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Research paper

In-situ synthesis of interconnected SWCNT/OMC framework on silicon nanoparticles for high performance lithium-ion batteries

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Abstract

In spite of silicon has a superior theoretical capacity, the large volume expansion of Si anodes during Li$^+$ insertion/extraction is the bottle neck that results in fast capacity fading and poor cycling performance. In this paper, we report a silicon, single-walled carbon nanotube, and ordered mesoporous carbon nanocomposite synthesized by an evaporation-induced self-assembly process, in which silicon nanoparticles and single-walled carbon nanotubes were added into the phenolic resol with F-127 for co-condensation. The ordered mesoporous carbon matrix and single-walled carbon nanotubes network could effectively accommodate the volume change of silicon nanoparticles, and the ordered mesoporous structure could also provide efficient channels for the fast transport of Li-ions. As a consequence, this hybrid material exhibits a reversible capacity of 861 mAh g^{-1} after 150 cycles at a current density of 400 mA g^{-1}. It achieves significant improvement in the electrochemical performance when compared with the raw materials and Si nanoparticle anodes.

Keywords: Silicon; Single-walled carbon nanotube; Ordered mesoporous carbon; Lithium ion battery

1. Introduction

Lithium ion batteries (LIBs) are urgently needed as power supply for today's hybrid vehicles, portable electronic and medical devices owing to its high energy density and rechargeable properties [1]. With the increasing demand of LIBs with higher energy density and prolonged lifecycle, various cathode and anode materials with higher storage capacity have been investigated during the latest years [2,3]. On the one hand, the commercially used graphite carbon anode has a limited theoretical capacity of 372 mAh g^{-1}, which restricts its further application. Silicon has a theoretical capacity of 4200 mAh g^{-1} and a relatively low working potential, making it one of the most promising candidates for the next generation LIBs [4,5]. But silicon has the problem of huge volume expansion (>300%) during lithium insertion and extraction processes. Along with the pulverization and the exposure of more silicon fragments that consume more electrolyte, the impairment of the electrical contact between the current collector and active materials and continuous formation of solid−electrolyte interface (SEI) layers result in intensified capacity fading with prolonged cycles.

In order to overcome these difficulties, numerous efforts have been tried to reduce the volume expansion of silicon anodes. One strategy is decreasing the silicon particle size to micro or nanometre scale [6], such as silicon nanowires [7−9], double-walled silicon nanotubes [6,10], silicon nanoparticles [11−15], and silicon nanospheres [16,17]. Owing to the small particle size and available void space, the abnormal pressure generated during lithiation/delithiation process in these silicon nanostructures can be buffered effectively. Another way is

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dispersing silicon nanoparticles into a matrix [6,18], which possesses high conductivity and good mechanical properties, such as silicon/single-walled carbon nanotube (SWCNT) composite paper [19], graphene-encapsulated silicon foam [20], graphene nanosheets [21,22], carbon nanotubes [6,23–26] and hollow or porous carbon [18,27]. These silicon/carbon composites can not only improve the electric conductivity of the Si, but also accommodate the volume expansion of Si anodes and facilitate the formation of a stable SEI layer.

Among all the carbon materials, the ordered mesoporous carbon (OMC) with porous structure and large surface area can increase the contact area between active materials and the electrolyte, while facilitating the lithium ion diffusion in the electrolyte. So the OMC can be expected to improve the rate capability of Si-based anodes owing to its high specific surface area, ordered mesoporous channels and high pore volume. The silicon nanoparticles trapped in the OMC can also achieve a good rate capability [28–31]. However, the OMC exhibits a rather poor electric conductivity [32,33], which is different from other carbon materials (eg, carbon nanotube, graphene), resulting in that the OMC cannot solely be used as a matrix or additive to make up for the poor electric conductivity of the silicon anode. Considering the SWCNTs, which have high electric conductivity and flexible properties. It is suitable for constructing network to accommodate the expansion of Si-based anodes, as well as increasing the electric conductivity of Si and OMC. Herein, we have fabricated a ternary Si/SWCNT/OMC nanocomposite through a self-assembly synthesis process, in which the OMC was prepared as previously reported [34]. The key synthesis procedure was mixing the Si nanoparticles and SWCNTs together in the F127/phenolic resol solution using the solvent evaporation-induced self-assembly method, thus the interconnected SWCNT/OMC framework was in-situ synthesized on silicon nanoparticles.

