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A high-performance ternary Si composite anode material with crystal graphite core and amorphous carbon shell

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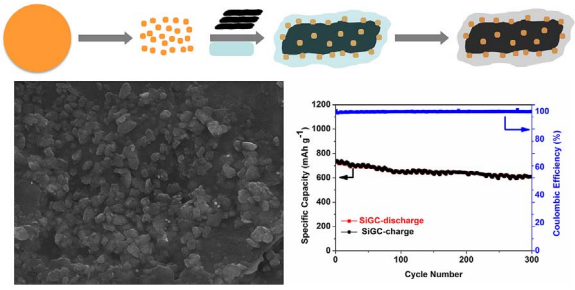
HIGHLIGHTS

- A ternary core/shell Si/graphite/pyrolytic carbon composite was prepared.
- Over 80% capacity retention was obtained after 300 cycles.
- High performance benefits from the peculiar structure of the composite.

GRAPHICAL ABSTRACT



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ABSTRACT

Si is a promising anode material for lithium-ion batteries, but suffers from sophisticated engineering structures and complex fabrication processes that pose challenges for commercial application. Herein, a ternary Si/graphite/pyrolytic carbon (SiGC) anode material with a structure of crystal core and amorphous shell using low-cost raw materials is developed. In this ternary SiGC composite, Si component exists as nanoparticles and is spread on the surface of the core graphite flakes while the sucrose-derived pyrolytic carbon further covers the graphite/Si components as the amorphous shell. With this structure, Si together with the graphite contributes to the high specific capacity of this Si ternary material. Also the graphite serves as the supporting and conducting matrix and the amorphous shell carbon could accommodate the volume change effect of Si, reinforces the integrity of the composite architecture, and prevents the graphite and Si from direct exposing to the electrolyte. The optimized ternary SiGC composite displays high reversible specific capacity of 818 mAh g^{-1} at 0.1 A g^{-1}, initial Coulombic efficiency (CE) over 80%, and excellent cycling stability at 0.5 A g^{-1} with 83.6% capacity retention (~610 mAh g^{-1}) after 300 cycles.

1. Introduction

In recent years, with the fast development of electric vehicles and portable electronics, lithium-ion batteries (LIBs) with higher energy density and better cycling performance are highly demanded and extensive efforts have been made to search for new cathode and anode

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materials with higher specific capacity [1–5]. For LIBs anode materials, graphite, which has dominated current commercial anode market for nearly three decades, suffers a relatively low capacity and safety problems. Among the potential anode candidates, Si-based anode materials are one of the most promising ones due to its extremely high specific capacity (3580 mAh g^{-1} vs. 372 mAh g^{-1} for graphite), abundant resource, and proper lithium-alloy potential (0.2 V vs. Li^+/Li) [6,7]. In spite of these superior advantages, the practical application of Si-based materials, especially bulk Si, is still severely hindered by some drawbacks, such as huge volume variation during lithium alloy/de-alloy, continues formation of solid electrolyte interface (SEI), and low intrinsic electric and ion conductivity [8]. To address these critical issues, several strategies have been successfully developed, including designing nano-Si structure, introducing carbon-buffering layer, and optimizing the choice of binder and electrolyte [9–14]. A variety of Si-based nano-materials, e.g. nanoparticles, nanowires, nanotubes, and core/shell nanostructures, show better electrochemical performance than pure bulk Si [7,12,15–19]. However, considering the cost, scalability, energy consumption and pollution, these strategies are rather hard to achieve commercial applications. Therefore, it is highly desirable to develop low-cost and scalable strategies to prepare Si-based anode materials with high capacity and cycling stability.

Fabricating Si/C composites are efficient approaches to circumvent the limitations of pure Si by introducing graphite and/or amorphous carbon, thus improving their electrochemical performance [12,14,20–26]. These carbon components not only enhance the conductivity of the composites, but also suppress the huge volume variation of Si, keep the integrity of electrode, and prevent direct contact of Si with the electrolyte. Herein, we developed a ternary Si/graphite/pyrolytic carbon (SiGC) composite with a structure of crystal core (graphite) and amorphous shell (sucrose derived pyrolytic carbon) by easy and scalable ball milling and spray drying process. The optimized SiGC composite with Si content of 12.8 wt% displays high initial reversible specific capacity of 818 mAh g^{-1} at 0.1 A g^{-1} and long cycle life up to 300 cycles at 0.5 A g^{-1} with 83.6% capacity retention. Moreover, high initial CE (over 80%) as well as good rate capability was achieved. Such super performance should be ascribed to the peculiar structure of the ternary SiGC composite and synergistic effect of the three components.

