



Micro-sized spherical silicon@carbon@graphene prepared by spray drying as anode material for lithium-ion batteries



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ARTICLE INFO

Article history:

Received 1 March 2017

Received in revised form

30 April 2017

Accepted 20 June 2017

Available online 21 June 2017

Keywords:

Lithium ion battery

Silicon

Spray drying

Graphene

Anode material

ABSTRACT

The micro-sized silicon@carbon@graphene spherical composite (Si@C@RGO) has been prepared by an industrially scalable spray drying approach and a subsequent calcination process. The obtained Si@C@RGO anode exhibits a high initial reversible specific capacity of 1599 mAh g⁻¹ at a current density of 100 mA g⁻¹ with a good capacity retention of 94.9% of the original charge capacity at a higher current density of 200 mA g⁻¹. Moreover, the Si@C@RGO anode shows a high reversible specific capacity of 951 mAh g⁻¹ even at a high current density of 2000 mA g⁻¹. The excellent cycling stability and superior rate capability are attributed to the unique structural design of carbon coating and wrapped by highly conductive graphene. The combination of carbon shells and flexible graphene can effectively enhance the electrical conductivity of the composite and accommodate significant volume changes of silicon during cycling. The presented spray drying strategy is adaptable for large-scale industrial production of Si-based composite, and it can be extended to the design of other promising micro-sized electrode materials.

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1. Introduction

Since mobile electronic products and electrical vehicles (EVs) have undergone rapid development in recent years, greater demands on lithium-ion batteries (LIBs) have been put forward [1–4]. Thus, electrode materials with high energy densities have attracted considerable attention. Presently, silicon is considered the most promising candidate for next generation anode material, owing to its extremely high theoretical capacity (at room temperature: Li₁₅Si₄: ~3600 mAh g⁻¹), low lithium insertion/extraction voltage, and abundance in nature [5–7]. However, silicon exhibits a limited cycle life due to severe volumetric changes (~300%) during the lithium insertion/extraction processes, hindering its practical applications [8,9]. The huge volume changes of silicon over repeated cycles result in pulverization, formation of unstable solid electrolyte interface (SEI) and conductive network breakage [10,11].

Extensive research has been done to avoid the known drawbacks of silicon-based anode materials through special structural designs (such as core-shell [12,13], porous [14,15] and yolk-shell structures [16,17]) and fabricating silicon-based composite

materials, leading to significant improvement of the electrochemical performance [2,18,19]. One of most promising strategies for practical application is to synthesize silicon/carbon composite anode materials with a well-designed structure. The introduction of a carbon phase is considered to enhance the electronic conductivity of the composite and accommodate significant volume changes of silicon during lithium insertion/extraction processes [20]. Because graphene exhibits superior electric conductivity, various hybrid nanomaterials of the graphene and active materials have been fabricated and used as electrode for LIBs recently [21–23]. Moreover, there are many well-designed Si/graphene nanocomposites that exhibit enhanced electrochemical performance. However, most of them show low initial Coulombic efficiency because of the large specific surface area of graphene and the direct contact between Si and electrolyte [24–26]. Recently, a carbon-coated Si nanoparticle/graphene composite was prepared via a freeze-drying approach and thermal annealing process, showing developed electrochemical performance and a high initial Coulombic efficiency of 83.7%, but the yield of the freeze-dried approach is limited for industrial production [27].

On the other hand, practical application of nano-sized silicon-based composite materials is stalled because of the low tap density and unfit scalability [28–31]. Therefore, a silicon-based composite with micro-sized design and scalable synthetic process is required to replace graphite anode materials. Spray drying technique has

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been widely used in industrial production of catalysts and drug carriers due to the high production efficiency [32–34]. Considerable efforts have been made towards synthesis of Si-based composites by spray drying processes [32,35–37].

In this paper, we present a unique micro-sized Si@C@RGO composite by an industrially scalable spray drying approach and a subsequent calcination process. The micro-sized Si@C@RGO composite delivers excellent cycling stability and superior rate capability due to the unique structure design of carbon coating and wrapped by highly conductive graphene.

2. Experimental

2.1. Fabrication

Typically, graphite oxide (GO) was synthesized from natural graphite powder via a modified Hummers method as previous report [38]. The micro-sized Si@C@RGO spherical composite was synthesized by an industrially scalable spray drying approach and a subsequent calcination process. In a typical synthesis, the silicon nanoparticles (~80 nm, Shuitian ST-NANO Science & Technology Co., Ltd, Shanghai, China) and as-prepared GO were homogeneously dispersed in a solution of sucrose assisted by ultrasonic treatment for 4 h. The GO content was adjusted to ~3 mg mL⁻¹ and the weight ratio of sucrose, silicon and GO was designed as 15:10:2. Subsequently, the precursor solution was dried by a spray dryer with an inlet air temperature of 180 °C to obtain the Si@C@RGO composite precursors. Finally, the as-prepared precursors were heat treated at 800 °C for 4 h under H₂/Ar₂ (10%) atmosphere to yield the Si@C@RGO composite. As a comparison, the preparation of the Si@C composite is similar to that of the Si@C@RGO composite but without the presence of GO.

