

Short Communication

Preparation and Electrochemical Performance of Polymer-derived SiCN-graphite Composite as Anode Material for Lithium Ion Batteries

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The composite of silicon carbonitride and graphite (SiCN-graphite) composite was synthesized by pyrolyzing the mixture of polysilylethylenediamine-derived amorphous SiCN and graphite powder at a temperature of 1000 °C for 1 h in argon. The as-prepared SiCN-graphite material, which was used as anode active substance in a lithium ion battery, showed excellent electrochemical properties. The SiCN-graphite anode exhibited a high initial specific discharge capacity of 975.6 mAh g⁻¹ and a steady specific discharge capacity of 425.0 mAh g⁻¹ after 30 charge-discharge cycles at a current density of 40 mA g⁻¹. Both of the abovementioned values are higher than that of pure polymer-derived SiCN and commercial graphite under the same charge-discharge condition. Additionally, the SiCN-graphite anode showed good high charge-discharge rate capability, which met the standard of commercial anode materials. It is considered that the less voids and cracks at the interface of the SiCN-graphite particles benefit the electron transfer, resulting in the improvements of the capacity and cycle stability.

Keywords: Silicon carbonitride; Polymer-derived ceramic; Anode; Li-ion battery

1. INTRODUCTION

As one of the alternative anode materials for lithium ion batteries, amorphous polymer-derived silicon carbonitride (SiCN) materials bring popular concerns recently, due to their many advantages such as structural steady, chemical inert and thermal stability [1-3]. This kind of polymer-derived SiCN material usually pyrolyzed at 1000-1700 °C using polysilazanes precursors. The max charge-discharge specific capacity of pure polymer-derived SiCN is about 600-760 mAh g⁻¹ [4-6] which higher than that of commercial graphite anode. The excellent electrochemical property comes from the

particular structure of SiCN material, which is suitable for Li-battery anode. The structure of the SiCN material is an amorphous three-dimension networks which consist of silicon, carbon and nitrogen atoms [7]. In these networks, there are amounts of nano-clusters and free dangling bonds of silicon and carbon, which are active sites for the inserting/extraction of lithium ion and the providing of high electrochemical capacity. Moreover, the nano-holes or nano-channels in SiCN network provide many smooth Li^+ transfer channels, which improve the electrochemical dynamic properties.

Although the initial charge-discharge capacity of SiCN anode is high, the cycle stability of this anode is not very good. After 30 cycles, the specific discharge capacity of the SiCN anode was below 170 mAh g^{-1} [4]. To improve the cycle stability of this polymer-derived SiCN anode, the adding of carbon component seemed to be feasible. Kolb et al [8] mixed commercial graphite powder with the cross-linked polysilazane and then pyrolyzed the polymer/graphite mixture in inert argon atmosphere resulting in the formation of an amorphous SiCN/graphite composite material. According to these studies above, the carbon is a beneficial component in SiCN anode for the improvement of capacity and cycle stability. However, the amount of graphite in their SiCN/graphite composite is too much (75 wt. %) that it is seemed the graphite is a main active substance and the SiCN only acts as a doping material.

In this work, to investigate the effect of graphite (below 10 wt. %) as doping material in SiCN composite for electrochemical test, we prepared SiCN-graphite composite by mixture of polysilylethylenediamine-derived amorphous SiCN and graphite powder at a temperature of $1000 \text{ }^\circ\text{C}$ for 1 h in Argon. Charge-discharge cyclic measurements, X-ray diffraction (XRD) and scanning electron microscope (SEM) are employed to investigate the electrochemical properties and structure performance of the as-prepared SiCN-graphite material.

2. EXPERIMENTAL

The SiCN material was synthesized by the pyrolysis of a polysilazane precursor, which was synthesized from the reaction of ethylenediamine and dichlorosilanes (99.9 %, Tianjin Kewei Corp., China), according to the method reported before [9]. The polysilazane precursor were placed in an Al_2O_3 crucible and pyrolyzed in an alumina tube furnace in an argon flow (100 sccm) at a heating rate of $5 \text{ }^\circ\text{C min}^{-1}$. The final temperature $1000 \text{ }^\circ\text{C}$ was held for 1 h and then the system was allowed to cool down to room temperature. The as-prepared SiCN products were grounded by hand and sieved down to $80 \text{ }\mu\text{m}$. Then the SiCN powder were homology separated into two parts, one part as compared blank sample, and the other part mixed with graphite (Tianjin Kewei Corp., China) at a weight ratio of 9:1 (SiCN:graphite). The SiCN and graphite powder were mixed in absolute ethanol at $60 \text{ }^\circ\text{C}$ with vigorous stir. Till all the liquid was evaporated, the remaining solid was dried at $120 \text{ }^\circ\text{C}$ in a vacuum for 1 h and followed by a heat treatment in an alumina tube furnace in an pure argon flow at $1000 \text{ }^\circ\text{C}$ ($5 \text{ }^\circ\text{C per minute}$ from room temperature) for 1 h to obtain SiCN-CNTs composite.