2. Experimental section

2.1. Synthesis of ternary SiGC composite with crystal core and amorphous shell

All the starting materials are commercially available low-cost products. Different mass ratio of Si, graphite and sucrose (1:4:5, 1:7:5, 1:10:5) were fabricated for systematic studies. Here is the typical synthesis process for the ternary SiGC composite with crystal core and amorphous shell. First, micro-sized Si powder with particle size of about 10 μm (1000 g, Xuzhou Lingyun Silicon Industry Co. Ltd.) was ball-milled in alcohol (3000 g) with Zirconia beads (0.1 mm diameter) for 8 h at 60 Hz via wet grinding (Labstar LMZ, Netzsch). Then, the as-obtained suspension (25 wt%, 200 g) of nano-Si in alcohol was mixed with graphite (350 g, Huaxin Energy Material Co. Ltd.), sucrose (250 g) and water (1180 g) by ball milling for 30 min at 30 Hz. The overall solid content of the mixture was adjusted to 30 wt%. After that, the resulting homogeneous suspension was spray dried with inlet temperature of 140 °C and outlet temperature of 80 °C at a rate of 1000 mL/h in a spray dryer (Shanghai Pilotech Instrument Equipment Co. Ltd.). Finally, the spray-dried solid precursor was calcined at 800 °C for 2 h under H_2/Ar (5:95 v/v) atmosphere at a heating rate of 5 °C min^{-1} to obtain the SiGC composite. For comparison, binary Si/graphite (SiG) composite without amorphous pyrolytic carbon shell was also prepared by similar procedure.

2.2. Material characterization

Thermogravimetric (TG) measurement (Netzsch-STA 449C) was conducted from room temperature to 900 °C at a heating rate of 10 °C min^{-1} in air. Powder X-ray diffraction (XRD) analysis was performed on a Rigaku D/Max-2500 diffractometer with Cu Kα radiation. Raman spectra were recorded using a Lab RAM HR Evolution with a 514.5 nm Ar-ion laser. Scanning electron microscopy (SEM) was carried out using a LEO 1530 VP field emission scanning electron microscope with an acceleration voltage of 10 kV. Transmission electron microscopy (TEM) as performed using a JEOL TEM-2100 electron microscope operated at 200 kV.

2.3. Cell fabrication and electrochemical measurements

Electrochemical performances were characterized using coin-type cells. To prepare working electrodes, the active materials, Super P carbon black, and poly(vinylidene fluoride) (5 wt% in N-methyl-2-pyrrolidone) were mixed with a mass ratio of 80:10:10 to produce a homogenous slurry which was then coated onto a Cu foil (10 μm in thickness) with areal density of about 1.1 mg cm^{-2}. After heating at 60 °C for 3 h and 150 °C for 1 h, the electrode sheet was punched into 11 mm diameter electrodes and then pressed under pressure of 10 MPa. The coin-type cells were assembled in an argon-filled glove box with lithium metal foil as the counter/reference electrode. The electrolyte was 1 M $LiPF_6$ in ethylene carbonate/diethyl carbonate/vinylene carbonate (1:1:0.02 v/v/v). The galvanostatic charge/discharge cycles were performed in the voltage window of 0.01–1.5 V at 25 °C using a battery test system (LAND CT2001A model, Wuhan LAND Electronics. Ltd.). Electrochemical impedance spectra (EIS) measurements were recorded using an Autolab system (Metrohm). The EIS measurements were carried out at AC amplitude of 10 mV in the frequency range from 100 kHz to 10 mHz.

3. Results and discussion

3.1. Structure and morphology

To synthesis the ternary SiGC composite with a peculiar core/shell structure, we developed a simple approach as shown in Fig. 1 and the

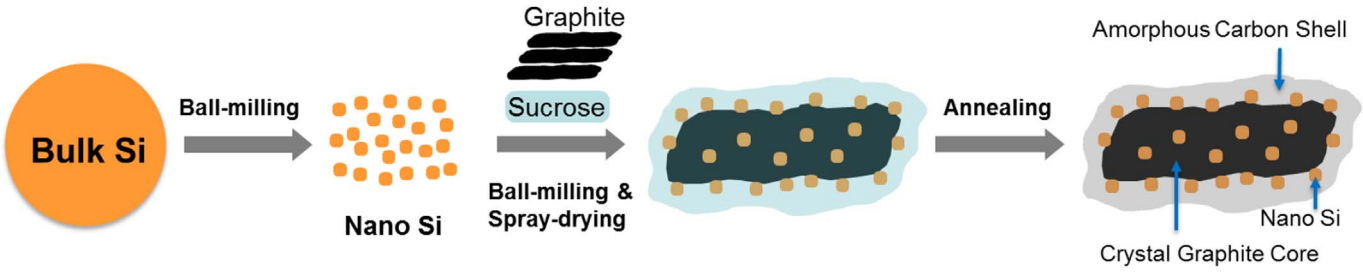

Fig. 1. Schematic of the synthesis process of the SiGC composite.