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SHORT COMMUNICATION

Preparation and electrochemical performance of SiCN–CNTs composite anode material for lithium ion batteries

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Abstract The composite of silicon carbonitride (SiCN) and carbon nanotubes (CNTs) was synthesized by sintering the mixture of polysilylethylenediamine-derived amorphous SiCN and multi-walled CNTs at a temperature of 1,000 °C for 1 h in argon. The as-prepared SiCN–CNTs material, which was used as anode active substance in a lithium ion battery, showed excellent electrochemical performance. Charge–discharge tests showed the SiCN–CNTs anode provided a high initial specific discharge capacity of 1176.6 mA h g^{-1} and a steady specific discharge capacity of 450–400 mA h g^{-1} after 30 charge–discharge cycles at 0.2 mA cm^{-2}. Both of the abovementioned values are higher than that of pure polymer-derived SiCN, CNTs, and commercial graphite at the same charge–discharge condition. It was deduced that the CNTs in the composite not only improved the electronic conductivity and offered channels and sites for the immigrating and intercalating of Li^+ but also stabilized the structure of the composite.

Keywords Silicon carbonitride · Polymer-derived · Carbon nanotube · Anode · Li-ion battery

1 Introduction

Polymer-derived silicon carbonitride (SiCN) materials are novel anodes for lithium ion batteries because of their high charge–discharge capacity and excellent electrochemical dynamics [1–3]. These SiCN materials, usually synthesized by pyrolysis of a polymer precursor such as polysilazanes analogues [4, 5] and polysilylcarbondiimides [6], have amorphous three-dimensional networks which consist of silicon, carbon, and nitrogen atoms [7]. These SiCN materials have two structural advantages which are suitable for active substance of anodes of lithium ion batteries. One, there are far more than sufficient nanocarbon clusters and free dangling bonds of silicon and carbon in the SiCN network, which are active sites for the intercalating/de-intercalating of lithium ions and provide high electrochemical capacity. The other, the nano holes or nano channels in SiCN network provide many smooth lithium ion transfer channels, which make the better electrochemical dynamic properties.

Despite the high initial discharge capacity, the cycle stability of the SiCN anodes is bad. After 30 cycles, the specific discharge capacity of the SiCN anodes was below 170 mA h g^{-1} [2]. The improvement of the cycle stability of these polymer-derived SiCN anodes was largely attributed to the carbon component in the SiCN material. Zonescu et al. [8] prepared SiCN/CNTs (carbon nanotubes) nanocomposites by dispersing multi-walled CNTs in a cross-linked polysilazane by means of a simple roll-mixing method. They found the conductivity of the composite was 7.6×10^{-2} S cm^{-1}, which was seven times larger than that of the pure SiCN material.

In this study, the SiCN–CNTs (10 wt% CNTs) composite was prepared by a 1 h heat treatment at 1,000 °C in argon. Charge–discharge cycle measurement, X-ray diffraction (XRD), and scanning electron microscope (SEM) were employed to investigate the electrochemical performance and structural properties of the as-prepared SiCN–CNTs material.

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2 Experimental

2.1 Preparation

The SiCN material was synthesized by the pyrolysis of a polysilazane precursor PSEDA, which was synthesized by the reaction of ethylenediamine and chlorosilane (99.9%, Tianjin Kewei Corp., China), according to the method reported before [9].

The SiCN product was pulverized and sieved with a 180 meshed standard sieve. Then, the SiCN powder (through the sieve) was used as blank sample for comparison and to prepare SiCN–CNTs composite. The multi-walled CNTs (Shenzhen Nanotech Port, China) were used as received without further treatment. The CNTs and as-prepared SiCN were mixed in absolute ethanol at 60 °C with vigorous stir (mass ratio CNTs:SiCN = 1:9). Till all the liquid was evaporated, the remaining solid was dried at 120 °C in vacuum for 1 h and followed by a heat treatment in an alumina tube furnace in an pure argon flow at 1,000 (5 °C $\min^{-1}$ from room temperature) for 1 h to obtain SiCN–CNTs composite.

