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Abstract

Silicon single walled carbon nanotube composite paper was modified by low energy ion implantation using Si to obtain a flexible composite paper. Raman and FE-SEM results show that structure of SWCNT could be destroyed by the implantation. Electrochemical measurements display that the implanted Si can improve the specific capacity and the reversible capacity of CNT paper. After 50 cycles, the specific capacity of Si implanted CNT paper is 30 per cent higher than the pristine CNT.

Keywords

batteries, ion, lithium, material, flexible, anode, nanotube, paper, irradiation, si, carbon

Disciplines

Engineering | Physical Sciences and Mathematics

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Irradiation Si on Carbon Nanotube Paper as a Flexible Anode Material for Lithium-Ion Batteries

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Silicon/single-walled carbon nanotube (SWCNT) composite paper was modified by low energy ion implantation using Si to obtain a flexible composite paper. Raman and FE-SEM results show that structure of SWCNT could be destroyed by the implantation. Electrochemical measurements display that the implanted Si can improve the specific capacity and the reversible capacity of CNT paper. After 50 cycles, the specific capacity of Si-implanted CNT paper is 30% higher than the pristine CNT.

Keywords: Silicon, Ion Implantation, Lithium-Ion Battery, Carbon Nanotube Paper, Flexible Electrode.

1. INTRODUCTION

Flexibility of the battery electrode is of great interest for the rapid development of portable devices and mobile equipments which requires their power supply to be designed to have not only high energy density but also high mechanical properties.^{1,2} Carbon nanotube (CNT) paper which is flexible and easy to prepare has been used as a flexible electrode for Li-ion batteries and supercapacitors.^{3–5} However, the limitations for CNT paper used as anode for lithium-ion battery are the low theoretical capacity (around 370 mAh g⁻¹) and large irreversible capacity,⁶ due to either the functional group on the surface of SWCNT or the formation of solid electrolyte interphase (SEI) layer. Since normally the SWCNT shows a high surface area, the formation of SEI layer is evitable. If we could remove the functional group from the surface of the SWCNT, the reversible capacity should be enhanced. On the other hand, silicon is the most promising doping material due to its abundance in nature, low discharge potential, and the highest known theoretical charge capacity (~3790 mAh g⁻¹).^{7,8} In addition, the big volume change (~300%) during lithium insertion and extraction results in capacity fading due to pulverization and loss electrical contact with substrate.⁹ In order to combine the advantage of both CNT paper and Si, we use ion implantation method to dope silicon into the SWCNT paper. The resulting CNT composite material is strong flexible and offer

a good conductive matrix which can not only accommodate the large volume change during the charge/discharge cycle, but also provide good electronic contact with Si-based material. The irradiated Si can enhance the total specific capacity of CNT paper and improve the reversible capacity due to the removal of the functional groups on the surface of SWCNT.

2. EXPERIMENTAL DETAILS

Single wall CNT paper was prepared using a filtration method reported previously.⁴ The CNT paper was irradiated at room temperature with Si ions perpendicular to its surface, using low energy and high fluxes. Si was produced using a direct extraction ion source, for which the average ion charge was +1.587,¹⁰ and implanted with an average energy of 7.93 KeV. At this energy, considering the average density of CNT as 0.5 g/cm³, SRIM calculations suggest that Si range in CNT is of the order of 450 Å. However, due to the nature of the sample and the orientation of the CNT's relative to the Si ion flux, this range value can be much larger. The total dose of Si ions implanted in CNT paper was 1 × 10²⁰ Si ions cm⁻².

The morphology and microstructure of as-prepared samples were characterized by scanning electron microscopy (SEM; JEOL FESEM-7500, 30 kV, equipped with energy dispersive X-ray (EDX) spectroscopy), and Raman spectroscopy. Raman spectra were recorded using a JOBIN Yvon Horiba Raman Spectrometer model HR800 employing a 10-mW helium/neon laser at 632.8 nm, which was

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Fig. 1. Raman spectra of pristine (top) and after Si implantation (middle) SWCNT paper, and carbon black (bottom).

filtered by a neutral density filter to reduce the laser intensity, and a charge-coupled detector (CCD).

To test the electrochemical performance, as-prepared Si/CNT composite paper was cut into 0.5 cm × 0.5 cm as a working electrode. The electrochemical cells (CR 2032 coin-type cell) contained as-prepared Si/CNT composite

paper as the working electrode, Li foil as the counter electrode and reference electrode, a porous polypropylene film as separator, and 1 M LiPF₆ (battery grade 99.99%, Aldrich) in a 1:2 (v/v) mixture of ethylene carbonate (EC, anhydrous 99%, Sigma-Aldrich) and diethyl carbonate (DEC, anhydrous 99+%, Sigma-Aldrich) as the electrolyte. The cells were assembled in an Ar-filled glove box. The cells were cycled at a current density of 25 mA g⁻¹ between 0.01 and 2.0 V using a computer-controlled charger system manufactured by Neware battery testers. The specific capacity was calculated based on the weight of the Si/CNT composite.

