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Synthesis of porous Si/graphite/carbon nanotubes@C composites as a practical high-capacity anode for lithium-ion batteries

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ABSTRACT

There are still several challenges to synthesize a practical, high capacity and stable Si-based anode materials. Here we report a porous Si-based composites, which consists of nano silicon (obtaining high capacity), graphite (gaining stable structure), carbon nanotube (increasing electron conductivity), and pitch (porous structure as well as a binder), by spray-drying method. We then optimize the content of pitch in the composites. The composite with 11.5 wt% carbonized pitch delivers excellent electrochemical performance. It shows an initial reversible capacity of 863.2 mAh g^{-1} at 100 mA g^{-1}, and exhibits capacity retention of 81.3% after 100 cycles. The composite also possesses good rate capability, and up to 89.3% of the reversible capacity can be recovered at 1 A g^{-1}.

1. Introduction

A considerable amount of research has been conducted to develop lithium-ion batteries (LIBs) with high energy capacities to be used for portable electronics and electrical vehicles [1–5]. Silicon is the most promising anode material because of its high specific capacity (3580 mAh g^{-1}), natural abundance, suitable operating potential, and good safety performance. Hence, it is a suitable replacement for graphite in LIBs [6,7]. However, the significant volume change (>300%) during alloying leads to particle fracture, pulverization of the material structure, and poor intrinsic electronic conductivity [8]. In this regard, scholars have focused on effectively accommodating volume expansion and securing the electrical conduction of Si-based materials. The electrochemical performance of Si-based materials can be effectively improved using nanostructures, active–inactive composites, and core–shell structures [9–12]; in particular, combining silicon with other carbon matrices is one of the most effective techniques. Carbon materials can improve the electronic conductivity of the Si electrode and be used as a soft medium to buffer volume changes.

Here, we synthesize a porous Si/graphite/carbon nanotube (CNT)@C composite through spray drying and subsequent carbonization. In the fabricated composite, CNTs work as interconnected conductive network and flake graphite works as carbon framework to ensure the structural stability of the composite. The CNTs and graphite also help the dispersion of Si particles. After spray drying and heat treatment, the CNT/graphite and Si particles are bonded by a carbonized pitch. The amorphous carbon layer derived from low-cost pitch cannot only protect Si particles from electrolytes but also alleviate volume changes in the particles during discharging/charging. We optimize the amount of pitch to obtain a composite with a porous sphere structure and investigate its electrochemical properties.

2. Experimental

Briefly, 1 g of nano-Si (~30 nm, Shuitian ST-NANO Science & Technology Co., Ltd., Shanghai, China) powder was dispersed in 60 mL of alcohol in an ultrasonic bath for 30 min. The solution was added with 0.3 g of pitch powder and ultrasonicated for 30 min to fully mix Si and powder. Subsequently, 5 g of the carbon nanotube suspension (6 wt%) and 1.5 g of flake graphite were dispersed in the suspension under continuous stirring. The mixture was diluted with 240 mL of deionized water. The resulting homogeneous suspension was spray dried by hot air to form a solid precursor. The inlet and outer temperatures of the spray dryer were maintained at 120 °C and 90 °C, respectively. The solid precursor was heated at 850 °C for 3 h under argon atmosphere at a heating rate of 5 °C min^{-1} to obtain the target composite (Pitch-C1). The composites were prepared through similar procedures using 15%, 20%, and 25% pitch (weight ratio) and denoted as C2, C3, and C4, respectively.

Thermogravimetric analysis of the precursor was performed on a SDT Q600 TG apparatus at a heating rate of 10 °C min^{-1}. The crystal structure of the as-prepared composites was characterized by

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X-ray diffraction analysis (XRD, Rint-2000, Rigaku) using CuKα radiation (λ = 0.15406 nm). The morphologies and microstructures of the samples were investigated by field-emission scanning electron microscopy (Nova NanoSEM 230) and transmission electron microscopy (TEM, FEI Tecnai G220) analyses.

The working electrodes were prepared by mixing the active material, Super P, and 5 wt% LA-132 binder (Chengdu Indigo Power Sources Co., Ltd, China) at a weight ratio of 8:1:1. Lithium foil was used as counter electrode. A polypropylene microporous film was used as separator. 1 M $LiPF_6$ in EC:EMC:DMC (1:1:1, v/v/v) was utilized as electrolyte. The cells were discharged and charged using a Neware battery tester (Neware, Shenzhen) within 0.01–2.00 V at room temperature. Cyclic voltammetry (CV) measurements and electrochemical impedance spectroscopy analysis were conducted on a CHI660A electrochemical analyzer.

