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Preparation of graphene supported porous Si@C ternary composites and their electrochemical performance as high capacity anode materials for Li-ion batteries

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Received 30 January 2015; received in revised form 11 March 2015; accepted 11 March 2015

Abstract

Graphene supported porous Si@C ternary composites had been synthesized by various routes and their structural, morphological and electrochemical properties were investigated. Porous Si spheres coated with carbon layer and supported by graphene have been designed to form a 3D carbon conductive network. Used as anode materials for lithium ion batteries, graphene supported porous Si@C ternary composites demonstrate excellent electrochemical performance and cycling stability. The first discharge capacity is 2184.7 mA h/g at a high current density of 300 mA/g. After 50 cycles, the reversible capacity is 652.4 mA h/g at a current density of 300 mA/g and the coulomb efficiency reaches at 98.7%. Due to their excellent electrochemical properties, graphene supported porous Si@C ternary composites can be a kind of promising anode materials for lithium ion batteries.

Keywords: Anode materials; Porous Si; Carbon layer; Graphene; Electrical performance

1. Introduction

Considering the fact that rechargeable Li-ion batteries almost dominate the portable electronic and electric vehicle markets, it is highly desired to further improve the battery performance by developing new electrode materials with higher specific capacity, better conductivity and better cycle stability [1]. However, the low theoretical capacity (372 A h/g) [2] and security of carbon-based anode materials for lithium ion batteries cannot meet the growing demand of high-energy application fields. Theoretical capacity of transition metal oxides is over 700 mA h/g, but the low electrical conductivity and the volume change make their cycling performance variation. At the same time, the formation of the SEI film causes a high irreversible capacity [3]. Tin-based materials have received considerable interests as high capacity (782 mA h/g). However, when Li is alloyed and de-alloyed or metal is reduced and oxidized, large expansion volume occurs [4]. Silicon is considered as a more promising lithium ion battery anode material because of a specific insertion capacity of 4200 mA h/g, abundance and environmental protection [5]. Like other materials, in the process of the lithium insertion and extraction, there exists a large volume change. In addition, low electrical conductivity of silicon electrode limits its application in anode materials [6].

Therefore, to overcome the volume expansion problem, many researchers have synthesized Si nanowires [7], Si nanotubes [8], Si nanospheres [9] and some other Si-based composites [10] used as anode materials. Recently, much work has been focused on the synthesis of carbon coated silicon materials as anode materials to enhance the lithium storage performance by introducing carbon as buffering matrixes. Carbon coating layer not only acts as a buffer layer against the volume change but also improves the electrical conductivity of Si anode material [11]. For example, Hong [12] prepared mesoporous Si/C composites anode materials by the

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http://dx.doi.org/10.1016/j.ceramint.2015.03.060
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Please cite this article as: X. Chen, et al., Preparation of graphene supported porous Si@C ternary composites and their electrochemical performance as high capacity anode materials for Li-ion batteries, Ceramics International (2015), http://dx.doi.org/10.1016/j.ceramint.2015.03.060

magnesium-thermal reduction process. Xu [13] synthesized nanosized core/shell silicon@carbon anode materials with polyvinylidene fluoride as carbon source. Wang [14] used nanostructured hybrid silicon/carbon nanotubes as anode materials, which showed a high reversible capacity.

Fabricating porous electrode is another approach to improve the cycling stability of anode materials because that the special structure could provide extra free space for alleviating the structural strain and accommodating the large volume variations during repeated Li-ion insertion/extraction processes [15]. For instance, Song [16] produced a novel porous coral-like $Zn_{0.5}Ni_{0.5}Co_2O_4$ by a facile co-precipitation method using oxalic acid as complex agent, which showed excellent electrochemical performance. Wang [17] prepared hollow porous SiO_2 nanobelts using CuO nanobelts as template. Used as a potential anode material for LIBs, they exhibited remarkable lithium-storage capability in terms of high specific capacity, excellent cycling performance and high rate capability.

Recently, graphene has been paid more attention in the field of materials science due to its superior electrical conductivity, high surface area and excellent structural flexibility [18,19]. For instance, Zhao [20] synthesized carbon-doped Li_2SnO_3/graphene composites for lithium-ion batteries by the hydrothermal route. Fan [21] prepared nanographene-constructed carbon nanofibers grown on graphene sheets high-performance anode materials. Flexible network of grapheme could improve the electron conductivity of the electrode material during the charge–discharge processes. In addition, acting as a good carbon matrix to construct the connection among the particles, graphene also effectively buffers the volume changes of the embedded particles with its wonderful confining structure [22].

