Self-assembly of porous-graphite/silicon/carbon composites for lithium-ion batteries

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ABSTRACT

The self-assembly of porous-graphite/silicon/carbon composites is fabricated by electrostatic attraction in solvent and pyrolysis method. Silicon carries a positive charge after surface modification and porous-graphite carries a negative charge after oxidation. Transmission electron microscopy reveals some Si nanoparticles encapsulated in pores of porous-graphite. X-ray diffraction shows that the structure of porous-graphite and silicon are not destroyed during oxidation of the graphite and surface modification of the silicon with APTES. Galvanostatic charge/discharge tests demonstrate that porous-graphite/silicon/carbon composites have much higher reversible charge capacity than flake graphite and better capacity retation than pristine silicon. The composites exhibit an initial reversible charge capacity of 778.8 mAh · g^{-1}.

1. Introduction

Lithium-ion batteries have attracted considerable attention owing to the increasing demands for portable electronics, electric vehicles and the storage of renewable energy [1–5]. But graphite, the commercial anode for Li-ion batteries, cannot meet the ever increasing energy density requirements for applications due to its limited theoretical specific capacity of 372 mAh · g^{-1} [6]. Silicon has attracted great attention since it has 10 times higher specific capacity than traditional carbon anodes, but the poor cycle ability due to the large volume change during insertion and extraction of lithium has been an impediment to its application [7,8].

Recently, graphene which has been used to coat silicon is becoming more and more appealing because of its unique properties, such as high two-dimensional electrical conductivity, superior mechanical flexibility, high chemical and thermal stability, and large surface area [9–14]. But we also know that graphene is difficult to prepare [15–18]. So we empoly porous-graphite which is easier to prepare than graphene replacing graphene to encapsulate silicon nanoparticles [19]. In this paper the graphite intercalating space has been enlarged due to oxidation for accommodating silicon nanoparticles. Silicon nanoparticles and porous-graphite are taken as opposite charges. Afterwards, silicon nanoparticles enter into graphite intercalating space automatically.

2. Experimental

2.1. Sample preparation

The scheme for the preparation of porous-graphite/silicon/carbon composites is presented in Fig. 1. The overall synthetic procedure involves three steps:

(1) Preparation of the porous-graphite and surface modification of the silicon samples

All the reagents in the experiments were analytically pure. Firstly, 2.7 g potassium dichromate was dissolved in 55 g sulfuric acid (>98%) with stirring in a flask. Secondly, 1.5 mL distilled water was also added to prepare chromic acid. Thirdly, flake graphite (>99%, 1.0 g, ~100 μm, Luo yang Guanqi Grapgite Co., Ltd, Henan, China) was added to the flask and the mixture was stirred gently. Then acetic anhydride (1.0 g) used as an intercalating agent was slowly dropped into the solution and stirred at 45 °C for 50 min. Then the solution was filtered and neutralized with 0.1 M sodium hydroxide and washed with distilled water until the pH of the solution reached a constant value of about 7.0. After washing, porous-graphite was dried in a vacuum oven at 60 °C overnight.

To functionalize the silicon surface, 1 mL (3-Aminopropyl) triethoxysilane(APTES) and 1 g silicon(>99.9%,~30 nm,Shuitian Materials Technology Co., Ltd, Shanghai, China) were added to 15 mL toluene with continuous stirring. The solution was stirred at room temperature for 1 h and refluxed at 130 °C for 2 h. After being cooled naturally to room temperature, the solution was

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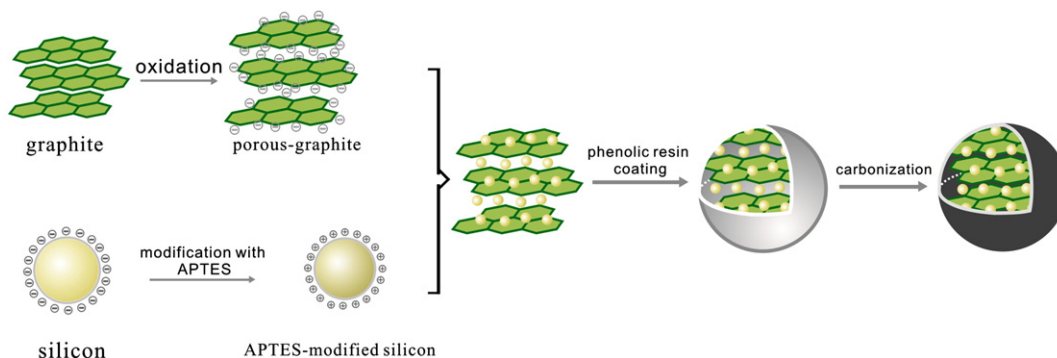E-mail address: hjguo_csu@163.com (H. Guo).

Fig. 1. The scheme for the preparation of porous-graphite/silicon/carbon composites.

filtered and washed with dry toluene. Finally, the modified-Si was dried overnight under vacuum.

