



Nano/micro-structured silicon@carbon composite with buffer void as anode material for lithium ion battery

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Abstract

A novel nano/micro-structured pSi@C composite with buffer void was successfully synthesized via a simple and scalable process with combination of the calcination, spray drying, carbonization and HF etching. The obtained pSi@C composite with this particular structure exhibits high reversible capacity of *ca.* 2200 mA h g⁻¹ and excellent cycling stability with 90.3% capacity retention after 300 cycles, which benefits from its void spaces between silicon and carbon layer and highly conductive carbon-layer. The simple and scalable synthesis technique and good electrochemical performance of this nano/micro-structured pSi@C composite make it a promising candidate for large capacity lithium ion battery anode material.

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1. Introduction

With the rapid development of electric vehicle and advanced electronic device, lithium-ion battery with high energy density and long life has attracted considerable attention [1,2]. For anode materials, silicon has been the focus of research for many years because of its extremely high theoretical capacity of about 4200 mA h g⁻¹, which is more than 10 times of commercial graphite (LiC₆, 372 mA h g⁻¹) [3]. However, the gigantic volume expansion of silicon (up to 300%) during Li repeated alloying/dealloying process leads to particles' crack and electrode's crumbling. The electrical deactivation and particles pulverization are consequently resulted in rapid capacity fading of silicon anode material and seriously hinders its practical application [4–6]. Besides, the semiconductive nature of silicon material also limits its application in high-

power lithium-ion batteries [7,8]. To overcome aforementioned issues, many researches have been conducted to minimize the volume expansion and improve the conductivity of silicon simultaneously [9–11]. For instance, Huang et al. [12] studied the lithiation of individual silicon nanoparticles in real time and discovered a strong size dependence of fracture. According to the research of Huang et al. when the particle size is below a critical value of 150 nm, neither cracking nor fracturing will happen upon first lithiation and delithiation. Moreover, extensive nanometer regimes including nanowires [2,13,14], films [15], nanospheres [16] and nanotubes [17] have also been investigated to reduce the volume expansion and some good results have been achieved as well. What is more, varieties of porous silicon-based composite receive considerable attention for the buffering effect provided by inner pores. For example, Wensheng Yang et al. [18] developed yolk-shell structured porous Si-C microspheres by magnesiothermic reduction of silica inside carbon shells. The composite exhibited a capacity of *ca.* 530 mA h g⁻¹ and the

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capacity retention after 100 cycles was *ca.*67%. The great improvement of the cycling stability can be ascribed to the well-designed porous yolk–shell structure. Similarly, another approach is to synthesize porous silicon and directly create pores inside the silicon particles. A novel lotus-root-like mesoporous Si/C composite material produced by magneto-thermic reaction and chemical vapor deposition (CVD) method was reported by Jun Yang et al. [19]. The uniform mesopores within the particles can accommodate the large volume changes of Si during lithiation and delithiation process, and the thin coated carbon layer can enhance the surface electric conductivity and stabilize the whole structure. Donghai Wang et al. [20] reported silicon core-hollow carbon shell nanocomposites with controllable voids between silicon nanoparticles and hollow carbon, which exhibited excellent electrochemical performances. In addition to creating pores inside the silicon particles, varieties of secondary Si-based particles with void spaces are also investigated. Gleb Yushin et al. [21] adopted a hierarchical bottom-up assembly route for the formation of nano-Si, which contains rigid and robust spheres with irregular channels for rapid access of Li ions into the particle bulk. Large Si volume changes on Li insertion and extraction are effectively accommodated by the secondary particle's internal porosity. Dae Soo Jung et al. [22] designed a void space between Si nanoparticles by the industrially-established spray drying method. The void space around the Si nanoparticles provides adequate space for Si expansion. As a result, the mechanical stability and sufficient contact with current collector can be retained during cycling, leading to the excellent electrochemical performance.

