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An easy way for preparing high performance porous silicon powder by acid etching Al–Si alloy powder for lithium ion battery

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ABSTRACT

We developed a novel, simple method to prepare porous silicon powder by acid etching Al–Si alloy powder. .The morphology and structure of the as-obtained material were investigated using scanning electron microscopy (SEM), X-ray diffraction (XRD), transmission electron microscope (TEM), and BET methods. It was found that the porous silicon powder (size about 15 μm) had a spongy structure, consisting of silicon nanobars with diameter about 50 nm and length of 1.5 μm. Its specific surface area was 102.8 $m^2\ g^{-1}$. The electrochemical properties of porous silicon electrode were evaluated by measuring voltammograms and charge and discharge curves. The porous silicon electrode with ratio of porous Si powder:Super P:binder = 1:1:1 was tested in button style lithium/Si cell. It was found that due to its ability to promote the formation of primal SEI film on the surface of electrodes, additive fluoroethylene carbonate (FEC) had an effect to improve the charge and discharge cycle stability of porous silicon electrodes. In solution 1 M $LiPF_6$, EC:DMC = 1:1 (V/V) containing 15% FEC, the first charge and discharge capacities of porous silicon electrode were 3450 mAh g^{-1} Si and 2072 mAh g^{-1} Si respectively, at current density 100 mA g^{-1}. The discharge capacity retained 66% as 1368 mAh g^{-1} Si after 258 charge and discharge cycles. In 1 M $LiPF_6$/EC:DEC = 1:1 (V/V) solution, the charge and discharge capacities of porous silicon electrode in first cycle were 3396 mAh g^{-1} Si and 2537 mAh g^{-1} Si respectively. At 69th cycle, the discharge capacity remained 59% as 1497 mAh g^{-1} Si. The high electrochemical performance of porous silicon powder could be attributed to its porous structure, which provides enough tiny space to buffer the huge volume change of Si anode during charging and discharging processes. The nano-size Si bars benefited the diffusion process of lithium in Li–Si alloy. Moreover, the firm connection between Si nanobars in spongy porous structure prevented the breakdown of porous Si particles. This new advanced method for preparing high performance porous Si material is simple and inexpensive, presenting a promising prospect for practical application.

1. Introduction

The demand for lithium ion batteries with high discharge capacity has been surging, especially for the recent development of electro vehicles. It is well known, that compare with anode material graphite (discharge capacity 372 mAh g^{-1}), as the challenge material metal lithium presents very high discharge capacity of 3862 mAh g^{-1} for lithium ion batteries. However, the lithium dendrite formed during charge process causes the powdering of lithium and the decline of discharge capacity, as well as the safety problem in charge and discharge process. In order to solve these problems, some lithium alloys, such as Li–Si, Li–Sn, Li–Al and Li–Mg et al. alloys, were suggested as new high capacity materials. Among them, Li–Si alloy shows the highest potential for the practical application, as its theoretic discharge capacity of $Li_{4.4}Si$ is as high as 4140 mAh g^{-1}. But the volume of $Li_{4.4}Si$ is 3.2 times as original Si material. The huge volume expanding/shrink phenomenon of Si during charge and discharge cycling process, could cause the breakdown of Si particles and the loss of contact between each particles, leading to quick decline of the charge and discharge capacities. Moreover, the low diffusion coefficient of lithium in Li–Si alloy and the low conductivity of Si particles limit its practical use in lithium ion battery. Various methods have been investigated in order to solve these difficulties, such as using nano size Si particles: nano-particles [1,2], nano-fibers and nano-tubers [3–9], mesoporous and porous silicon materials [10–14], and Si–C composites [15,16,13,17,18]. But in general, these methods are not simple and cost high. It has been known that same surface additives, such as fluoroethylene carbonate (FEC) [19] and vinylene carbonate (VC) [19,20], have the abilities to improve the electrochemical

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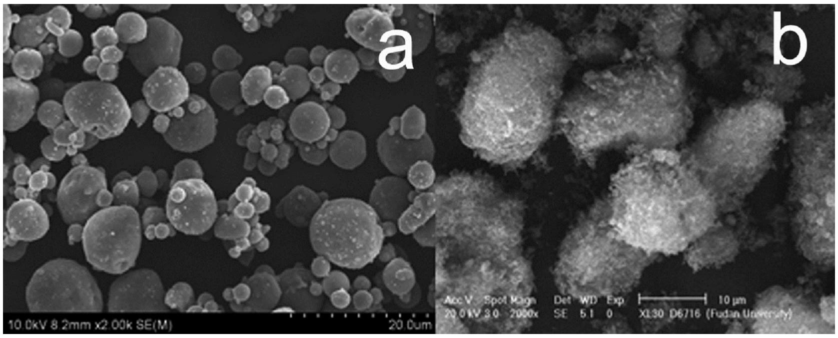

Fig. 1. SEM images of Al–Si alloy powder (a), and as-prepared porous silicon powder (b).

stability of Si electrode, due to the improvement of solid electrolyte interface (SEI) film. These additives could be decomposed in first charge process to form a so called additional second SEI film on the surface of electrode, to improve the stability of SEI film [19]. It is also known that water soluble CMC binder is suitable for the use in preparing Si electrodes [21].