For electrochemical tests, anode electrodes were prepared by mixing the active material (SiCN-graphite), conductive additive (acetylene black, ENSACO, Switzerland) and binder (polytetrafluoroethylene, PTFE, Sigma-Aldrich, Switzerland) in a weigh ratio of 85:10:5. The

materials, as a anode, were assembled into lithium batteries in an argon filled glove box, with the use of Celgard 2300 (Celgard, Charlotte, NC) as a separator, Li foil as counter and reference electrodes, and $1.15 \text{ mol}\cdot\text{dm}^{-3}$ LiPF_6 in ethylene carbonate (EC), propylene carbonate (PC) and dimethyl carbonate (DMC) (1:1:1 by volume, Jinniu, China) as electrolyte, to form laboratory-made coin-type cells (size: CR 2032). Galvanostatic charge-discharge cycle tests were performed on a LAND 2001A battery testing system (Jinnuo, China) in the potential range of 0-3.5 V vs. Li^+/Li . To investigate the electrochemical performance of the SiCN-CNTs composite anodes, a pure SiCN and a pure graphite powder (99.9 %, Tianjin Kewei Corp., China) was used as a compared anode under the same charge-discharge conditions.

The structures of the materials were analyzed by X-ray diffraction (XRD) using Rigaku X-ray powder diffractometer (Rigaku D/MAX 2500 V/PC, Tokyo, Japan) with graphite monochromatic $\text{CuK}\alpha$ radiation in the 2θ range of $3\text{-}80^\circ$. Morphologies of the materials were investigated by scanning electron microscopy (SEM, JEOL JSM-6700F, Japan) using an accelerating voltage of 15 kV.

3. RESULTS AND DISCUSSION

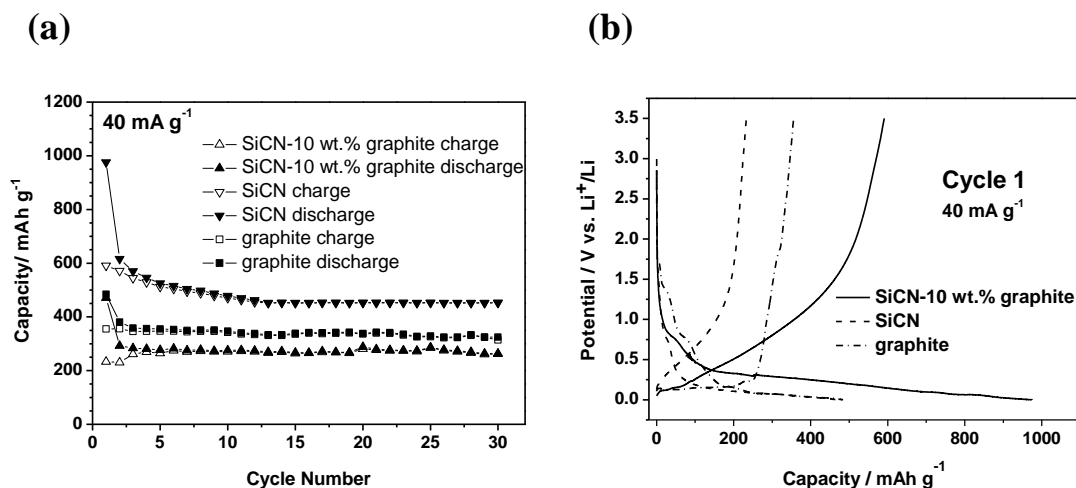


Figure 1. (a) Specific capacity versus cycle number of the SiCN-10 wt. % graphite, SiCN and graphite at a current density of 40 mA g^{-1} ; (b) The specific capacity-potential curves of the first cycle for SiCN-10 wt. % graphite, SiCN and a graphite anode at current density of 40 mA g^{-1} .

