Nano-Si/graphite/N-doped biocarbon hybrid anode material for high-performance lithium-ion batteries

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Abstract. Improving the cycle life of silicon-based anodes is extremely important to the development of Li-ion batteries. Nano-silicon / graphite / Nitrogen-doped carbon composites are prepared as hybrid anode material in this work. The nano-silicon particles are distributed in the graphite framework, which improves the electrical conductivity of the composite. The amorphous nitrogen-doped carbon layer of the composite could be a buffer structure for the volume change of Si while providing a fast transport channel for lithium ions and further enhancing the electrical conductivity of the composites. The specific capacity of the composite electrode is 656.5 mAh g\(^{-1}\) at 500 mA g\(^{-1}\). The capacity retention rate is 91\% after 100 cycles. The composite electrode could deliver a specific capacity of 497.3 mAh g\(^{-1}\) after 200 cycles even at a large current density of 1A g\(^{-1}\).

1. Introduction

After being extensively used in different electronic devices, lithium-ion batteries have reached an unprecedented height in electric vehicles. At present, the demand for better batteries has increased with the progress of industry and technology [1]. Compared with the 372 mAh g\(^{-1}\) of traditional carbon anode, the specific capacity of 4200 mAh g\(^{-1}\) of the silicon-based anode materials has drawn great attention [2]. However, its volume change is about 400\% during the lithiation/delithiation, which makes the anode material pulverized and cracked, leading to a rapid capacity decline and low Coulombic efficiency.

In order to address the above challenges of silicon-based anodes, Carbon materials are widely used to form silicon-carbon composites due to their good electrical conductivity, stable lithium intercalation ability, and tiny volume expansion [3]. The widely accepted strategy for silicon anodes is carbon coating. Organic compounds such as sucrose, citric acid, phenolic resin, glucose, and pitch can be used as precursors for carbon coating [4]. Chitosan is a functional biomaterial with great application potential [5]. In addition, there is more than 7\% nitrogen element in chitosan, which can make nitrogen dope in pyrolytic carbon after heat treatment. Nitrogen doping is an available method to enhance the conductivity of the material remarkably [6].

In this work, nitrogen-doped biocarbon layer coated nano-silicon/graphite (Nano-Si / Graphite / CTS-C) composites anode materials have been prepared by mechanical ball milling, evaporative drying, and pyrolysis. Nano-silicon is distributed between flake graphite which could be the first buffer structure to
relieve the great volume expansion of Si. Besides, the outer amorphous N-doped carbon layer could be a barrier to separate the silicon particles and the electrolyte, limiting the volume expansion of silicon, further forming a cross-linked conductive network, and providing a fast electron transfer channel. Combining these advantages, the Si / Graphite / CTS-C anode could attain better electrochemical capability.

2. Experimental section

2.1 Material Synthesis
Nano-silicon/graphite/nitrogen-doped biocarbon composite precursors were obtained via the following processes: First, 1 g chitosan powder (<200 mPa.s, Shanghai Mindray Chemical Technology Company) was dissolved in a 2% (m/V) acetic acid aqueous solution (Beijing Tongguang Fine Chemical Company) with continuous stirring to obtain 2% (m/V) chitosan acetic acid aqueous solution. Then 0.25 g nano-silicon (50 nm, Shanghai Ailan Chemical Technology Co. Ltd.) and 0.25 g flake graphite (Shanghai Ailan Chemical Technology Company) were added into the corundum ball mill jar, with a zirconia balls/materials mass ratio of 30:1 for 6 hours. After adding the product to the above acetic acid aqueous solution, the precursor was obtained after stirring for 12 h and drying at 80 °C. Then the precursors were pyrolyzed at 800 °C under an argon-filled atmosphere for 3 hours to obtain Si/Graphite/CTS-C composite.

2.2 Material characterization
An X-ray diffractometer (XRD, Rigaku Ultima IV-185) was applied to X-ray diffraction analysis from 10° to 90° with the scan speed of 8° min⁻¹. Raman spectra were acquired from a Raman spectrometer (HORIBA Scientific LabRAM HR Evolution), and the wavelength of laser is 532 nm. By using scanning electron microscopy and transmission electron microscopy, the morphological features of the composites were observed (FE-SEM, Hitachi S-4800, TEM, Tecnai G2 F30 S-TWIN). Thermogravimetric curves (TG, Netzsch STA 2500) were obtained at 10 °C min⁻¹ in the range of 10 to 1000 °C.

