

A facile synthesis of graphite/silicon/graphene spherical composite anode for lithium-ion batteries[☆]



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ABSTRACT

The Graphite/Silicon@reGO composite was synthesized via spray drying and subsequent annealing. According to XRD, Raman spectroscopy and FT-IR, graphene was demonstrated to be existed in the composite. Moreover, SEM and TEM were also used to illustrate the morphology of Graphite/Silicon@reGO. Used as anode for lithium-ion battery, it exhibited good cyclability with a high reversible charge capacity of 575.1 mAh g⁻¹ and showed a capacity retention ratio of 73.1% after 50 cycles at a current density of 50 mA g⁻¹. It also presented good rate capability at different rates of 50–1000 mA g⁻¹. EIS test showed that the composite electrode had a lower SEI resistance and charge-transfer resistance due to the existence of graphene.

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1. Introduction

Lithium-ion battery is a key component of portable equipment, especially in cell phones, digital cameras, notebook computers and electric vehicles (EV) [1–3]. But graphite, the commercial anode for Li-ion batteries, cannot meet the ever increasing energy density requirements for applications due to its limited theoretical capacity of 372 mAh g⁻¹ [4]. Various materials (such as hard carbons [5], Sn-based anodes [6,7], Si-based anodes [8,9], and metal oxides [10,11]) capable of storing lithium reversibly were investigated to increase the specific capacity of negative electrodes. Because of the abundance in nature, low cost and high theoretical capacity, silicon becomes an attractive candidate for anode of lithium-ion batteries. However, due to the repeated alloying and de-alloying process of Li with silicon, silicon particles show severe volumetric changes (about 300%) which results in the crumbling of active materials and conductive network breakage, leading to poor cycle performance [12]. Considerable efforts have been made to reduce the irreversible capacity and the capacity fading of the electrode upon prolonged cycling. And most work on Si-based anode materials has been focused on the issues of volume, conductivity and particle

morphology changes during charge–discharge cycling. Some effective methods are as follows: (1) Developing synthetic strategies which use nanostructure Si-based anode materials to release the structural stress, such as well-dispersed nanoparticles without aggregation [13], 3D porous bulk Si particles [14], and Si nanotubes [15]; (2) Developing composite materials where Si is dispersed homogeneously within an electrochemically inactive matrix [16]. The electrochemically inactive phase usually comprises a ductile and conductive matrix which can compensate mechanical stresses/strains by the active Si-based phase; (3) Developing the composite materials where nano-sized silicons are dispersed homogeneously within electrically conductive and also electrochemically active matrix. Among them, Si-carbon composite anode materials seem to be the most promising for practical application in LIBs.

The cycling stability had been greatly enhanced by employing amorphous carbon [17], graphite [18], carbon nanotube [19], and mesoporous carbon [20] as carbon matrix. Due to its superior electronic conductivity, large specific surface area and excellent structural flexibility, graphene can act as a good carbon matrix to buffer the volume change of silicon particles and maintain a stable conductivity network. Many researchers have obtained graphene and nano-silicon composites through chemical reduction of graphene oxide solution containing nano silicon, such as graphene/nanosized silicon composites [21] and silicon nanoparticles–graphene paper composites [22].

Compared to other carbon matrix, graphene can easily fold and deform to a flexible, 3D macroscale graphene networks which can act as a wonderful confining structure to construct the connection

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network of graphite and silicon [23]. The networks can buffer the volume change of silicon particles and also provide pathways for transportation of electrons and lithium ions, improving both the electrical conductivity and the lithium ion diffusion rate of the electrode [24]. Meanwhile, other than simply synthesizing Si-graphene composites, graphite was added as a main matrix of the composites in this work with following considerations. Firstly, graphite is also a good supporting host matrix because of its small volume expansion (9%) on lithium intercalation and ideal cycle stability. These features are further helpful for accommodating the volume change of silicon. Secondly, the addition of graphite can scatter nano-silicon particles and prevent the agglomeration of these particles which can be often found in Si-graphene composites [22]. Thirdly, in Si-graphene composites, too low graphene content cannot ease the volume effect of the silicon particles while high graphene content will reduce the overall reversible capacity and coulombic efficiency because of the furious reaction between the graphene with high surface area and the electrolyte [21]. The introduction of graphite as the third phase will promote to find a balance between cycle stability, overall reversible capacity and coulombic efficiency.

In this research, we presented a spherical Graphite/Silicon@reGO composite synthesized by a spray drying and subsequent annealing approach. Thermal reduction of graphene oxide was used to obtain graphene other than chemical reduction. This makes a shorter treatment process and much more green synthesis method. And graphene is firstly used as carbon matrix to connect flake graphite and nano silicon. The structure, morphology and electrochemical performance of the composite were investigated.

