Energy 85 (2015) 159–166

Contents lists available at ScienceDirect

Energy

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

Mesoporous silicon/carbon hybrids with ordered pore channel retention and tunable carbon incorporated content as high performance anode materials for lithium-ion batteries

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ARTICLE INFO

Article history:
Received 7 November 2014
Received in revised form
10 March 2015
Accepted 11 March 2015
Available online 21 April 2015

Keywords:
Mesoporous silicon
Hybrid
Anode material
Lithium ion battery

ABSTRACT

In-situ magnesiothermic reduction reaction route was developed to synthesize mesoporous Si/C (silicon/carbon) hybrids with ordered pore channel retention and tunable carbon incorporated content as high performance anode materials for LIBs (lithium ion batteries). The effect of carbon incorporation on the microstructures and electrochemical performance of the Si/C hybrid LIBs anodes is investigated. The incorporation of carbon in the Si/C hybrids not only prevents the ordered structure of mesoporous silicon from collapsing, but also increases the electrical conductivity of the synthesized Si/C hybrids. The as-prepared Si/C hybrid LIBs anode with an optimal carbon content of 7.05 wt%, displays improved electrochemical performance with a high reversible specific capacity, rate capability and excellent cyclic performance, showing a higher specific capacity of up to 1452 mAh g^{-1} at a current density of 200 mA g^{-1} after 100 cycles and a high coulombic efficiency of up to 99.2%. The great improvement of the electrochemical performance of the ordered mesoporous Si/C hybrid LIBs anodes can be attributed to the unique ordered structure, large surface area, the homogeneously incorporated carbon in the Si/C hybrids. The synthesized ordered mesoporous Si/C hybrids are promising for potential applications as LIB anode materials with enhanced electrochemical performance.

1. Introduction

Today, depletion of fossil energy sources and environmental pollution are becoming the severe problems. To replace the traditional fossil fuels, renewable energy generation (wind, wave, solar) becomes more and more critical in future. Among the present energy conversion and storage devices, LIBs (lithium ion batteries) have been widely used in energy storage field because of their high energy density, high open-circuit voltage and no memory effects [1,2]. However, current commercial anode material based on graphite is limited by its low theoretical specific capacity of 372 mAh g^{-1} and limited rate capability. To obtain high energy and power density essential to meet the future challenges of energy storage, many researchers began to seek for new generation electrode materials, including transition metal oxides, silicon (Si) and tin etc. [3–15]. For instance, Yang et al. synthesized $Li_4Ti_5O_{12}$/carbon hybrid electrodes, displaying a reversible capacity of approximately 160.8 mAh g^{-1} at a current density of 30 mA g^{-1} [3]. Pang et al. reported MnOx@carbon hybrid nanowires with core/shell architecture as highly reversible anode materials for lithium ion batteries. The novel MnOx@carbon hybrid nanowires exhibit a reversible capacity of approximately 541 mAh g^{-1} after 54 cycles [4].

Compared with the transition metal oxides, Si has also attracted particular attention because of its high theoretical capacity, abundant resources and non-poisonousness as LIBs anode material. Si can theoretically accept 4.4 Li^+ ($Li_{4.4}Si$) per atom leading to a capacity of 4200 mAh g^{-1}, which is an order of magnitude higher than that of conventional graphite anode materials. However, its application for LIBs anode materials has been hindered by large volume change (>300%) and low intrinsic electrical conductivity. The large volume change during lithium ion insertion/extraction process can

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http://dx.doi.org/10.1016/j.energy.2015.03.090

induce enormous mechanical stress, and then leads to pulverization of the Si electrode materials and loss of electrical contact with current collector, which may result in decreasing in reversible capacity. Furthermore, the low electrical conductivity of Si is not favorable for the fast lithium ion transport, leading to capacity loss and poor rate capability [6].

To overcome these obstacles and obtain high energy storage performance, several attempts have been implemented to enhance capacity and improve the cycling stability performance of Si electrode. Among these strategies, rational design of Si nanostructures and coupling of Si with carbon to form Si/C hybrids are the promising techniques [6,7]. So far, variety of nanostructured Si anode materials with different dimensionalities, such as nanoparticles [8], nanocable arrays [9], nanowires [10,11], and nanotubes [12,13], have been reported to improve the cycle life and rate capacity. However, most of these Si nanostructures are fabricated by chemical vapor deposition or physical vapor deposition routes, and these methods usually need higher temperature and gas precursor, the Si nanostructures are difficult to be controlled and synthesized in large scale [14,15]. Si/C hybrid synthesized strategy can combine the appealing merits of both Si (high theoretical capacity) and carbon (good electrical conductivity and mechanical stability) [7]. Up to now, Si–graphite [16], Si/graphene [17], Si/carbon fiber [18], and Si/C core/shell nanocomposites [19] are reported. However, nanostructured Si electrode materials tend to aggregate easily, greatly inhibiting the penetration of electrolyte into electrochemically active materials for Li storage [6].