2.2 Measurements

For electrochemical tests, anode electrodes were prepared by the following procedure: Blend the mixture of the as-prepared SiCN–CNTs composite (active material), ENSACO (conductive additive, Sigma-Aldrich, Switzerland), and PTFE (binder, Sigma-Aldrich, Switzerland) in a mass ratio of 85:10:5 with absolute ethanol to form a slurry; Coat the slurry on copper foil; Evaporate all the alcohol, water, and other volatile content. So far, the electrode foil was obtained. Coin-type cells (model CR2032) were assembled in argon-filled glove box. The electrode foil prepared above, lithium foil, Celgard 2300, and 1.15 mol dm^{-3} LiPF_6 complex carbonate (volume ratio: EC:PC:DMC = 1:1:1) solution were, respectively, used as working electrode, counter and reference electrode, separator, and electrolyte in the test cells. Galvanostatic charge–discharge cycle tests were carried out on a LAND 2001A battery test system (Wuhan Jinnuo, China) in the potential range of 0–3.5 V versus $\mathrm{Li}^+/\mathrm{Li}$.

The structures of the materials were analyzed by powder XRD (Rigaku D/MAX 2500 V/PC, Japan) with Cu $K\alpha$ radiation by means of a graphite monochromator in the 2θ range of 3–80° and SEM (JEOL JSM-6700F, Japan) with an accelerating voltage of 15 kV.

3 Results and discussion

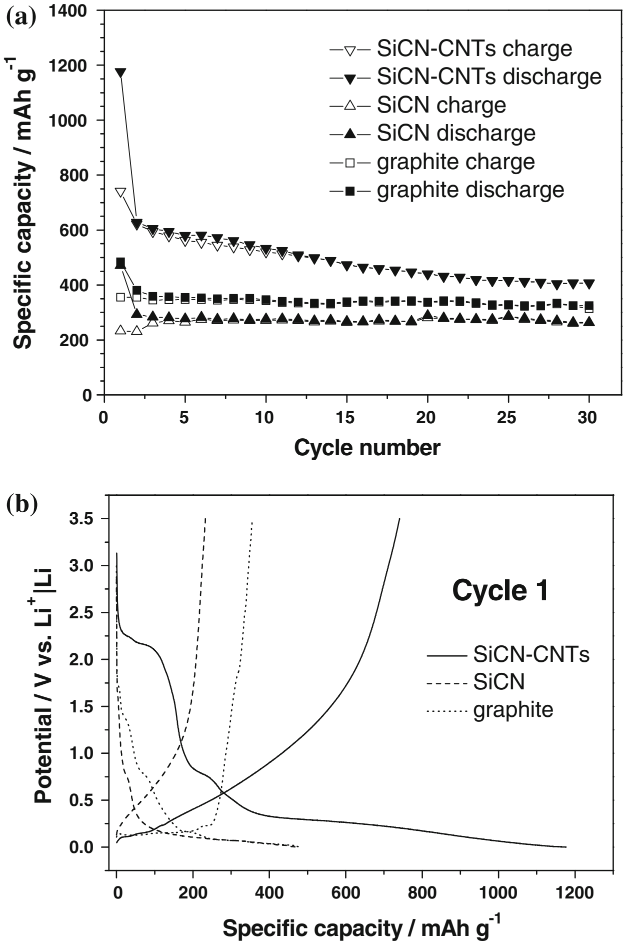

Fig. 1 **a** Specific capacity versus cycle number of the SiCN–CNTs, SiCN, and graphite at a current density of 0.2 mA cm^{-2}; **b** the specific capacity–potential curves of the first cycle of SiCN–CNTs, SiCN, and graphite at a current density of 0.2 mA cm^{-2}

Figure 1a shows the specific charge and discharge capacity versus cycle number of the SiCN–CNTs composite, pure SiCN, and graphite at a current density of 0.2 mA cm^{-2}. The initial specific discharge capacity of the SiCN–CNTs anode was 1176.6 mA h g^{-1}, which was about 1.5 times higher than that of pure SiCN and 1.4 times higher than that of the graphite. From the 1st to 5th cycle, the decrease of the discharge capacity was fast. Whereafter, the discharge capacity decreased gently. After 30 cycles, the discharge capacity met a plateau, which was between 450 and 400 mA h g^{-1}. This value was larger than the previous SiCN-type materials [1–3]. The curves had the same trend as the discharge curves. Obviously, the CNTs improved the reversible charge–discharge capacity of SiCN.

