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Hard carbon coated nano-Si/graphite composite as a high performance anode for Li-ion batteries

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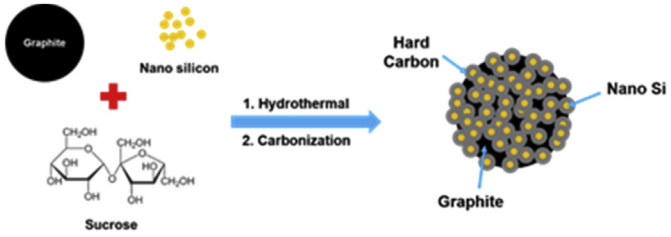
HIGHLIGHTS

- Hard-carbon-nano-Si/Graphite composite was prepared by hydrothermal method for LIBs anodes.
- Hard carbon plays important role buffering the volume expansion of silicon and as active material.
- It also provided an efficient pathway for electron transfer between nano-Si to graphite.
- High specific capacity and excellent cycling stability was demonstrated at high areal capacity.

GRAPHICAL ABSTRACT



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ABSTRACT

With the ever-increasing demands for higher energy densities in Li-ion batteries, alternative anodes with higher reversible capacity are required to replace the conventional graphite anode. Here, we demonstrate a cost-effective hydrothermal carbonization approach to prepare a hard carbon coated nano-Si/graphite (HC-nSi/G) composite as a high performance anode for Li-ion batteries. In this hierarchical structured composite, the hard carbon coating not only provides an efficient pathway for electron transfer, but also alleviates the volume variation of Si during charge/discharge processes. The HC-nSi/G composite electrode shows excellent performance, including a high specific capacity of 878.6 mAh g^{-1} based on the total weight of composite, good rate performance, and a decent cycling stability, which is promising for practical applications.

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1. Introduction

Li-ion batteries (LIBs) have been widely used in electric vehicles (EVs) due to their high energy density, long-term cycle life, and environmental benignity. However, the limited specific capacity (~350 mAh g^{-1}) of graphite anode used in the state-of-the-art LIBs is one of the key barriers to the development of high energy density batteries. Batteries with graphite electrodes have an energy density of <200 Wh kg^{-1}. As a result, the driving range of EVs using these batteries is limited to <200 km in a single charge [1]. Li-ion batteries with high energy density of 300 Wh kg^{-1} are required to meet the need for long range EVs [1,2]. Therefore, alternative high capacity anode are urgently needed for large-scale market penetration of EVs. In this aspect, silicon has been regarded as one of the

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most promising anode material with its high theoretical specific capacity (~4200 mAh g^{-1}) at room temperature [3]. However, because of the large volume expansion (>300%) of Si during lithiation/delithiation processes, silicon particles will be easily pulverized, which would lead to fast capacity fading [4,5]. To circumvent these problems, Si with various nanostructures have been designed. These nanostructures include nanowires [6], nanotubes [7], nanoparicles [8], yolk-shell [9], and core-shell structure [10], which minimize the intrinsic problem of silicon during lithiation/delithiation processes. Recently, a novel sandwich-structured Si/graphene composite has been developed which included ordered magnesiothermo-reduced Si nanoparticles and thermally reduced graphene oxide and demonstrated good stability [13]. Although these nano-structured Si can provide high capacity and good cycling stability, they often suffer from the high production costs and are difficult to scale up. Therefore, a low cost, scalable process of making Si based anode materials is needed. Considering the typical capacity of 150–200 mAh g^{-1} for the state of the art cathode material, a practical anode capacity of ~600 mAh g^{-1} with a long term stability is a reasonable compromise between the high capacity and high stability requirement for anodes [11–13].

Here, we propose a facile and scalable strategy for preparation of the interconnected structure consisting of a hard carbon coated nano-Si/graphite (HC-nSi/G) composite. In this hierarchical architecture, hard carbon plays an important role in buffering the volume expansion of silicon during lithiation and providing the effective pathway for electron transfer, as well as functioning as active material. Furthermore, it is expected that nano-Si adhesion on graphite is well maintained by the hard carbon coating, which has strong mechanical properties.