2.3 Electrochemical measurements
The composite electrode was coated on copper foil after mixing active material, carboxymethyl cellulose, styrene-butadiene rubber, and Super P with a mass ratio of 8:0.5:0.5:1. The 2025 coin-type cells were fabricated under an inert atmosphere, which included a Celgard 2325 membrane and a lithium sheet. The electrolyte was made up of 1 mol L⁻¹ LiPF₆ in EC : DMC : DEC with a volume ratio of 1:1:1 and 10 wt% FEC additive. Cyclic voltammetry test was performed on the CHI660E workstation between 0.01V and 1.5V at 0.1 mV s⁻¹. The charge-discharge test was performed on a LAND CT2001A test system with the voltage ranging from 0.01 to 1.5 V.

3. Result and discussion
Figure 1 shows the preparation and structure of the composite. The silicon nanoparticles were attached to the surface and layers of the flake graphite by the method of mechanical ball milling. Then the aforementioned raw materials were uniformly dispersed in a chitosan acetic acid aqueous solution. The interaction between chitosan and silicon nanoparticles is shown in Figure 1c. During the process of ultrasonic stirring, the chitosan containing a large number of hydroxyl groups can be associated with silicon nanoparticles through the hydrogen bonds. Therefore, based on hydrogen bonding and electrostatic interactions, a uniform chitosan coating layer linked to the silicon nanoparticles and graphite is formed. After that, the Si / Graphite/ CTS-C composites were finally obtained through evaporative drying and carbonization processes, as shown in Figure 1b. In this structure, silicon nanoparticles are embedded on the surface and layers of flake graphite, with an amorphous carbon layer doped with nitrogen covering the outermost layer.
The XRD patterns of the Si, Graphite and the composite are shown in Figure 2a. Clearly, the diffraction peak of the composite corresponds to the characteristic peaks of silicon and graphite, respectively, which confirm the existence of graphite and silicon, indicating that during the pyrolysis process, the silicon particles remain in the composite materials. As presented in Figure 2b, a sharp peak at 512 cm\(^{-1}\) was observed in the Raman spectra, corresponding to the lattice vibration of Si. Moreover, D-peak and G-peak around 1335 cm\(^{-1}\) and 1585 cm\(^{-1}\) were observed, which confirmed that the chitosan had been converted into carbon [7]. The D-peak is attributed to the amorphous carbon, while the G-peak is related to the sp atomic vibration process of the graphite layer [8]. The ratio of \(I_D/I_G\) is 0.95, demonstrating that the degree of graphitization of the carbon layer is moderate. Since the composites contain graphite, the pyrolyzed amorphous carbon reduces the graphitization of the material. The amorphous structure could facilitate the transmission of lithium-ions [9], correspondingly, the higher degree of graphitization demonstrates better conductivity. The co-existence of the two structures could incorporate both advantages.

Figure 2. (a) XRD patterns (10-90°, 8° min\(^{-1}\)), (b) Raman spectrum of the hybrid materials.

Figure 3a and Figure 3b present the SEM images of the composites. The particle size is approximately 5-10 µm. TEM and HRTEM further elucidated the microstructure of the samples. As shown in Figure 3c and Figure 3d, silicon is distributed among the flake graphite, with an amorphous carbon layer about 2.5 nm tightly coated on the outer layer. It could be observed that the interplanar distance is associated with the (111) crystal plane of Si, which is 0.31 nm. Silicon nanoparticles, flake graphite, and amorphous pyrolytic carbon constitute Si / Graphite / CTS-C composite particles. The
Graphite could enhance the conductivity of Si, and function in limiting the volume expansion in the course of the Si-Li alloying/dealloying. Besides, the pyrolyzed amorphous carbon layer also prevents the silicon from direct contact with the electrolyte. The element distribution (Figure 3g, 3h, 3i, 3j) shows that Si is distributed among C, indicating that Si particles are distributed in the conductive network which is made up of the graphite and the amorphous carbon. Moreover, the similarity of the distribution of nitrogen and carbon indicates that the chitosan pyrolytic carbons are N-doped carbons. Since the only source of N element is chitosan, the above results confirm that the carbon layer which is derived from the chitosan is a kind of nitrogen-doped layer. Notably, the defects on the N-doped carbon layer are conductive to facilitate the transport of Li-ions on the interface.

Figure 3. (a)(b) SEM, (c)(d) TEM, (e)(f) HRTEM images, and (g)(h)(i)(j) elemental mapping of Si/Graphite/CTS-C composite.

