Powder Technology 331 (2018) 52–59

Contents lists available at ScienceDirect

Powder Technology

journal homepage: www.elsevier.com/locate/powtec

Graphene-chambered interconnected nano-Si@N, P, S–codoped C spheres as anodes for lithium ion batteries

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ARTICLE INFO

Article history:
Received 10 October 2017
Received in revised form 12 January 2018
Accepted 7 March 2018
Available online 08 March 2018

Keywords:
Silicon
Composite
Anode
Lithium-ion batteries
Electrochemical performance

ABSTRACT

A facile and controllable material preparation method is developed to fabricate a graphene-chambered interconnected nano-Si@N, P, S-codoped C spheres anode composite for lithium ion batteries. Interconnected carbon shells improve the electronic contact of neighbor spheres, while flexible graphene networks ensure high electrical conductivity for the entire structure and provide extra void spaces for the volume expansion of Si. At 200 mA g^{-1}, the discharge capacity of the composite is still as high as 1086 mAh g^{-1} after 200 cycles. At 1600 mA g^{-1}, a stable discharge capacity of about 821 mAh g^{-1} can be obtained. The enhanced electrochemical performance is ascribed to the composition and special microstructure of the fabricated material, which significantly improve the structural stability and conductivity of the electrodes.

1. Introduction

The increasing worldwide demand for high-performance lithium-ion batteries has evoked large amounts of research to search novel lithium-stored materials. Si has been considered as an optimal anode material due to the highest theoretic capacity among the known electrode materials, satisfying lithium insertion/extraction potential plateaus and rich resources [1]. However, both large volume change and low electronic conductivity severely hamper the electrochemical performance of Si electrodes. To overcome the two drawbacks, numerous efforts have been devoted to developing novel nanostructural Si anodes [2–9], employing stronger binders [10,11] and adding electrolyte additives [12,13]. Among them, Si nanoparticle-based composites have received much attention due to facile production and relatively low cost [14]. Especially, core-shell Si nanocomposites have demonstrated obviously improved cycling performance because the outer shell can not only improve the conductivity of Si, but also suppress the volume change of Si particles to some degree [14–16]. However, since the outside shell tends to fracturing in a prolonged cycling process, simple core-shell structure is not enough to accommodate the volume change of Si. To obtain further enhanced electrochemical performance, it still needs to be combined with other measures.

Graphene has widely been used to improve the electrochemical performance of lithium storage materials because of high conductivity and excellent mechanical properties [17–21]. However, the influence of graphene on the electrochemical performance of Si electrodes is closely associated with the distribution and existence state of graphene in the composites. The nano-Si/graphene composites synthesized by simple self-assembly usually show limited improvement in cycling performance because nano-Si particles tend to fall off from graphene after the repeated expansion/contraction, resulting in the loss of electronic contact [21,22]. Carbon or conductive polymer coated nano-Si/graphene composites show further improved cycling performance [23]. However, a thick carbon/polymer coating layer easily bereaves graphene of high elasticity. To overpass this problem, sandwich-structural graphene/nano-Si@C/graphene composites and graphene coated nano-Si@C composites have been fabricated [24]. However, the preparation of the aforementioned composites experiences either a troublesome manual operation procedure or takes a long reaction time. On the other hand, it has been demonstrated that N, O or S doping can not only significantly improve the conductivity of carbon, but also contribute to lithium insertion because of higher electronegativity than C [25,26].

In this work, we fabricate a graphene-chambered interconnected nano-Si@N, P, S-codoped C spheres anode composite for lithium ion batteries by the combination of rapid hydrogel coating, self-assembly, lyophilization and carbonization techniques. Compared with the previously reported method, the suggested synthesis routine is more facile and controllable. In the as-prepared composite, the high elasticity of graphene is maintained and the interconnected nano-Si@C spheres keep compact contact with graphene. Lyophilization ensures the porous

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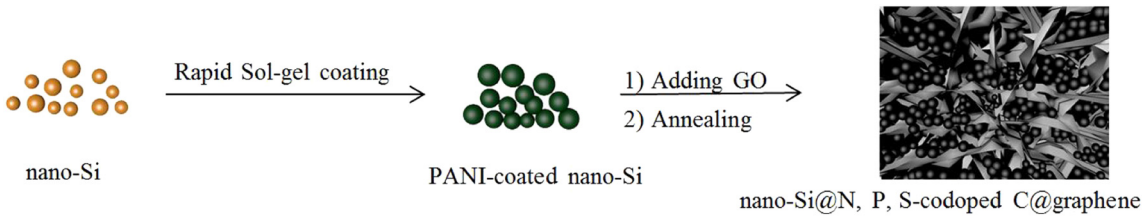
https://doi.org/10.1016/j.powtec.2018.03.006
0032-5910/



Scheme 1. Formation process of the graphene-chambered interconnected nano-Si@N, P, S codoped-C spheres.

structure of the resultant composite, which provides extra room for the volume change of nano-Si. Besides, since N, P and S are from the reactants, there is no need for adding extra dopants. When used as anode for lithium-ion batteries, the as-prepared composite shows high reversible capacity with significantly enhanced cycling performance.

