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Multi-layered carbon coated Si-based composite as anode for lithium-ion batteries

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ABSTRACT

Si-based composite with multi-layered structure composed of multicomponent carbon was successfully prepared via a two-step in-situ carbon coating process. The physicochemical properties of the composite were characterized by TG-DTA, XPS, XRD, SEM, TEM, Raman and electrochemical measurements. XPS reveals the presence of reduced graphene oxide. SEM and TEM images demonstrate that the nano-Si particles are well dispersed in multi-layered carbon matrix constructed by resin-pyrolyzed carbon and reduced graphene oxide. Used as anode material for lithium-ion batteries, the prepared Si@C@RGO composite exhibits improved electrochemical performance. The electrochemical results indicate that the composite exhibits a high initial charge capacity of 1474.9 mAh g^{-1}, with an initial columbic efficiency of 74.57%. The composite also delivered a higher charge capacity at various current densities, and show good rate performance, which is partly attributed to the stable multi-layered structure.

1. Introduction

Owing to their high energy-storage density, long-term cycle life, and ambient temperature operation, lithium-ion batteries (LIBs) have been considered to be the most promising candidates for advanced clean energy storage devices [1–3]. As one of the components of LIBs, anode material plays an important role in LIBs' operation. However, along with the developments of large-scale EV, HEV and PHEV and the requirement of high energy densities, many efforts have been made in search of high capacity anodes to replace existing carbon-based materials due to their limited capacity (372 mAh g^{-1}). Lithium-alloying materials (Si, Ge, Sn, Al, Sb, etc.) have much higher Li storage capacity than the conventional carbon-based materials. Among all the alloy anodes, Si materials have attracted people's attention because of their high specific capacity (3579 mAh g^{-1}), environmental compatibility and low cost [4,5]. Moreover, Si also has a massive volumetric capacity of 8322 mAh cm^{-1} [6]. However, the use of Si is severely hampered by its huge volumetric change (~300%) during the alloying/dealloying process and low intrinsic electrical conductivity [6,7]. To overcome these issues, tremendous research have been focused on reducing the particle size of silicon and designing suitable Si-based composites [8–10].

Graphene has become a spotlight in the field of energy conversion due to its superior electronic conductivity, large specific surface area, excellent structural flexibility and high surface to volume ratio [11,12]. Graphene has been proven to be the primary candidate for use as the buffering/conducting matrix for silicon anodes owing to its exceptional physicochemical properties [13–15]. Various graphene-based materials such as graphene hydrogels, aerogel, foams, and networks have been prepared via hydrothermal and chemical vapor deposition (CVD) methods. As known, though the structures described above could greatly improve the electrochemical performance of silicon anodes, these methods always involve harsh preparation conditions and complex synthetic procedures [16]. Furthermore, the compact density of the materials is also an issue in terms of the requirement of high volumetric capacity [17]. Hence, a simple and convenient method to prepare Si-based anode materials with high adjustability is very necessary [18].

In this report, we propose a novel two-step in-stiu carbon coating technology to prepare multi-layered carbon coated Si@C@RGO composite. Phenolic resin-pyrolyzed carbon was in-situ formed from organic residue carbonization under high-temperature pyrolysis in the first step, and reduced graphene oxide was obtained by thermal reduction during the following step. The as-prepared composite Si@C@RGO was preliminarily studied in respect of physicochemical and electrochemical properties.

2. Experimental

2.1. Materials preparation

Graphene oxide (GO) was synthesized by a modified Hummers' method, just as described in our previous study [11]. Si@C@RGO

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composite was prepared by a two-step in-stiu carbon coating process using the following procedure. Commercially available nano-Si particles (0.4 g, ~80 nm, Shuitian ST-NANO Science & Technology Co., Ltd., Shanghai, China) and phenolic resin (0.2 g) were put into acetone (30 mL) and sonified with ultrasonic stirring for dispersion. The solution was heated to 50 °C for hours with mild magnetic stirring to get a solid blend precursor of Si@C composite. Then, the precursor was sintered at 750 °C for 2 h under argon atmosphere in a tube furnace to yield Si@C composite. Subsequently, the obtained Si@C powders were dispersed uniformly into GO suspension (100 mL of 4 mg mL^{-1}) with the existence of additive agent C and evaporated at 80 °C to get a solid blend precursor Si@C@GO. Finally, the precursor was heated to 500 °C for 3 h under argon atmosphere in a tube furnace to yield Si@C@RGO composites. As contrast, the sample Si/C/RGO prepared by one-step in-stiu carbon coating process was prepared following the similar method and denoted as Si/C/RGO. The nano-Si powder and phenolic resin were dispersed into graphene oxide suspension. After, the suspension was vigorously stirred and evaporated to get the precursor of Si/C/GO composites. The Si/C/RGO composite was obtained after annealing.

2.2. Materials characteristics

Thermal analysis of the blended precursor was performed on a SDT Q600 DSC-TGA (TE, USA) apparatus between room temperature and 900 °C at a heating rate of 10 °C min^{-1} in argon atmosphere. The powder X-ray diffraction (Rint-2000, Rigaku, Japan) measurement using Cu $K\alpha$ radiation ($\lambda = 0.15406$ nm) was employed to identify the crystalline phases of the materials. The morphology of the composites was observed by scanning electron microscopy (SEM, JEOL, JSM-5600LV). Raman spectra from 180 to 2000 cm^{-1} were obtained from WiTec Alpha300 system applying 632.8 nm laser light. The microstructure of the composite was examined by a Tecnai G12 transmission electron microscope (TEM).