Here, we present a facile way to synthesize high performance porous Si@C/graphene composites. In the Si@C/graphene composites, the special structure, the carbon coating layer and the flexible graphene network work together to effectively accommodate the volume expansion of Si during the Li-insertion/extraction process. Meanwhile, carbon coating layer and graphene network could improve the electrical conductivity of the electrode. The structure, morphology and electrochemical performance of the composites were tested and the results showed that porous Si@C/graphene composites exhibited a better electrochemical performance than Si and Si@C electrode.

2. Experiment

2.1. Sample preparation

2.1.1. Preparation of hollow SiO_2 spheres

Solid SiO_2 spheres were synthesized by a well-known StÖber process. In a typical experiment, 152 ml ethanol, 36 ml ultrapure water and 195 ml ammonia (28%) were mixed completely to form a uniform solution, then 16.8 ml tetraethyl orthosilicate (TEOS) was added into the above solution quickly and then the mixed solution was stirred at room temperature for 6 h. The resulting products were centrifuged and were washed with deionized water and ethanol, and then they were dried in a vacuum at 60 °C for 12 h.

The hollow SiO_2 spheres were prepared via a simple sodium borohydride etching method. 1.2 g solid SiO_2 spheres were dispersed in 40 ml polyvinyl pyrrolidone aqueous solution (2.91%), 2.4 g $NaBH_4$ was added into the above mixture slowly and then the mixed solution was stirred at 51 °C for 6 h. The products were separated by centrifugation and were washed with ultrapure water and ethanol. Finally, the hollow SiO_2 spheres were obtained after drying in a vacuum at 60 °C for 12 h.

2.1.2. Synthesis of porous Si@C composites

The hollow SiO_2 spheres were coated with a thin layer of glucose-derived carbon-rich polysaccharide (GCP) through a direct hydrothermal synthesis. 0.6 g prepared hollow SiO_2 spheres were dispersed in aqueous glucose solution under the magnetic stirring. The solution was then transferred into a 100 ml Teflon-lined stainless steel autoclave. The autoclave was kept in an oven at 180 °C for 12 h. After cooling down to the room temperature, the products were washed with ultrapure water and ethanol, and then were dried at 60 °C for 12 h to obtain the GCP coated hollow SiO_2 spheres. The porous Si@C composites were prepared by thermal treatment, that is the mixture of GCP coated hollow SiO_2 spheres and Mg powder at 650 °C under Ar atmosphere for 3 h at a heating rate of 3 °C min^{-1}, and the generated MgO and the remaining Mg powders were removed using HCl aqueous solution. Si was also synthesized as the control sample. The synthetic process of the Si was just the same as that of the porous Si@C composites except that the GCP coated hollow SiO_2 were replaced by the as-prepared hollow SiO_2 in the process of thermal treatment.

2.1.3. Synthesis of porous Si@C/graphene composites

Graphite oxide (GO) was prepared with a modified Hummers method [23]. 0.125 g GO was dispersed in 50 ml ultrapure water and the hollow SiO_2@GCP (0.25 g) was dispersed in 25 ml ultrapure water, respectively. The hollow SiO_2@GCP aqueous solution was then slowly added into the GO aqueous solution and then the mixed solution was stirred for 30 min. Subsequently, the above solution was transferred to a 100 ml Teflon-lined stainless steel autoclave. The autoclave was kept in an oven at 180 °C for 18 h. After the reaction was finished, the resultant products were centrifuged and then were dried in a vacuum at 60 °C for 12 h. The above dried products were mixed with Mg powder, and then the mixture was calcined at 500 °C under Ar atmosphere for 3 h with a slow ramp rate of 3 °C min^{-1}. Subsequently, HCl aqueous solution gets rid of the generated MgO and the remaining Mg powders to obtain the final porous Si@C/graphene composites.

2.2. Materials characterization

The X-ray diffraction (XRD) was employed to analysis the characterize structures of the porous Si@C/graphene composites, which was recorded on a model D/max-2500VL/PC system equipped with Cu-Ka radiation at 40 kV and using 100 mA. The Fourier transform infrared spectroscopy (FTIR) spectrums of the samples were obtained by using a Model NIcolETiS10 Fourier transform spectrometer (Thermo SCI-ENTIFIC CO., USA) in the range of 400–4500 cm^{-1}. The Raman spectrums were measured

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