Recently, much attention had been paid to the hierarchically porous structure composed of primary nanocrystals tightly interconnected to form three dimensional channels. Hierarchically porous Si can combine the advantages of the high specific capacity from nanoscale Si and good stability from hierarchical structure. The application of the hierarchically porous Si is mainly hampered by the tedious process of template technology [20,21], and low yield of chemical etching method [22,23]. It was previously reported that silica material can be reduced to nanostructured Si by magnesiothermic reduction action [24–27]. However, the reported structures of ordered porous Si are usually destroyed and collapsed, increasing the interface resistance for the lithium ion transfer and resulting in low capacity retention. Up to now, scalable synthesis of ordered mesoporous Si nanostructures as high performance LIBs anodes with tunable microstructures and carbon incorporation content is still challenging.

Herein, we developed a facile route to fabricate ordered mesoporous Si/C hybrid materials as anode materials for high performance LIBs. The synthesized Si/C hybrid materials can retain mesoporous silica ordered channel efficiently, and the specific surface area can be enhanced remarkably. The capacity of the Si/C hybrid material can also be tuned by optimization of the weight ratio of Si to C. The Si/C hybrid sample with the optimal microstructure and chemical composition, displays a higher specific capacity of 1452 mAh g^{-1} at the current density of 200 mA g^{-1} after 100 cycles, showing its potential applications as anode material in LIBs.

2. Experimental section

2.1. Synthesis of Si/C hybrids

The mesoporous silica SBA-15 was synthesized using triblock copolymer Pluronic P123 as a template and tetraethoxytitane (TEOS) as a silica source [28]. In a typical synthesis of SiO_2/C hybrid, 1.0 g of SBA-15 was added to a solution obtained by dissolving 0.156 g of sucrose and 0.14 g of H_2SO_4 in 5.0 g of deionized water. The mixture was treated in a drying oven at 100 °C and 160 °C for 6 h, respectively. After the addition of 0.1 g of sucrose, 0.09 g of H_2SO_4 and 5 g of deionized water, the sample was treated again at 100 °C for 6 h and 160 °C for another 6 h. The carbonization process was performed by heating the sample to 900 °C and maintaining for 6 h under a nitrogen protection gas flow [29].

0.3 g SiO_2/C and 0.3 g magnesium powders were mechanically mixed and put in a corundum boat, and then heated in a tube furnace at 670 °C with an increasing temperate rate of 5 °C min^{-1} for 5 h under Ar atmosphere. The ordered mesoporous Si/C nanohybrids were obtained by soaking the obtained powders in HCl solution to remove MgO [24–26]. The prepared samples were denoted as mesoporous Si, Si/C-1 (0.165 g sucrose first and 0.1 g sucrose second), Si/C-2 (0.312 g sucrose first and 0.2 g sucrose second), Si/C-3 (0.625 g sucrose first and 0.4 g sucrose second).

2.2. Material characterization

The crystal structure of the synthesized samples was determined by powder XRD (X-ray diffraction, Rigaku D/Max-KA diffractometer with Cu Ka radiation). XPS (X-ray photoelectron spectroscopy, ESCALAB 250 with 150 W Al Ka probe beam) was used to characterize the chemical composition and chemical bonding state. Raman spectroscopy measurement was performed using a JY HR800 micro Raman spectrometer under ambient conditions with an excitation wavelength of 632.8 nm. TGA (Thermogravimetric analysis) was carried out under a flow of air with the temperature ramp of 10 °C min^{-1} from 40 to 800 °C using thermogravimetric analyzer (SDTQ600). SU-70 FESEM (field emission scanning electron microscope) was employed to analyze the surface morphology. The microstructures of the synthesized products were observed in TEM (Transmission electron microscope) JEM-2100. The specific surface area was determined by N_2 adsorption/desorption on a V-Sorb 2800P series analyzer (Gold APP Co. Ltd.).

2.3. Electrochemical measurements

The electrochemical measurements were conducted using standard 2025 type coin cells with copper foil as the current collectors, lithium foil as counter electrode and reference electrodes and 1.0 M $LiPF_6$ in a 1:1 (V/V) mixture of EC (ethylene carbonate) and DEC (diethyl carbonate) as the electrolyte. The cutoff voltage window is 0.01–2.0 V. The working electrode mixture slurry was prepared by mixing 80 wt% active materials, 10 wt% acetylene carbon black, 10 wt% binder (styrene butadiene rubber/sodium carboxymethyl cellulose, 1:1 by weight), and an adequate amount of H_2O [25]. Galvanostatically cycled test was carried out on a LAND CT2001A instrument (Wuhan, China) at room temperature. Electrochemical workstation (PARSTAT2273) was used to study CV (cyclic voltammetry) characteristics in a potential window of 0.01–3.00 V at a scan rate of 0.1 mV s^{-1}. EIS (Electrochemical impedance spectroscopy) measurements were performed in the frequency between 100 kHz and 10 mHz and the amplitude is 5 mV [29].

3. Results and discussion

The schematic fabrication process of ordered mesoporous Si/C hybrid material is illustrated in Fig. 1. The mesoporous silica template SBA-15 was firstly synthesized. The carbon precursor (sucrose) was impregnated into the mesoporous silica of SBA-15, and then carbonized to synthesize the SiO_2/C composites. In the impregnated process, the carbon can embed into the pore channel of the SBA-15 and coated on the surface of the SBA-15. The Si/C hybrid anode materials were fabricated by in-situ magnesiothermic reduction of the SiO_2/C composites.