2. Experimental

2.1. Material synthesis and characterization

Sample preparation and Characterization: The synthesis of the interconnected HC-nSi/G was carried out with a hydrothermal process followed by a carbonization step, as shown in Fig. 1a. In detail, the solution of nano-Si powders (size ~50 nm, Alfa-Aesar) was prepared in 1.5 M of sucrose solution with a few drops of ethanol to uniformly disperse the powder. After the addition of graphite (size ~10 μm, Superior graphite), the mixture was stirred for 1 h at 50 °C and then placed in Teflon-lined stainless steel autoclave. The hydrothermal reaction was carried out at 190 °C for 6 h. The product was further dried at 110 °C overnight to remove the residual water, followed by being carbonized at 1000 °C for 6 h in Ar atmosphere to produce hard carbon structure. The final product was composed of 45.8 wt% of graphite, 14.6 wt% of nano-Si and 39.6 wt% of hard carbon. For pre-lithiation step, the stabilized lithium metal powder (SLMP, FMC Inc.) was scattered on the dried electrode prior to cell assembly and compressed. As a reference sample, mechanically blend graphite/nano-Si/hard carbon (BGSH) was prepared by simply mixing the graphite, nano-Si, and hard carbon with same weight ratio of HC-nSi/G sample. Powder X-ray diffraction (XRD) of the synthesized samples was performed on a Rikagu MiniFlex II with Cu Kα radiation operated at 30 kV and 15 mA. Data were collected in the 2θ range of 10–80° at 0.5° min^{-1}. Scanning electron microscopy (SEM) studies were performed on a FEI Quanta FE-SEM at an accelerating voltage of 5 kV. Transmission electron microscopy was performed on a JEOL-2010.

2.2. Electrochemical measurements

Electrochemical performance measurements were carried out with R2032 coin-type cells. The electrodes were prepared by casting the homogeneous slurry consisting of active materials, carbon black, and sodium carboxymethyl cellulose (CMC) in a weight ratio of 70:10:20 or 80:10:10. A typical loading of the active material is 1.5–2.0 mg cm^{-2}. After drying, the electrodes were punched into disks with an area of 1.27 cm^2, and then dried at 70 °C under vacuum overnight. Electrochemical cells were assembled with the electrode as prepared in an Ar-filled glove box using metallic Li chips as negative electrode, Celgard 2500 as separator, and 1 M $LiPF_6$ in ethylene carbonate (EC)/diethyl carbonate (DEC) with 10 wt% fluoroethylene carbonate (FEC) additive as electrolyte. Charge-discharge experiments were performed galvanostatically on an Arbin BT-2000 battery tester at room temperature (~25 °C). The voltage range for cycling stability and rate performance tests is between 0.005 and 1.5 V vs. Li/Li^+. A 1C rate corresponds to a current density of 600 mA g^{-1} in the present work. Cyclic voltammetry (CV) was tested using a CH Instruments at a scan rate of 0.1 mV s^{-1} in a voltage range of 0.005–1.5 V. Electrochemical impedance spectroscopy was measured using the CHI660d workstation (CH Instruments, US) with a perturbation amplitude of ±5 mV at a frequency range between 10^5 Hz and 10 mHz.

3. Results and discussion

Fig. 1a describes schematically the detailed synthesis process for the HC-nSi/G composites. In order to coat the interconnected hard carbon/nano-Si on a graphite surface, a mixture solution of graphite (size ~ 10 μm), nano-Si (size ~ 50 nm) and 1.5 M of sucrose in water was subjected to a hydrothermal process, followed by a carbonization step to produce hard carbon structure from sucrose. The morphology of the prepared HC-nSi/G composite was examined using SEM, and the images are presented in Fig. 1b and c. At low magnification, HC-nSi/G exhibits agglomerated secondary particles with particle size of ~10 μm (Fig. 1b). Higher magnification SEM images reveal that the surface of these large particles consist of interconnected nano-Si/hard carbon (Fig. 1c). Elemental mapping analysis was carried out to better understand distribution of hard carbon and nano-Si at the surface of HC-nSi/G composite. The individual elemental mapping result is shown in Fig. S1. The overlaid C/Si elemental maps as presented in Fig. 1d reveals that nano-Si particles are well wrapped with hard carbon and the thickness of nano-Si particles/hard carbon the layer on graphite surface is ~1 μm. The hard carbon coated nano-Si has good adhesion to the graphite surface because of the hydrophobicity of carbon and graphite [14]. The carbon coating layer on nano-Si particles is believed not only to be beneficial for an efficient electron transport but also to serve as a buffering zone to accommodate the volume change of nano-Si during lithiation/delithiation processes [15]. The crystalline structure of HC-nSi/G as characterized by XRD (Fig. 1e) shows XRD peaks that can be indexed to graphite (hexagonal phase, JCPDS# 98-007-6767) and silicon (cubic phase, JCPDS# 00-027-1402) without any SiC by-product detected.

CV was first carried out to understand the electrochemical properties of HC-nSi/G composite and the results are shown in Fig. 2a, in which the CV curves of mechanically blended graphite/nano-Si/hard carbon (BGSH) mixture is also shown for comparison. In the CV scan of HC-nSi/G after formation cycles, two cathodic peaks (~0.05 and ~0.15 V) are observed in the negative scan while five anodic peaks (~0.13, ~0.215, ~0.28, ~0.34 and ~0.53 V) are observed in the positive scan. The cathodic peaks at ~0.15 and ~0.05 V can be attributed to the continuous lithiation of nano Si and graphite (stage III + IIL), respectively [16–18]. The anodic peaks at ~0.13 and ~0.22 are ascribed to the delithiation of graphite, and the peaks at ~ 0.28 V, ~0.34 and ~0.53 V are characteristic of the delithiation of amorphous Si (the crystalline structure of Si becomes

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