(2) Preparation of self-assembly of porous-graphite/silicon/carbon composites

The mass ratio of functionalized silicon, porous-graphite and amorphous carbon was designed as 2:7:1. Firstly, 0.7692 g phenolicresin was added to 30 mL alcohol and the pH value of the solution was adjusted to 2 by diluted hydrochloric acid [20]. Secondly, 0.2 g modified-silicon and 0.8 g porous-graphite were added into the above-mentioned solution under vigorous stirring and dispersed uniformly. Thirdly, the solution was evaporated at 80 °C to get a solid blend precursor. Then the dried precursor was pyrolyzed at 750 °C for 2 h under argon atmosphere in a tube furnace to yield porous-graphite/silicon/carbon composites.

2.2. Material characterization

The morphologies of the particles were examined by scanning electron microscopy (SEM, JEOL, JSM-6360LV). The microstructures of the particles were observed by transmission electron micro-scope (TEM, Tecnai, G12). The phase components of the materials were investigated by powder X-ray diffractometry (XRD, Rint-2000, Rigaku) with Cu Kα radiation. Zeta potential was examined by Malvern instruments Nano ZS.

2.3. Electrochemical measurements

The electrochemical characterizations were performed by CR2025 coin-cells with pure Li as the counter electrode, a Celgard 2400 film as the separator and a solution of 1 M $LiPF_6$ in EC/EMC/DMC (1:1:1 by volume) as electrolyte. And the working electrodes were prepared by pasting a homogeneous slurry of 80 wt.% active material, 10 wt.% super P and 10 wt.% PVDF binder dissolved in a certain amount of N-methyl pyrrolidinone (NMP) onto a copper foil, and then dried at 120 °C in vacuum oven for 12 h. Electrodes were punched in the form of 12 mm diameter disks and then pressed under the pressure of 20 MPa. The loading density of electrode was about 1 mg/cm^2. After that the electrodes were heated to 300 °C in a tube furnace with a flowing argon atmosphere to further remove water content and attach to copper foil tightly. The cells assembled in Ar-filled glove box. The cells were charged and discharged using a Neware battery tester (Neware Shenzhen) between 0.01 and 2.0 V (vs. Li/Li$^+$). Cyclic voltammetry (CV) were carried out using a CHI660A electrochemical workstation at a scan rate of 0.1 mV s^{-1} with a voltage range of 0.01–2.0 V (vs. Li/Li$^+$) at room temperature.

3. Results and discussion

3.1. ZETA measurements of modified-Si and porous-graphite

To survey the assembly process, zeta potential measurements were carried out. The results show that the zeta potentials of APTES-modified silicon and porous-graphite are +22.6 and −8.75 mV, respectively. Attraction between the positive charge of modified-Si and negative charge of porous-graphite provided a driving force that allowed silicon nanoparticles to enter into porous-graphite intercalating space automatically.

3.2. Structure and morphology of the materials

Fig. 2 shows the XRD patterns of the porous-graphite/silicon/carbon composites. The porous-graphite/silicon/carbon composites show pure Si crystalline diffraction peaks, implying that the silicon nanoparticle crystals in porous-graphite/silicon/carbon composites are not destroyed during surface modification of the silicon samples with APTES and thermal reduction processes. Due to the oxidation, the intensity of the graphite diffraction peak near $2\theta = 26.38°$ became weak. These indicate that the multilayer structure still exists, but the layer-to-layer distance (d-spacing) of 0.376 nm is larger than the d-spacing (ca. 0.34 nm) of flake graphite [21].

The morphology of porous-graphite/silicon/carbon composites was characterized by SEM and TEM in Fig. 3. The SEM image shows that porous-graphite has become swollen after oxidation (Fig. 3a). The distance between two graphite layers is about 3 μm. It's easy for silicon particles with a diameter of about 30 nm inserting into the pores of porous-graphite automatically. Fig. 3b shows that some of the silicon particles were adhered to the surface of the porous-graphite. The pores of the porous-graphite were blocked by the amorphous carbon which came from carbonization of phenolic resin. In order to isolate electrolyte, accommodate the volume change of the silicon during insertion and extraction of lithium and enhance the electrical conductivity, the pores of the porous-graphite were blocked by the amorphous carbon which came from the carbonization of the phenolic resin. Fig. 3c verified that
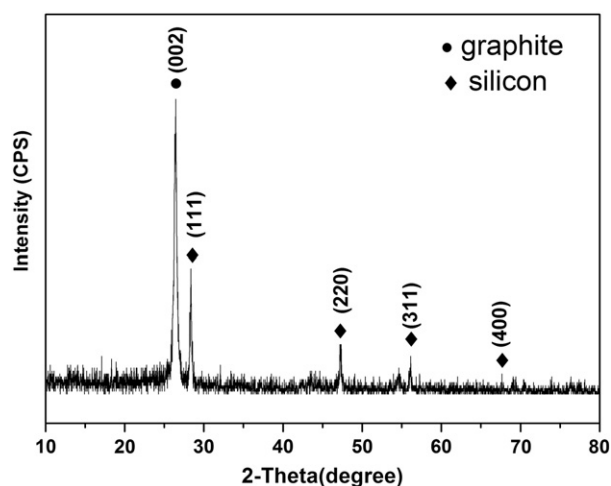

Fig. 2. XRD patterns of porous-graphite/silicon/carbon composites.