, In, Sn and $Al(OH)_3$ and washed for several times. Then the resulting product was immersed in 5% hydrofluoric acid for 1 h to remove SiO_2 with subsequent washing with DI water. The collected R-Si was dried in oven at 60 °C.

For comparison, micro-sized porous Si (MP-Si) was produced by a typical acid etching method. The Al-Si alloy powder was added into 2 M HCl solution slowly. The etching time was 24 h for remove Al completely. After filter, the deposition was immersed in 5% hydrofluoric acid for 1 h. Finally, after being washed several times with DI water, the powder was dried in vacuum at 80 °C.

2.2. Characterization

The microstructures of the samples were characterized by field emission scanning electron microscopy (SEM, Nova NanoSEM230) and field emission transmission electron microscopy (TEM, JEOL JEM-2100F). X-ray diffraction (XRD) patterns were collected with Rigaku-TTRIII with Cu Kα radiation at a scanning rate of 10° min^{-1}. The Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) analyses were performed on a SPECTRO BLUE SOP spectrometer. Energy dispersive X-ray spectroscopy (EDS) mapping was measured on a FEI Titan G2 60–300 electron microscope.

2.3. Electrochemical characterization

The working electrodes were prepared by mixing the Si material, Super P and sodium alginate binder at a weight ratio of 60:20:20 in water solvent for 2 h. The slurry was pasted on a cooper foil evenly with scrape and then dried at 60 °C for 12 h. The electrodes were punched into small wafer, and the Si mass loading is typically 0.61–0.76 mg cm^{-2}. Before cell assembly, the electrodes were dried at 60 °C for 2 h. Coin-type cells (CR2025) were assembled in an argon-filled glove box (Super 1220/750, Shanghai Mikrouna Co. Ltd) with a

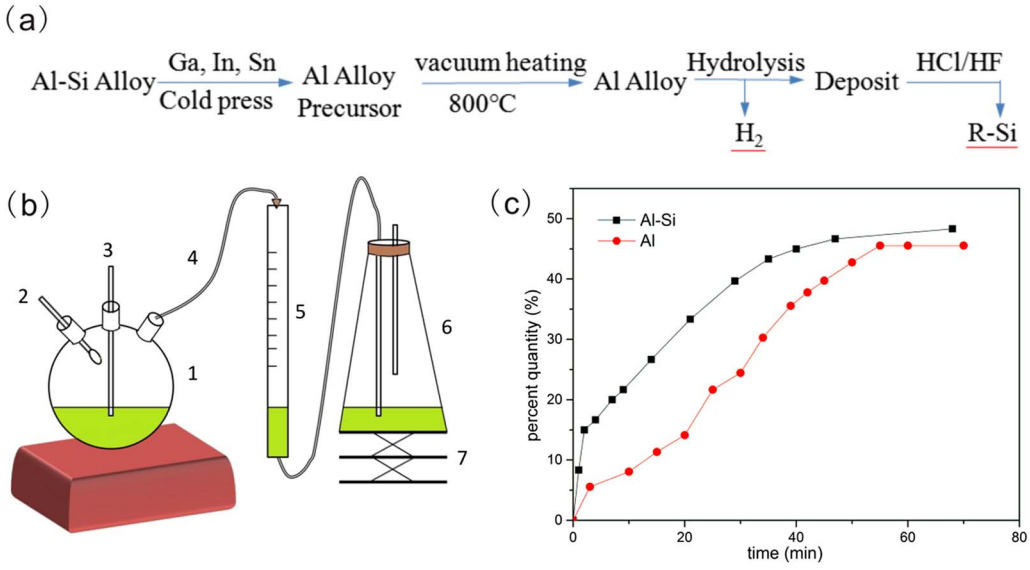

Fig. 1. (a) Flow chart of the process for producing hydrogen and recovering R-Si. (b) Schematic diagram of equipment used for hydrogen production and measurement, 1-flask; 2-spoon; 3-thermometer; 4-gas pipe; 5-gas burette; 6-calibrated bottle; 7-lifting platform. (c) Hydrogen production curve of Al-Si and Al on 25 °C.