2. Experimental

2.1. Synthesis of materials

Firstly, 0.3 g of nano-Si was dispersed in the solution composed of 20 mL of distilled water, 0.69 mL of aniline monomer and 1.97 mL of 35 wt% phytic acid via ultrasonication. Secondly, 3 mL of ammonium persulfate was added into the above mixture under ultrasonication. Only after several minutes, the hydrogel was formed, and then a desired amount of graphene oxide aqueous solution was added and sonicated for another 20 min. The obtained mixture was stirred for 5 h to complete self-assembly. The solid product was recovered by filtration and subsequently freeze-dried for 8 h. The resultant nano-Si@N, P, S codoped-C/graphene was obtained by annealing the dried sample in a tube furnace with an argon flow of 80 mL min^{-1} at 1000 °C for 2 h. The ramp rate was 10 °C min^{-1}. For comparison, the composite without graphene was also synthesized by similar method (labeled as nano-Si@N, P, S codoped-C).

2.2. Physical characterization of materials

Field-emission scanning electron microscopy (SEM, Leo-1530, Zeiss), transmission electron microscopy (TEM, JEOL 3010) and energy dispersive spectrometer (EDS) were used to characterize the morphology, structure and composition of the samples. X-ray diffraction (XRD, D8 Discover, Bruker) patterns were recorded employing Cu Ka ($\lambda = 0.15406$ nm) radiation at a scan rate of 5° min^{-1} from 10 to 80°. Raman spectra were recorded on a Raman micro spectrometer (InVia, UK) with an excitation wavelength of 560 nm. Elemental analysis of the composite was measured on an Elementar Vario EL III Elemental Analyzer. XPS analysis was performed by a multi-technique ultrahigh vacuum Imaging XPS Microprobe system (ESCALab 250, Thermo VG Scientific) and the CasaXPS software (Version 2.3.16) was used to fit the spectra. The N_2 adsorption and desorption isotherms were collected at 77 K with a Micrometrics ASAP2010 Gas Adsorption Analyzer.

2.3. Cell assembly and electrochemical characterization

Coin-type half cells were assembled to evaluate the electrochemical performance of the as-prepared samples. For the nano-Si@N, P, S codoped-C and nano-Si@N, P, S codoped-C/graphene, the working electrode was the mixture of the tested sample, carbon black and sodium alginate at a mass ratio of 75:10:15. The mass loading of active material was 1.2–1.3 mg cm^{-2}. For the raw nano-Si, the working electrode was composed of 60 wt% nano-Si, 10 wt% carbon black and 30 wt% sodium alginate, and the mass loading of nano-Si was 0.7–0.8 mg cm^{-2}. A lithium foil was used as the counter electrode and 1 M $LiPF_6$ in ethylene carbonate/dimethyl carbonate/ethyl methyl carbonate (1:1:1, V/V/V) was used as the electrolyte. To form stable SEI film, vinylene carbonate (VC) and fluoroethylene carbonate (FEC) as additives were added into the electrolyte above at mass ratios of 2% and 10%, respectively. Cell assembly was carried out in a recirculating argon glove box (LabMaster, BRAUN) where the moisture and oxygen contents were both below 1 ppm. The cells were cycled at room temperature in a voltage window of 0.02–1.2 V on a Neware battery tester. Electrochemical impedance spectra (EIS) and cyclic voltammetry (CV) measurements were performed on an electrochemical workstation (VMP3, Bio-logic). The scan rate for the CV measurement was 0.2 mV s^{-1}. EIS measurements were carried out over the frequency range from 100 kHz to 0.1 Hz by applying a sine wave with an amplitude of 10 mV. The coating thicknesses on the current collectors before and after cycling were measured by a micrometer scale in the above glove. The coating thickness was obtained by subtracting the collector thickness from the electrode disc thicknesses.

3. Results and discussion

Scheme 1 illustrates the formation process of the graphene-chambered interconnected nano-Si@N, P, S codoped-C spheres. The phosphoric acid groups in the phytic acid molecules can potentially bind with the SiO_2 on the Si particle surfaces via hydrogen bonding, which results in the conformal coating of phytic acid molecules on the Si particle surfaces [27]. In subsequent polymerization process, these phytic acid molecules further crosslink with aniline monomers to generate a conformal coating. Additionally, the negatively charged surface oxide may electrostatically interact with the positively charged polyaniline (PANI) doped by the phytic acid. The interactions above result in the formation of a 3D continuous hydrogel network, trapping the coated Si particles inside. This hydrogel polymerization reaction can be completed in several minutes. Under ultrasonication, PANI coated Si hydrogels are partly dispersed and then electrostatically interact with the negatively charged graphene oxide. After annealing, PANI is carbonized while graphene oxide is reduced. It should be mentioned that although PANI coated Si hydrogel have directly been pasted on the collector as working electrodes [27], owing to poor binding between PANI and the collector, the mass loading of nano-Si is very low (0.2–0.3 mg cm^{-2}), limiting the areal energy density.

From Fig. 1(a), the raw Si nanoparticles are 30–100 nm in sizes. In the synthesized nano-Si@N, P, S codoped-C composite (Fig. 1(b)), Si nanoparticles have been coated by pyrolytic carbon to form core-shell spheres which are interconnected into small aggregates by the outer-shell carbon. Compared with monodisperse nanospheres, the interconnected outer-shell carbon contributes to electronic transfer between neighbor spheres. The synthesized nano-Si@N, P, S codoped-C/graphene composite shows interesting microstructure (Fig. 1(c, d)). The graphene sheets are assembled on the surfaces of the interconnected nano-Si@N, P, S codoped-C sphere aggregates to form lots of compartments with different sizes. The TEM and HRTEM images in Fig. 1(e, f) further confirm that crystalline Si nanoparticles are coated by an about 5 nm amorphous carbon layer, and neighbor spheres are interconnected together by carbon shells. Moreover, graphene sheets keep good contact with Si@N, P, S codoped-C spheres. This unique nanostructure can not only improve the electronic conductivity, but also provide much more voids/spaces to accommodate the volume changes of Si during cycling while