For this ternary Si/SWCNT/OMC hybrid material, the Si nanoparticles are well distributed into the interconnected SWCNT/OMC framework, through hydrogen bonds formed between large number of hydroxyl groups on the surface of Si nanoparticles and the F127/phenolic resol [34,35], possessing a number of advantages: 1) The Si nanoparticles are trapped inside the OMC framework and are not in direct contact with the electrolyte solution, the SEI films can be regarded as forming on the surface of the outmost OMC only. 2) The abundant ordered mesopores in the OMC can provide enough void space to accommodate the volume change of Si in the charging/discharging processes. 3) The SWCNTs possess unique 1-D tubular structure, excellent mechanical properties, and high electric conductivity. Meanwhile, its flexible properties could alleviate the volume expansion of Si, thus making sure of an improved cycling performance.

2. Experimental

2.1. Experimental chemicals

Triblock copolymer Plurnoic F127 (Mw = 12,600, PEO_{106}-b-PPO_{70}-b-PEO_{106}) was purchased from Sigma-Aldrich. Silicon nanoparticles (~50 nm) were purchased from Alfa Aesar. Original SWCNTs were purchased from XF nano. Formalin solution (37 wt.%) was purchased from Aladdin Reagent Crop. Phenol. NaOH, HCl, and ethanol were purchased from Sinopharm Chemical Reagent Crop.

2.2. Synthesis of ternary Si/SWCNT/OMC nanocomposite

The Si/SWCNT/OMC composite was prepared by the solvent evaporation-induced self-assembly process. The fabrication process consisted of four steps, preparation of F127/phenolic resol precursor solution, dispersion of silicon nanoparticles and SWCNTs in the F127/phenolic resol solution, thermopolymerization and calcination.

2.2.1. Preparation of F127/phenolic resol

The phenolic resol precursor was prepared by polymerizing phenol and formaldehyde (37 wt.%, 2.1 ml) under alkaline conditions [22]. The phenol (0.61 g, 6.48 mmol) was melted at 42 °C in NaOH aqueous solution (0.1 M, 15 ml) under stirring in a 250 ml flask, followed by the addition of 2.1 ml formaldehyde (37 wt.%). This was followed by violently stirring of the mixture for 1 h at 70 °C. Subsequently, the mixture was cooled to room temperature, and the pH was adjusted to 7.0 using HCl (0.6 M). During this whole process, a colour transition was observed, and the aqueous solution changed its colour from transparent to crimson and finally to yellow. The prepared mixture was dried under vacuum evaporation at 45 °C. The yellow polymeric liquid was dissolved in ethanol, centrifuged, and filtered to remove the precipitated NaCl. At the end, the polymeric liquid was dissolved in an appropriate amount of ethanol prior to be used. The F127 (1.0 g) was dissolved in 10.0 g of ethanol and stirred at 40 °C to form a clear solution. The precursor solution was mixed with the solution of F127, stirring for 10 min to get the F127/phenolic resol.

2.2.2. Preparation of acid-functionalized SWCNTs

The original SWCNTs had an average diameter of 1–2 nm and an average length of 5–30 μm. The SWCNTs were milled with in a mixture of concentrated HNO_3/H_2SO_4 (40 ml, 1:3/V:V), and sonicated for 3 h to prepare carboxylic acid-functionalized SWCNTs [36]. Finally, the suspension was filtered using deionized water until the pH reached 7. The acid functionalized SWCNTS were dried at 100 °C for 12 h under vacuum.

2.2.3. Preparation of ternary Si/SWCNT/OMC hybrid composite

Silicon nanoparticles had an average particle size of less than 50 nm and a purity of more than 98%. Si NPs and SWCNTs were dispersed in ethanol by sonicating for 3 h. This was followed by the addition of SWCNTs and Si NPs solution into the F127/phenolic resol, with a continuous stirring for 8 h. After mixing up the solutions, the mixture was transferred into petri dishes, waiting for about 12 h until the ethanol was