3. Results and discussion

Fig. 1(a) presents the thermal gravimetric result of pitch in argon atmosphere. The main decomposition starts at 400 °C. The weight change is negligible at temperatures above 800 °C, indicating the completion of pitch pyrolysis. Hence, we select 850 °C for heat treatment; at which, the total weight loss of pitch is 47.8%. The CNTs, graphite, and Si are stable in argon atmosphere. Any weight loss of the precursor can be attributed to pitch pyrolysis. Pitch-C1, C2, C3, and C4 contain 5.5%, 8.4%, 11.5%, and 14.8% carbonized pitch, respectively. The XRD patterns of pure Si and Pitch-C composites are shown in Fig. 1(b). All reflections are well indexed to the peaks of pure Si and graphite, indicating that the composites are composed of Si and graphite [13]. The peaks of the carbonized pitch and CNT patterns are not detected in the com-

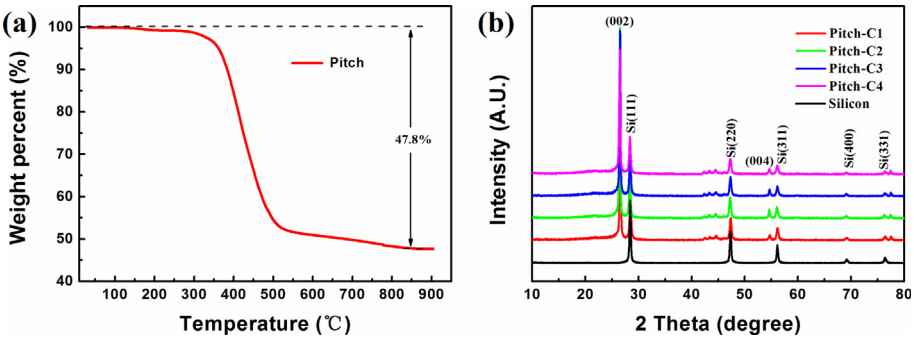

Fig. 1. (a) Thermogravimetric result of pitch in argon atmosphere; (b) XRD patterns of Pitch-C1, C2, C3, C4, and Si.

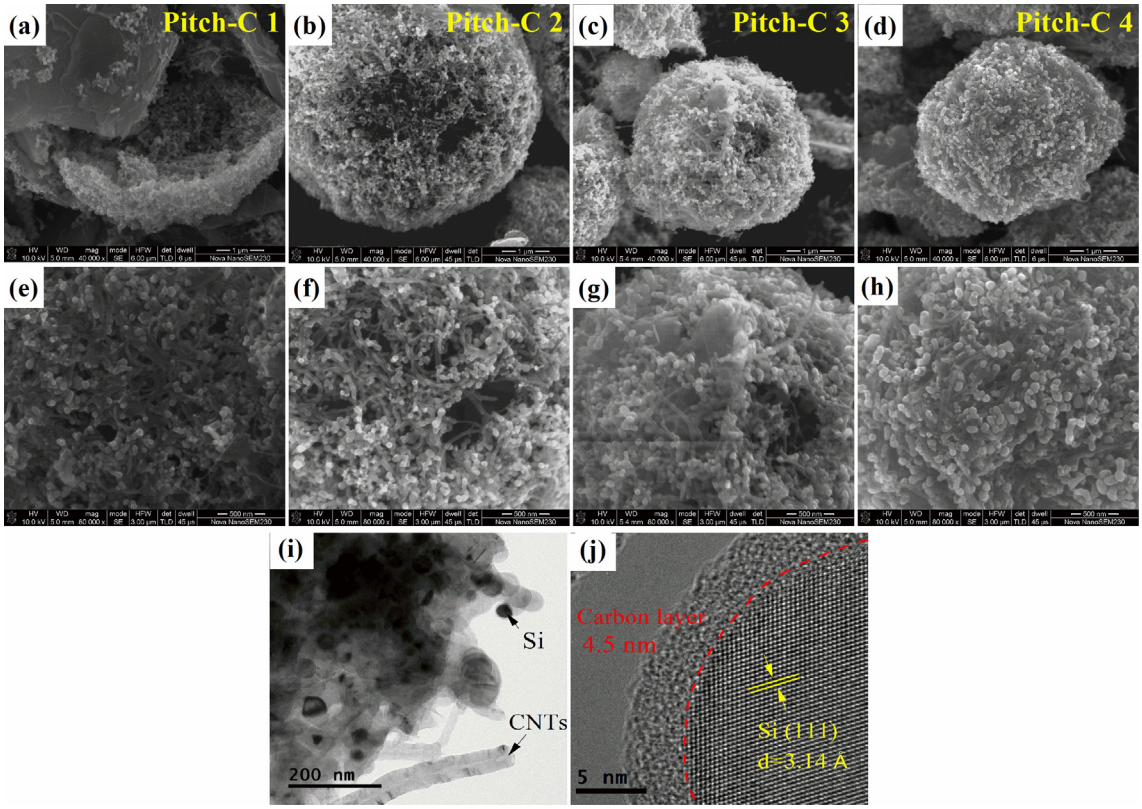

Fig. 2. (a, e) SEM images of Pitch-C1, (b, f) Pitch-C2, (c, g) Pitch-C3, and (d, h) Pitch-C4; (i) TEM images of Pitch-C3; (j) HRTEM image of Si particle in Pitch-C3 composite.