3. RESULTS AND DISCUSSION

Raman spectra of pristine CNTs film, carbon black and Si implanted SWCNT paper are shown in Figure 1. The pristine CNTs film shows a typical Raman spectrum of the SWCNT structure with three main features, which are assigned as the radial breathing mode (below 400 cm⁻¹), the D-band (1300–1350 cm⁻¹), and the G-band (1500–1600 cm⁻¹), respectively.¹¹ After high energy Si implantation, the intensity of the D-band is increased, which is related to the formation of amorphous carbon, the RBM peaks disappeared which indicate that the surface of the SWCNT structure was destroyed.

FE-SEM images and energy dispersive X-ray (EDX) spectrum are shown in Figure 2. It can be seen that after low energy Si implantation the carbon nanotubes are fused into networks or bundles, which is in good agreement with

Fig. 2. (a, b) FESEM images of SWCNT paper before (a) and after (b) Si implantation. (c) EDX spectrum of SWCNT paper after Si implantation. Photos of SWCNT paper before (d) and after (e) irradiation.

Raman result and previous report.¹² The EDX spectrum (Fig. 2(c)) shows that the Si/CNT composite paper contains C, Fe, Si, and O, indicating the presence of implanted Si, whilst Fe is the catalyst used for the preparation of CNTs. The EDX amount of silicon and Fe are similar, approximately 2%. Photos of SWCNT paper before and after irradiation are shown in Figures 2(d) and (e), respectively. It can be found that after the irradiation the surface of CNT turns into a little bit grey comparing to the black surface of pure SWCNT paper. Both of the electrodes show great flexibility.

The charge discharge curves from electrochemical tests are shown in Figure 3. The first discharge capacity for pristine CNT paper and Si-implanted CNT paper is 2400 mAh g⁻¹ and 2561 mAh g⁻¹, respectively. The reversible capacity for pristine CNT paper and Si-implanted CNT paper is 316 mAh g⁻¹ and 416.4 mAh g⁻¹, respectively. The reversible capacity of Si-implanted CNT paper is around 15.7% of initial discharge capacity, and is higher than that of pristine CNT paper (13.2%), suggesting a beneficial influence of Si doping into CNT by ion implantation.

The dQ/dV profiles show that the Si implantation has significantly reduced the intensity of peak at around 1.2 V, which is due to the removal of surface species containing oxygen on SWCNTs,¹³ indicating the structure change of CNT paper, and is in good agreement with SEM observation. The broad peak at 0.8–0.9 V versus Li/Li⁺ is attributed to the formation of the solid electrolyte interphase (SEI) layer.¹⁴ Another broad peak at lower potential (below 0.5 V vs. Li/Li⁺) mainly arises from the Li-ion intercalation into the graphitic-type layers. No obvious peak can be observed in the following cycles, indicating the large irreversible reaction. No typical silicon peaks were observed from dQ/dV plots due to the limited amount of Si doping (Fig. 4).

The cycle stability curves are shown in Figure 5. After 50 cycles, the specific capacity for pristine CNT paper and

Fig. 3. Typical discharge-charge curves of the pristine CNT paper (bottom) and Si-implanted CNT paper (top) electrodes.

Fig. 4. Differential charge-discharge capacity versus potential between 0.01 V and 2.0 V for pristine CNT paper (top) and Si-implanted CNT paper (bottom).

Si-implanted CNT paper is 108 mAh g⁻¹ and 139 mAh g⁻¹, respectively. This indicates that Si-implanted CNT paper shows 30% higher capacity than pristine one. Since the Si amount is very small in the composite, it is hard to determine the capacity from Si. Therefore, the capacity contribution from Si may be quite small. Our previous report¹⁵ used pulse laser deposition (PLD) method to deposit the Si onto the SWCNT. The results show that the Si charge-discharge curve can be clearly seen in the 2.2% Si composite. Here, the Si contents would be much less. Therefore, the higher capacity of Si-implant/CNT could be due to the change of the morphology as shown in Figure 2. The possible reason for the enhancement of specific capacity can be assigned to the removal of surface species containing oxygen on SWCNTs, producing more defects on the SWCNT surface, and the formation of the carbon network due to the partial fusion of CNT during Si irradiation.

Fig. 5. The cycle life the pristine CNT paper (triangles) and Si-implanted CNT paper (circles) electrodes.

4. CONCLUSIONS

Silicon/SWCNT composite electrodes were prepared via low energy silicon ion implantation into the CNT paper to obtain a flexible composite material. The implanted Si can improve the specific capacity and the reversible capacity of CNT paper. After 50 cycles, the specific capacity Si-implanted CNT paper is 30% higher than the pristine CNT.

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