Figure 1b shows the initial charge and discharge properties of SiCN–CNTs, SiCN, and graphite. For SiCN–CNTs, there were three discharge plateaus: 2.2, 0.75, and 0.2 V. The 0.2 V discharge plateau was similar to pure SiCN and graphite. The 0.75 V discharge plateau was considered as the formation of the solid electrolyte interface (SEI) film. The film, which was formed by the reaction

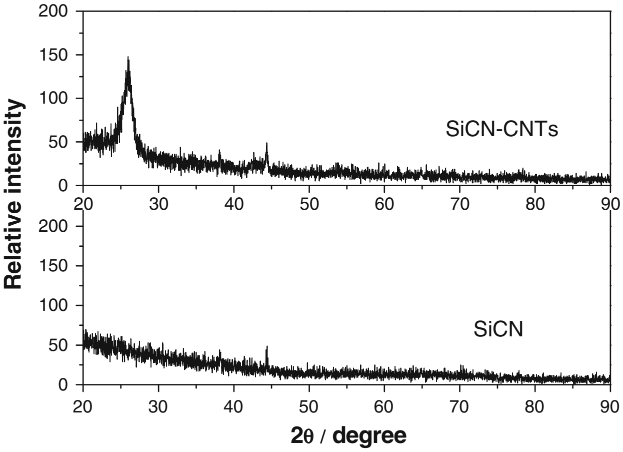

Fig. 2 XRD patterns of SiCN–CNTs and SiCN

of electrode material and electrolyte, usually occurred on the electrode surface at first charge–discharge cycle [10]. According to the reference [11], the formation potential of the SEI film on carbon anode material is about 0.8 V, which is consistent with the deduction above. The 2.2 V discharge plateau of SiCN–CNTs was unique, which might be attributed to the dangling bonds, nano vessel, and other active point which could accommodate lithium ion physically or chemically. The discharge plateau of SiCN–CNTs was longer and higher than pure SiCN and graphite. Longer plateau indicated higher discharge capacity. Higher plateau potential could prevent the formation of lithium dendrites and provide better safety. Comparing with graphite, no notable charge plateaus exist on the charge curves of SiCN–CNTs and SiCN. The acclivitous potential curves of SiCN–CNTs and SiCN were ascribed to the amorphous structures of active materials, which were confirmed by the XRD (discussed in the following paragraph).

The XRD patterns of the SiCN–CNTs composite and pure SiCN are shown in Fig. 2. The peaks of the pure SiCN material are broad, which suggests an amorphous structure, which is consisted of the SiCN structure in previous researches [12, 13]. In the XRD pattern of SiCN–CNTs composite, there is a strong diffraction peak at $2\theta = 26°$, which is indexed to the crystal plane (002) of typical graphite [14]. This peak is the witness to that the CNTs distorted the SiCN 3D network. The latter deduction will be further proved by the SEM investigation in the following paragraph.

Figure 3 is the SEM images of SiCN–CNT composite, pure SiCN, and raw CNTs. Figure 3a shows an irregularly configured structure of SiCN. The fitful particles, the particle size of which differed from 1 to 5 μm, delivered low electronic and ionic conductivity. Figure 3c and d suggest that the CNTs are about 10–20 μm in length and about 80–100 nm in external diameter. In SiCN–CNTs composite, SiCN and CNTs were well combined with each other, since no gaps were observed at the interfaces. Because of that, the electronic conductivity was increased and