2.3. Electrochemical measurements

The electrochemical characterizations were evaluated using CR2025 coin-type cell. The working electrodes were prepared by mixing the active material with 15 wt% Super P and 15 wt% LA-132 binder (Chengdu Indigo Power Sources Co., Ltd., China) to form a slurry. Then, the blended slurry was pasted onto a Cu foil current collector and dried at 120 °C for 12 h. After that, it was punched in the form of 12 mm diameter disks. Lithium foil was used as counter electrode and reference electrode. A polypropylene micro-porous film was used as the separator. The electrolyte was 1 mol L^{-1} $LiPF_6$ in EC, EMC and DMC (1:1:1 in volume). The assembly of the cells was carried out in a dry Ar-filled glove box. Galvanostatic charge–discharge tests were carried out using a Neware battery tester (Neware. Shenzhen) with a potential range of 0.01–2.00 V at room temperature. The cyclic voltammetry measurements and electrochemical impedance spectroscopy measurements were carried out with a CHI660A electrochemical analyzer. The electrochemical impedance spectra (EIS) were recorded by applying an AC voltage of 5 mV amplitude in the 0.01 Hz–100 kHz frequency range.

3. Results and discussion

3.1. Thermal analysis of the precursor

The TG-DTA curves of the two precursors are shown in Fig. 1. Fig. 1(a) is the TG-DTA curves of the precursor of Si@C composite. It is clear that three mass loss stages appear at 25–75 °C, 200–275 °C and 325–600 °C, which represent the loss of moisture, residual crystallized water and decomposition of phenolic resin, and the corresponding endothermic peaks are displayed in DTA curve. The weight loss is ~27.37%. The TG-DTA curve of the precursor of Si@C composite is similar to the TG-DTA curve of phenolic resin, since nano-Si is stable in the temperature range under argon atmosphere; any weight change of the precursor mainly corresponds to the pyrolysis of phenolic resin [19–21]. According to the above analysis, 750 °C was selected as the thermal treatment temperature. Fig. 1(b) is the TG-DTA curve of the precursor Si@C@GO. There are three mass loss stages appear at 25–125 °C, 150–225 °C and 225–450 °C, which represent the weight loss of physically absorbed and crystallized water, pyrolysis of the labile oxygen-containing functional groups in GO and the further reduction of GO, and the deposition of GO corresponds to the sharp exothermic peak at 200 °C DTA curve. The weight loss is about 59.24%. Hence, 500 °C was estimated to be the thermal reduction temperature of GO.

3.2. Structure and morphology of the materials

To investigate the compositions change of GO before and after reduced by annealing, the XPS spectrum was performed on GO and RGO. As shown in Fig. 2, the presence of the three distinct peaks (284.7, 286.3 and 288.4 eV) in the C1s spectrum were attributed to carbon atoms in C—C/C═C, C—O and C═O bands [22–24]. After annealing at 500 °C for 3 h, the C—C/C═C band becomes predominant. Both C—O and C═O bands were significantly reduced, demonstrating that most of the oxygen-containing functional groups have been removed after heat treatment, which means that GO was transformed into RGO.

Fig. 3 shows the XRD patterns of nano-Si, Si@C, Si/C/RGO and Si@C@RGO particles. We can see that nano-Si remains its crystal structure in both Si/C/RGO and Si@C@RGO particles [25], and all the XRD patterns of the composite exhibit similar curves to pure nano-Si. The broad diffraction peak observed at ~23° in Si@C composite corresponds to phenolic resin-pyrolyzed carbon, which is homogeneously distributed in the hybrids without agglomeration [26,27] and also exists in XRD patterns of Si@C@RGO composite. However, no diffraction peaks are observed for crystalline carbon; therefore, carbon in the sample is amorphous. There is also no obvious peak for reduced graphene oxide

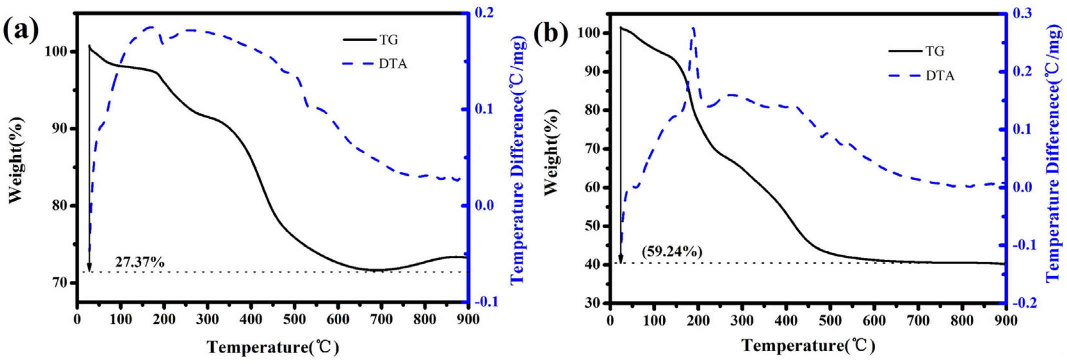

Fig. 1. TG and DTA curves of the (a) Si@C and (b) Si@C@RGO precursor recorded from room temperature to 900 °C at a heating rate of 10 °C min^{-1} in Ar atmosphere.