Inspired by the above-mentioned approaches of designing various void spaces for buffering silicon volume expansion and aimed at facile up-scaling production, herein, we conceive and prepare a new nano/micro-structured silicon@carbon (pSi@C) material with void spaces via facile and up-scaling production process. There are two types of void spaces, one is inside the silicon and the another is between silicon@carbon particles. Void spaces among the silicon@carbon particles are created via spray drying granulation. Moreover, plenty of void spaces between silicon core and carbon shell are formed via combination of calcination, carbonization and HF etching. A notable feature of this material is that the plenty of void spaces and uniform carbon layer with excellent mechanical properties, which can efficiently buffer the volume expansion of silicon during repeated lithiation and delithiation process and obtain excellent cycle performance. The pSi@C composite demonstrated high reversible capacity of 2269.7 mA h g⁻¹ and minimal capacity fading was observed over 300 cycles at a current density of 0.3 A g⁻¹ (90.3% capacity retention with 98.5–99.0% Coulombic efficiency).

2. Experimental

2.1. Materials synthesis

Phenolic resin (Shandong Shengquan Chemical Co., Ltd., PF-4012) was first dissolved in ethanol, then the nano-Si

powder (50–200 nm, Alfa-Aesar) after calcined at 800 °C for 2 h in air was added. After dispersing uniformly (the mixture was ultrasounded for 0.5 h), the mixture was spray-dried to form the secondary particles of nSi@SiO₂@PF containing SiO₂ and phenolic resin. In the spray drying process, ethanol was evaporated instantaneously, leaving phenolic resin uniformly coated on the surface of nSi@SiO₂ in nSi@SiO₂@PF secondary particles. The interconnected phenolic resin on the surface then stacked the particles together, leading to the secondary particles with good mechanical strength. Finally, the secondary particles were calcined at 900 °C for 2 h under Ar atmosphere and the phenolic resin in situ transferred to amorphous carbon at the same time. The resulting composite was denoted as nSi@SiO₂@C.

The synthesis of nSi@SiO₂@C powder was immersed in 5 wt% HF solution for 10 min, then washed with deionized water for several times and isolated by filter, followed by vacuum drying at 100 °C for 2 h, and finally naturally cooled down to room temperature. The SiO₂ layer was removed and the void space between silicon and carbon was eventually created. The obtained composite was designated as pSi@C composite.

The synthesis of nSi@C composite used as the control sample was similar to the process above. Phenolic resin was first dissolved in the ethanol, then nano-Si powder was added. After ultrasonic dispersion treatment, the spray drying and carbonization were followed and the composite was obtained. The obtained composite was designated as nSi@C composite.

2.2. Structural and morphological characterization

X-Ray diffraction (XRD) measurements were carried out using a Rigaku D/MAX-2200/PC X-ray diffractometer at 40 kV and 30 mA, with a Cu K α radiation source. The morphologies and microstructures of the samples were investigated using a FEI Nova SEM 230 ultra-high resolution FESEM and a JEM-2100F TEM (JEOL Ltd., Japan). Thermogravimetric analysis (TG) was performed using a STA 449F3 analyzer (NETZSCH Co., Germany) to evaluate the carbon. BET specific surface areas of the samples were obtained on a Brunauer–Emmett–Teller surface area analyzer (BET, ASAP 2010M+C, Micromeritics Inc.). The electronic conductivity of the composite was measured by a four-point probe method (RTS-8 Four-Point probe meter).

2.3. Electrochemical characterization

The working electrodes were composed of active material, Super P conductive carbon black (40 nm, Timical) and styrene butadiene rubber/sodium carboxymethyl cellulose (SBR/SCMC, 1:1 by weight) as binder at a weight ratio of 80:10:10. After casting the mixture onto a copper foil and drying, the electrodes were cut to Φ 12 mm disks, pressed at 3 MPa and finally dried at 80 °C in vacuum for 4 h.

Coin-type CR 2016 cells were assembled in an Argon filled glove box (MBraun, Unilab, Germany) using ENTEK ET20-26 membrane as separator and lithium-foil as counter

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