2.2. Characterization

The crystal structure, morphology and micro-structural morphology of the as-obtained samples were investigated by X-ray powder diffractometry (XRD, Empyrean, Cu-K α radiation, $\lambda = 1.5406$ nm), scanning electron microscopy (SEM, FEI Helios Nanolab 600i) and high resolution transmission electron microscopy (HTTEM, Hitachi, Japan). The content of each component was characterized by thermal gravimetric analysis (TGA, STA449 F3 Jupiter) under atmospheric conditions.

For electrochemical measurements, 2025 coin-type cells were assembled in a high purity argon-filled glove box with lithium foil as the counter electrode. The working electrodes were prepared by mixing active material, Super P carbon black, and sodium carboxymethyl cellulose (CMC) in a weight ratio of 8:1:1 and casting onto copper foil. The obtained electrodes were then dried at 100 °C overnight in vacuum and subsequently pressed with the mass loading of the active materials at approximately 1 mg/cm². The electrolyte was a solution of 1 mol L⁻¹ LiPF₆ dissolved in a solvent mixture of ethylene carbonate (EC), ethyl methyl carbonate (EMC) and dimethyl carbonate (DEC) (1:1:1, v/v/v) electrolytes. A galvanostatic cycling experiment was conducted from 0.01 to 1.5 V using a computer-controlled battery testing system (Neware, BST-5V5mA) at the various current densities. Cyclic voltammetry (CV) was conducted at a scan rate of 0.1 mV s⁻¹ between 0 and 1.5 V and electrochemical impedance spectroscopy (EIS) measurements were performed on an electrochemical workstation (CHI660D).

3. Results and discussion

Schematic illustration of the synthesis of Si@C@RGO and Si@C composites is shown in Fig. 1. The Si nanoparticles were

homogeneously dispersed in the solution of sucrose assisted by ultrasonic treatment, and the mixing solution was subsequently sprayed and dried to form the spherical precursor with an average size of several micrometers. Finally, the m-Si@C composite was obtained by heat treatment of the precursor, and carbon was introduced to coat the Si nanoparticles and form an active matrix that can accommodate volume changes of silicon and enhance the electrical conductivity of the Si@C composite. In the presence of GO, Si nanoparticles were wrapped by GO nano-sheets during the spraying process, and GO could be reduced to graphene during the calcination process under H₂/Ar₂ atmosphere. As a result, micro-sized Si@C@RGO spheres were obtained with carbon coating and graphene wrapping.

Fig. 2 shows the XRD patterns of GO, Si@C and Si@C@RGO. From the diffraction pattern of GO, only an intense diffraction peak at approximately 12° appears, indicating the successful oxidation of graphite [36]. There is no appreciable difference between the spectra, and sharp diffraction peaks corresponding to crystalline silicon appear in the XRD patterns of both Si@C and Si@C@RGO. No peaks ascribed to the SiC phase are observed, indicating that no other impurities are introduced during the calcination process. The intense peak ascribed to GO disappears completely in the XRD pattern of Si@C@RGO, which suggests that GO is successfully converted to graphene during the calcination process.

TGA (shown in Fig. 3) was used to determine the thermal properties and the composition of Si nanoparticles, Si@C and Si@C@RGO under air atmosphere at a heating rate of 10 °C min⁻¹. Si nanoparticles are found to be relatively stable during the heating process and only a 3.6% increase in mass is observed when the temperature is increased to 700 °C. The Si@C and Si@C@RGO composites mostly lost weight between 450 °C and 650 °C, due to the combustion of graphene and pyrolytic carbon in air, and then slightly increased in weight above 650 °C due to the oxidation of Si nanoparticles [39,40]. According to TGA data, the mass content of C and Si in the Si@C is calculated to be 21.5 wt % and 78.5 wt%, respectively, and the mass content of C, graphene and Si in the Si@C@RGO is calculated to be 71.5 wt%, 8.9 wt% and 19.6 wt%, respectively.

The morphologies of precursors of Si@C and Si@C@RGO, Si@C@RGO composite and Si@C composite have been analyzed with SEM. As observed in Fig. 4a and (b), the precursor materials for Si@C@RGO and Si@C with the average size of 2–6 μ m show homogenous spherical structure, which is mainly related to the introduction of sucrose and the spray drying process. The Si@C@RGO (Fig. 4c, d) and Si@C (Fig. 4e, f) composites prepared by the calcination of the precursors remain similar spherical structure. The Si nanoparticles in Si@C are surrounded by the pyrolytic carbon which will act as the conductive network and lower the contact area of Si with the electrolyte. In the presence of GO, it can be also clearly seen that the GO nano-sheet was homogeneously distributed in the precursor and the corresponding Si@C@RGO material (Fig. 4c, d). Graphene nano-sheet can further improve the electrical conductivity of composite and accommodate the volume expansion of silicon during the cycling. It suggests that the electrochemical performance of Si@C@RGO composite with the unique structure will be enhanced significantly in comparison with Si@C composite.

Elemental mapping analysis (shown in Fig. 5) more directly visualizes the uniform distribution of Si nanoparticles (purple color) in the matrix of graphene and carbon (yellow color). The structure of the samples was further investigated by TEM. Fig. 6 (a, b) shows that Si nanoparticles in the Si@C composite are coated by carbon with a thickness of approximately 5 nm. The lattice fringe of Si with a spacing of 0.31 nm corresponding to a (111) plane can also be observed. Fig. 6 (c, d) confirms the structure of the carbon coating and graphene wrapping. The addition of graphene does not hinder

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