Fig. 1a shows the specific charge and discharge capacity versus cycle number of the SiCN-graphite composite, pure SiCN and graphite at a current density of 40 mA g^{-1} . The initial specific discharge capacity of the SiCN-graphite anode is 975.6 mAh g^{-1} , and this value is much higher than that of pure SiCN (470.7 mAh g^{-1}) and pure graphite anode (484.3 mAh g^{-1}). The discharge capacity of SiCN-graphite stabilizes at 425.0 mAh g^{-1} , which are higher than those of pure SiCN (263.4 mAh g^{-1}) and the graphite (324.6 mAh g^{-1}), which shows that the graphite adding improves the reversible capacity of SiCN. From fig.1a, the first cycle coulombic efficiency of the SiCN-graphite anode is 60.6% which is lower than that of graphite (73.4%), but higher than that of pure SiCN (49.5%). From the 2nd

to 12th cycle, the coulombic efficiency of SiCN-graphite is obviously increased to 100%. From the 12th to 30th cycle, the coulombic efficiency stay at 100%. This exhibits an excellent reversible Li⁺ inserting/extracting behavior.

Fig. 1b shows the specific capacity-potential curves of the 1st cycle for SiCN-10 wt. % graphite, pure SiCN and graphite anodes at current density of 40 mA g⁻¹. The discharge plateau of SiCN-graphite anode is about 0.2 V. The discharge plateau of the pure SiCN anode is about 0.15 V, which is almost similar to the graphite anode. The discharge plateau of the SiCN-graphite is longer than pure SiCN anode indicating the higher discharge capacity, which is the advantage of anode material. Additionally, the discharge plateau of the SiCN-graphite is higher than pure SiCN, which can prevent the formation of lithium dendritic crystal and thus improve the safety properties. Moreover, in fig. 1b, there is a little plateau on 0.75-0.80 V of the SiCN-graphite anode and it is considered as the formation of a solid electrolyte interphase (SEI). SEI is formed by the reaction of electrode material and electrolyte usually occurred on the electrode surface at first charge-discharge cycle [10]. The 0.76 V in the pure SiCN curve and 0.78 V in the graphite curve are also caused by SEI formation. According to the previous reports [11], the SEI formation of carbon anode material is about 0.8 V, which accords with our SiCN-type anodes. This indicates the interactive layer structure of our SiCN anodes is similar to that of carbon anodes.

From Fig. 1b, neither the SiCN-graphite nor the SiCN material has a distinct charge plateau unlike the pure graphite anode. At 0.1-2.0 V charge voltage range, the potential of the SiCN-graphite increases slowly with the capacity increasing. It is considered that the amount of Li⁺ extracts from this voltage range. The slop voltage curves of our SiCN anodes are ascribed to the amorphous state of active materials, which is consistent with their XRD patterns in fig. 3 in the following.

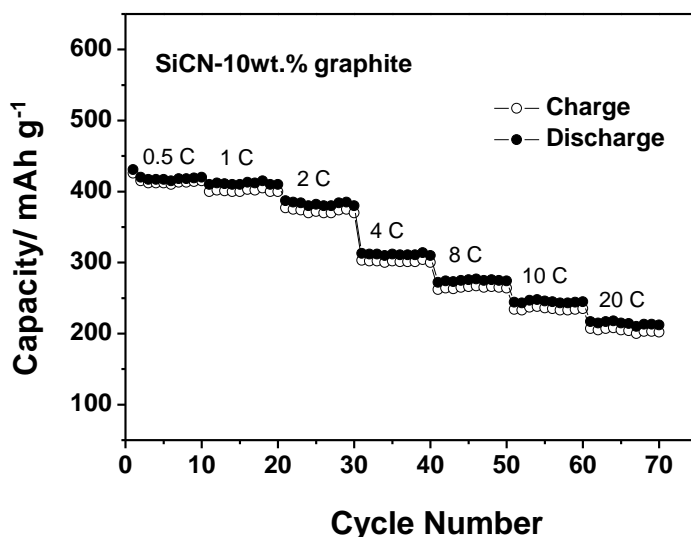


Figure 2. Specific capacity versus cycle number of the SiCN-10 wt. % graphite at different rates.

Fig. 2 shows the capacity variation with cycle number of the SiCN-10 wt. % graphite at different rates. As the figure shown, the SiCN-10 wt. % graphite has good electrochemical properties

at high rates. At 4 C rates, the charge-discharge capacity can stable at 300 mAh g^{-1} . At 20 C rates, the capacity is above 200 mAh g^{-1} which is ever better than pure graphite anode.