The thermogravimetric (TG) analysis curve of Si/Graphite/CTS-C is shown in Figure 4. The carbon in the composites is about 74.35 wt%, so the weight percentage of amorphous carbon is 48.7%, based on the same ratio of Si and graphite.

Figure 4. TG curve of the composite (10 °C min⁻¹).

Figure 5a presents the discharge-charge curves of the composite electrode. There is a flat voltage plateau around 0.1-0.2V which is associated with the lithiation of the graphite and the crystalline silicon. The plateau of 0.1V is related to the graphite in the course of the delithiation of the electrode while the delithiation of LiₓSi is associated with the plateau of 0.5V [10]. The initial Coulombic efficiency is
73.05%, for which the initial lithiation/delithiation capacity of the electrode is 1015.2/741.6 mAh g\(^{-1}\). Significantly, the irreversible capacity that appears in the initial lithiation exists in various silicon-based materials, which depend on the electrochemical chemical reduction reaction between Li\(^+\) and electrolyte to form an irreversible SEI film. As presented in Figure 5b, we further measured the CV curves of the composite electrode. Corresponding to Figure 5a, the broad peak of 0.8V is realted to the formation of the solid electrolyte interface (SEI) film, c. In subsequent tests, the broad peak disappears, indicating that the SEI film remains stable. When the potential is gradually decreased, a clear and sharp reduction peak at around 0.01V is interrelated to the lithiation of the silicon and the graphite. The oxidation peak around 0.16V corresponds to the delithiation of graphite, and the other two oxidation peaks at around 0.34V and 0.54V are attributed to the delithiation process of Li\(_{15}\)Si\(_4\) and Li\(_2\)Si [11]. The lithiation of amorphous silicon is corresponding to the new reduction peak at 0.19V in the 2nd cycle [10]. Besides, the new oxidation peaks at 0.12V and 0.16V both correspond to the delithiation of graphite.

![Figure 5](image_url)

Figure 5. (a) Charge-discharge curves, (b) CV curves (0.1 mV s\(^{-1}\)) of the composite electrode.

As shown in Figure 6a, the reversible specific capacities of the composite electrode at 0.1, 0.2, 0.5, 1, 2, and 5 A g\(^{-1}\) are 780.5, 754.3, 667.5, 569.4, 410.6 and 163.0 mAh g\(^{-1}\). The specific capacity could be returned to 733.9 mAh g\(^{-1}\) after several cycles even though the current density sharply dives to 100 mA g\(^{-1}\). The results of the discharge-charge tests at different current densities are displayed in Figure 6b and Figure 6c. The Si / Graphite / CTS-C composite anode has a reversible capacity of 656.5 mAh g\(^{-1}\) at 500 mA g\(^{-1}\). The Coulombic efficiency could remain above 99% after 15 cycles, revealing the good electrochemical reaction reversibility and structural stability of the composite electrode. The electrode exhibits a specific capacity of 596.6 mAh g\(^{-1}\) after 100 cycles, and the capacity retention rate is 91%. Moreover, a reversible specific capacity of 497.3 mAh g\(^{-1}\) could be achieved with a capacity retention rate of 81% after 200 cycles when the current density increases to 1 A g\(^{-1}\), showing durable cycling stability on fast lithium storage. In conclusion, the Nano-Si / Graphite / CTS-C hybrid anode exhibits good electrochemical performance as a potential material to replace graphite.
**Figure 6.** (a) Rate performance, (b)(c) Cycle performance of the composite electrode (500 mA g\(^{-1}\) & 1 A g\(^{-1}\)).

### 4. Conclusion

In summary, nano-silicon / graphite / nitrogen-doped carbon hybrid materials are successfully synthesized by mechanical ball milling, liquid phase stirring, and evaporative drying process. The Si / Graphite / CTS-C composites anode material delivers a reversible capacity of 656.5 mAh g\(^{-1}\) at 500 mA g\(^{-1}\) with the capacity retention of 91% after 100 cycles. When the current density increases to 1 A g\(^{-1}\), the Si / Graphite / CTS-C anode could still afford a specific capacity of 497.3 mAh g\(^{-1}\) after 200 cycles with the Coulombic efficiency maintains at 99% and also exhibits great rate capability. In the structure of the composites, Nano-silicon is embedded in flake graphite, which could increase the conductivity of silicon notably and act as the first buffer layer for silicon during cycling. The dense N-doped carbon layer derived from chitosan could also increase the electric conductivity of the hybrid anode, effectively maintain structural stability and separate the silicon and the electrolyte, providing a faster lithium-ion transport channel. These factors successfully make Si / Graphite / CTS-C anode achieve better electrochemical performance.

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