In this paper we provide, for the first time, a simple method to prepare high performance porous silicon powder using acid etching Al–Si alloy powder for lithium-ion batteries. The advantages of this method are easy and low cost, making it suitable for practical application as a valuable challenge.

2. Experimental

2.1. Preparation of porous Si electrodes

Porous silicon micro powder was prepared by acid etching Al–Si alloy powder (consisted of 80% Al, 20% Si, for metallurgy use, Jieweixin Co., China). The Al–Si alloy powder was added into 8% HCl (AR) solution step by step while stirring. The etching time was about 8 h until aluminium was completely dissolved from Al–Si alloy. Then after filter, the powder were washed by ion free water and immersed in 2% HF alcohol solution for 2 h to remove traces of SiO_2 present on the surface of porous Si powder. Finally after being washing several times using ion free water, the powder was dried in vacuum at 80 °C.

Porous Si electrodes were prepared using carbon Super P as conducting material, water soluble glue as binder. The water soluble glue consisted of SBR (water system styrene butadiene rubber emulsion) and CMC (sodium carboxymethylcellulose) water solution. The ratio of dry SBR to CMC was 1:1. The proportion of materials in the porous Si electrode was at the ratio of porous Si powder:Super P:binder = 1:1:1. The mixture were spread on a thin copper foil and then dried in vacuum oven at 80 °C. Each working electrode with diameter of 14 mm contained about 0.3 mg silicon. The test coin cell (Model CR2016) with a metal lithium foil as counter electrode, Celgard 2300 membrane as separator was assembled in a dry argon glove box (Super 1220/750, Mikrouna). Two kinds of organic solutions (produced by Guotai Huarong Co., China) were used in this study: one was 1 M $LiPF_6$/EC (ethylene carbonate):DMC (dimethyl carbonate) = 1:1 (V/V) with or without additive 15% FEC, the other was 1 M $LiPF_6$/EC:DEC (diethyl carbonate) = 1:1 (V/V).

2.2. Measuring the morphology and electrochemical behaviour of porous Si powder

The morphology of porous Si powder was observed by using scanning electron microscope (SEM) (Philip XL30) and transmission electron microscope (TEM) (JEM-2100F). For crystal structure detection, XRD measurement was carried out using Bruker D8m Advance X-ray diffractometer using Nickel filter Cu-Ka radiation. BET method was used to analyze the pore structure and the surface area of porous Si samples by using Micromeritics ASAP 2010 System.

The cyclic voltammetry of porous Si electrodes was carried out on a CHI 660A electrochemical workstation at scan rate of 0.2 mV s^{-1} in the potential range: 0.01–1.5 V (vs. Li/Li^+). The charge and discharge tests were carried out galvanostatically at the current density of 100 mA g^{-1} based on Si amount in working electrode. The cutoff potentials for charge (intercalation of lithium) and discharge (deintercalation of lithium) processes were 0.01 V and 1.5 V (vs. Li/Li^+) respectively.

3. Results and discussion

3.1. The structure of porous silicon particles

Fig. 1 shows representative SEM images of raw material Al–Si alloy powder (a), and as-prepared porous Si powder (b) respectively. It clearly shows that Al–Si alloy powder was spherical particles, with the diameter about 15 μm or less. The as-prepared porous silicon was a spongy composition. The pores produced by the loss of aluminium from Al–Si alloy during etching process distribute uniformly. In Fig. 2 the TEM image of an as-prepared porous silicon particle indicates that the porous particle composed of silicon nanobars with diameter about 50 nm, length of 1.5 μm, and intertwined.

The peaks at the XRD pattern as pointed at $2\theta = 28.5°$, 47.4°, 56.2°, 69.3°, 76.5° and 88.2° correspond to the characteristic crystal peaks of Si (Fig. 3). They support a good crystalline structure of the sample. N_2 adsorption/desorption isotherms of porous silicon particles (Fig. 4a) show the similar type IV adsorption isotherm behaviors. The surface area of porous Si powder 102.8 $m^2 g^{-1}$ was calculated from Brunauer–Emmett–Teller (BET) equation. The pore

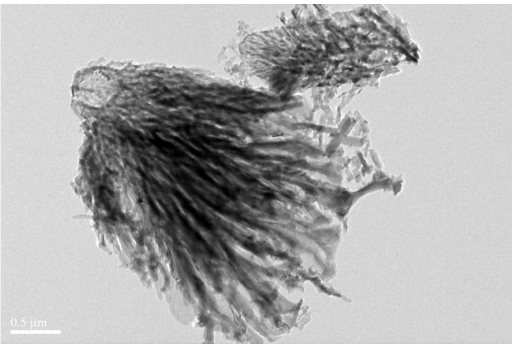

Fig. 2. TEM image of as-prepared porous silicon powder.