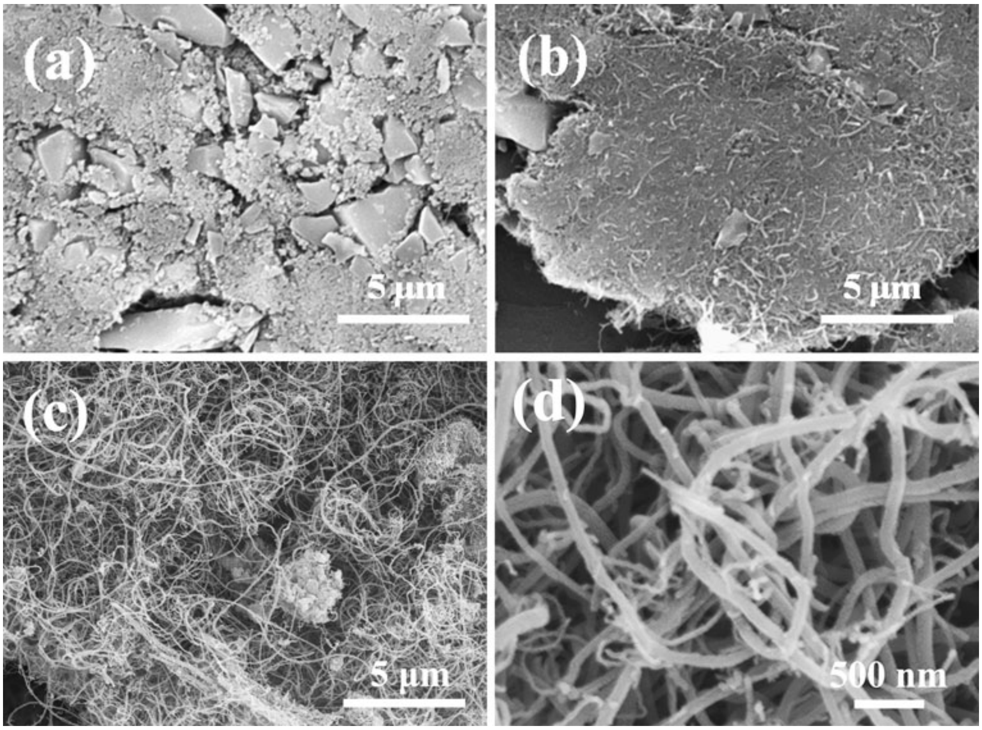

Fig. 3 SEM images of SiCN (**a**); SiCN–CNTs materials (**b**) and CNTs (**c**, **d**). Magnification: **a**–**c** ×5,000; **d** ×40,000

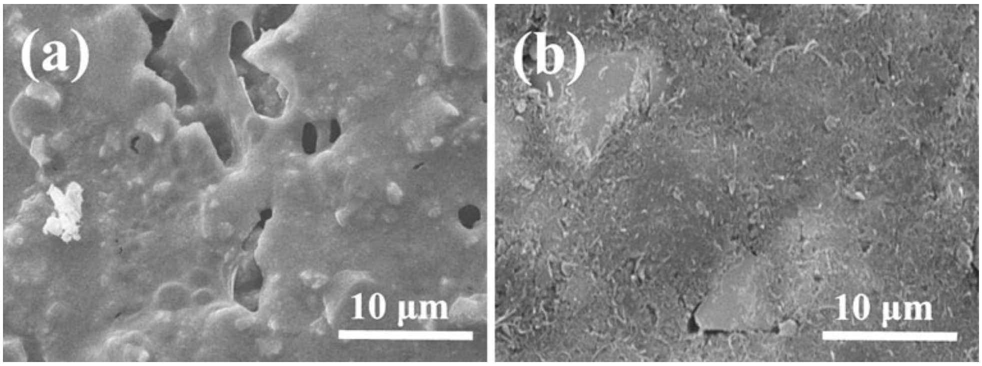

Fig. 4 SEM images of SiCN (**a**) and SiCN–CNTs (**b**) after 30 charge–discharge cycles. Magnification: ×5,000

the volume change during charge–discharge cycle was restricted. After 30 cycle charge and discharge, the SiCN anode had some obvious structural decays while the SiCN–CNTs anode, which was stabilized by CNTs, exhibited no evident structural change. The structural decays, mainly pulverization, caused the decrease of the specific electrochemical capacity and even the electrode failure. The CNTs 3D network in the composite stabilized the structure of the composite, which lengthened the cycle life of SiCN–CNTs (Fig. 4).

4 Conclusions

A novel anode material for lithium ion batteries SiCN–CNTs composite was synthesized with SiCN and multi-walled CNTs. At the current density of 0.2 mA cm^{-2}, the initial specific discharge capacity of the SiCN–CNTs was as high as 1176.6 mA h g^{-1}. The specific discharge capacity remained higher than 400 mA h g^{-1} by cycle 30. These values are both higher than those of SiCN-type materials and graphite in previous researches. The improvement of the reversible charge–discharge capacity was because of the introduction of CNTs. The 3D network of CNTs stabilized the structure of the composite and improved the conductivity of the material.

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