2. Experimental

2.1. Preparation of Graphite/Silicon@reGO composite

Graphite oxide was synthesized by the Hummers' method [25]. The delamination of graphite oxide into graphene oxide (GO) was achieved by ultrasonic treatment. The final suspension of GO was concentrated to a content of $\sim 3.5 \text{ mg mL}^{-1}$. Then, commercial nano-Si (>99.9%, 1 g, $\sim 30 \text{ nm}$, Shuitian Materials Technology Co. Ltd, Shanghai, China) and graphite (>99%, 9 g, $\sim 3 \mu\text{m}$, Qingdao Tianhe Graphite Co., Ltd, Shandong, China) were dispersed in the as-prepared GO suspension by ultra-sonication for 2 h. The mass ratio of graphite, nano-Si and GO was designed as 9:1:1.4. After that, the obtained suspension was spray dried in a spray dryer unit at a rate of 20 mL min^{-1} with inlet and outlet temperatures maintained at 150°C and 100°C , respectively. The spray-dried precursor (denoted as Graphite/Silicon@GO) was calcined at 600°C for 2 h in a tube furnace with a flowing Ar atmosphere, then cooled naturally to ambient temperature. And the final obtained sample was denoted as Graphite/Silicon@reGO. For comparison, the as-prepared GO suspension was processed in the same procedure as described above to get graphene oxide powder (GO) and thermally reduced GO (reGO). The graphite/silicon composite (Graphite/Silicon) with the mass ratio (9:1) was prepared by mechanical blending.

2.2. Material characterization

The structure of as-prepared samples was characterized by powder X-ray diffraction (XRD, Rint-2000, Rigaku) with $\text{Cu K}\alpha$ radiation ($\lambda = 0.15406 \text{ nm}$) and Raman spectroscopy (514.5 nm, Ar-Ion laser on LabRAM Aramis). Fourier transform infrared spectra (FT-IR) of the samples were recorded on a WQF-410 spectrophotometer (Beijing Secondary Optical Instruments, China). The morphology was measured by scanning electron microscopy (SEM, JEOL, JSM-6360LV) with accelerating voltage of 20 kV and transmission

electron microscope (TEM, Tecnai, G12). TG-DTA (SDT Q600 V8.0 Build 95, Universal V4.0C TA Instruments, USA) was conducted under Ar atmosphere with a flow rate of 40 mL min^{-1} from room temperature to 800°C at $10^\circ\text{C min}^{-1}$.

2.3. Electrochemical measurements

The electrochemical characterizations were performed by CR2025 coin-cell 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 90 wt.% active material and 10 wt.% PVDF binder dissolved in 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 14 mm diameter disks and then were pressed under the pressure of 20 MPa. The cells were fabricated in Ar-filled glove box and galvanostatic cycled between 0.01 and 2.0 V (vs. Li/Li^+) on a multi-channel cell tester. 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. The AC impedance was also performed by a CHI660A electrochemical workstation, with the frequency range and voltage amplitude set as 100 kHz to 0.01 Hz and 5 mV, respectively.

3. Results and discussion

3.1. Structure and morphology of Graphite/Silicon@reGO composite

In order to investigate the change of GO powder thermal reduction process, the TG-DTA curve of GO is shown in Fig. 1. There is a small mass loss (20 wt.%) corresponding to an endothermic peak around 100°C . This is mainly caused by the loss of absorbed water. A huge mass of 40 wt.% has been lost and a sharp exothermic peak appears during the temperature range of $100\text{--}300^\circ\text{C}$ which is due to pyrolysis of the labile oxygen-containing functional groups in GO [26]. According to the results from Fig. 1, 600°C was selected as the thermal reduction temperature. At this temperature, the mass loss ratio of GO is about 60% and the conversion rate of graphene oxide to graphene is estimated to be 40%. As the mass ratio of graphite, nano-Si and GO in Graphite/Silicon@GO was designed as 9:1:1.4, it can be deduced that the mass ratio of graphene in Graphite/Silicon@reGO is about 5.3% with the assumption that the

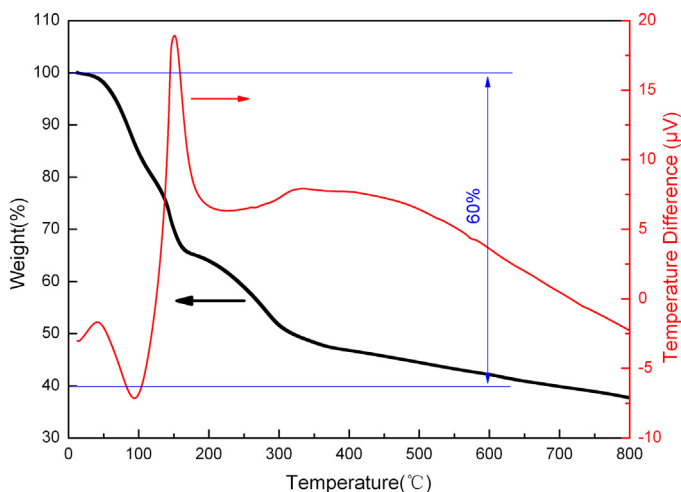


Fig. 1. TG-DTA plot of GO.

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