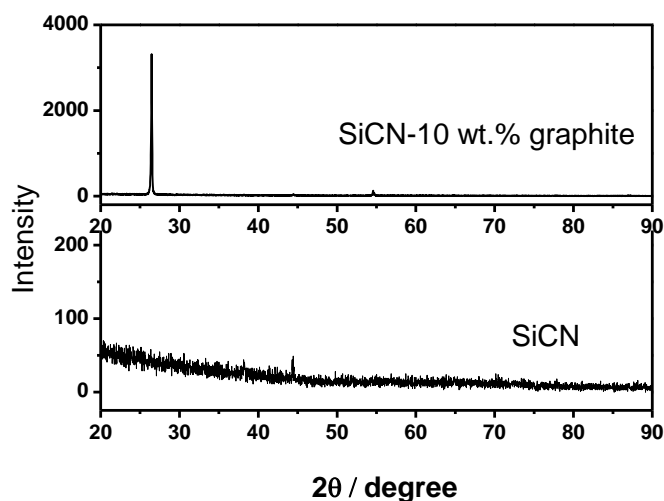


Figure 3. X-ray diffraction patterns (XRD) of SiCN-10 wt. % graphite and SiCN materials.

Fig. 3 shows the XRD patterns of the SiCN-graphite and pure SiCN materials. From the XRD figures, the peaks of pure SiCN material are broad, suggesting an amorphous structure which is consisted with the SiCN structure in previous research [12]. As shown in the XRD pattern of SiCN-graphite composite material, there is a strong diffraction peak at $2\theta=26^\circ$, indicating a (002) lattice of typical graphite [13]. This graphite peak covers the amorphous peak of SiCN material, and comes from the graphite adding in preparation of the SiCN-graphite composite.

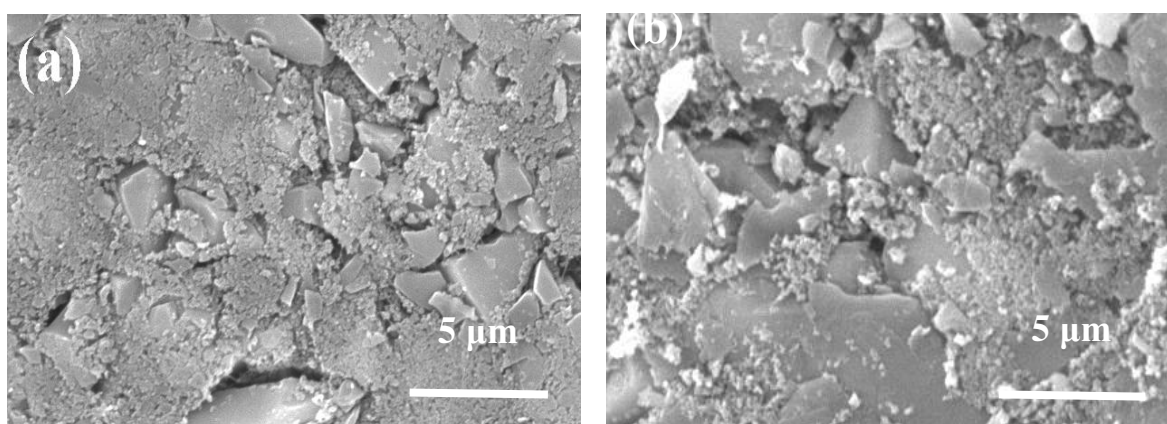


Figure 4. Scanning electron microscopy (SEM) images of the SiCN (a) and SiCN-graphite electrodes (b) Magnification: $\times 5,000$.

Fig. 4 is the SEM images of SiCN-graphite composite and pure SiCN anode. From fig. 4a, we can see that the particles of pure SiCN material are not homogeneous, about $1\text{-}5 \mu\text{m}$. The fillers among

the SiCN particles are acetylene black and PTFE which respectively act as conductive additive and binder in the preparation process of the material. However, they are not completely filled in all the interfaces of SiCN particles, forming many voids and cracks among SiCN particles. This results a bad electron transfer. Nevertheless, as shown in fig. 4b, the SiCN-graphite composite has no distinct crack, in favor of electron transfer. The particle sizes are larger than 3-5 μm , which bigger than the pure SiCN material which is benefited to the resistance of capacity decay during cycling.

4. CONCLUSIONS

A new SiCN-graphite composite anode for lithium ion batteries has been synthesized and shows promising electrochemical properties. The improvements of electrochemical performance owes to the graphite introduction in SiCN structure. Compared to pure SiCN material, the bigger particle sizes of SiCN-graphite can resist the capacity decay during cycling. The less voids and cracks at the particle interfaces of SiCN-graphite composite benefit the electron transfer. The following work should be aimed at further investigating the microstructure of SiCN-graphite and the combined function of graphite and SiCN nanocluster.

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