Single-Walled Carbon Nanotube/Carbon Black Composite Paper for Li-Ion Battery Anodes

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Novel single-walled carbon nanotube (SWNT) bucky papers containing carbon black powder were successfully synthesized by simply adding the carbon black powder to the starting solution of SWNT/Triton X-100 standard dispersion, followed by the filtration technique via positive pressure. The SWNT/carbon black composite paper anode demonstrated a reversible capacity of 200 mAh g^{-1} beyond 100 cycles.

1. Introduction

The discovery of carbon nanotubes by Iijima [1] has created a great deal of interest due to the exceptional properties they exhibit. Porous mats of carbon nanotubes, referred to as bucky paper, fabricated by a filtering procedure from highly stable suspensions of single-walled carbon nanotubes (SWNTs) has exhibited possible uses as hydrogen storage material, anode materials in lithium ion batteries, and actuators [2-4]. In this paper, we report on the synthesis of SWNT/carbon black (CB) composite papers and their first studies as anode in lithium-ion rechargeable batteries. The effect of the composite paper's thickness on the electrochemical performances was also investigated.

2. Sample preparation

SWNT/Triton X-100 standard dispersions were prepared by adding 40-60 mg of single-walled carbon nanotubes (SWNTs) (Supplied by Carbon Nanotechnologies Incorporated, USA) and 0.5 g Triton X-100 to 50 mL Milli-Q water, followed by ultrasonication for 2 hrs. A polyvinylidene fluoride (PVDF) filter membrane with pore size of 0.22 μm was cut to fit the filtration cell, after it was wetted with a 50:50 v/v Milli-Q water to ethanol solution. Subsequently, the prepared standard dispersion was filtered with the wetted PVDF membrane in a filtration cell under a nitrogen gas pressure of 400 kPa. The resultant SWNTs mat was washed with 200 mL of Milli-Q water followed by 100 mL of methanol to remove the remaining Triton X-100. Finally, the SWNTs mat was dried in a vacuum oven for overnight, and later peeled off from the PVDF filter. For the SWNT/CB composite paper, the dispersion was prepared by substituting 10 wt. % of the SWNTs with carbon black. The SWNT/CB paper was then prepared using the same procedures as that for the SWNT paper.

The electrochemical characterizations were carried out using coin cells. CR 2032 coin-type cells were assembled in an argon-filled glove box (Mbraun, Unilab, Germany) by stacking a porous polypropylene separator containing liquid electrolyte between the SWNT/CB composite paper and a lithium foil counter electrode. The electrolyte used was 1 M $LiPF_6$ in a 50:50 (v/v) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) provided by MERCK KgaA, Germany.

3. Results

3.1 Structure and morphology analysis

Fig. 1 shows XRD patterns of carbon black and SWNTs precursors and SWNT papers. For all samples, the XRD patterns indicate the persistence of the main reflection of the original SWNTs. This result strongly suggests that the length of the C-C bonds has remained unchanged. That is, when only the SWNTs were dispersed and deposited as a paper, almost no changes in the structure of SWNTs are observed. Most of the SWNT papers have nearly equal, interlayer (*d*(002)) values, and full width-half maximum (FWHM).

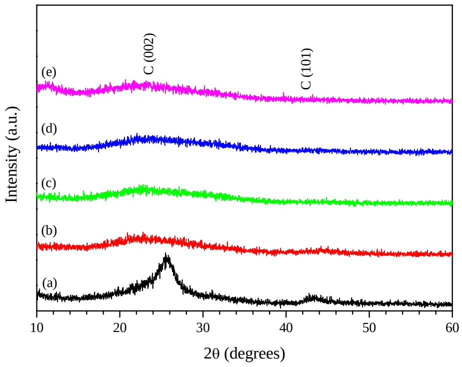


Fig. 1. XRD patterns of (a) carbon black powder, (b) SWNTs precursors, (c) thin SWNT paper with thickness of 30 μm, (d) SWNT paper with thickness of 180 μm and (e) SWNT/CB composite paper with thickness of 120 μm.

Fig. 2(a) shows the TEM image of the SWNTs used as precursors. The SWNTs are very long and reveal a highly entangled network structure. After being prepared as SWNT papers, the papers exhibit a very dense structure with a coarse surface (Fig. 2(b)). Since it was difficult to disperse the SWNT paper in solvent again, TEM was not conducted on SWNT paper in this study.

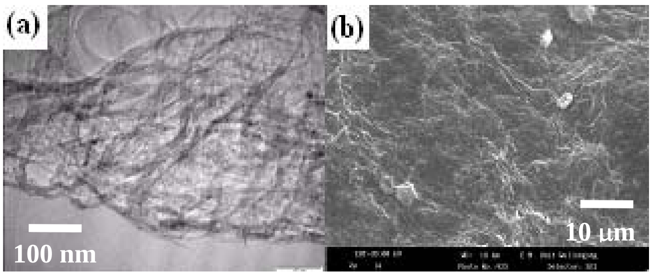
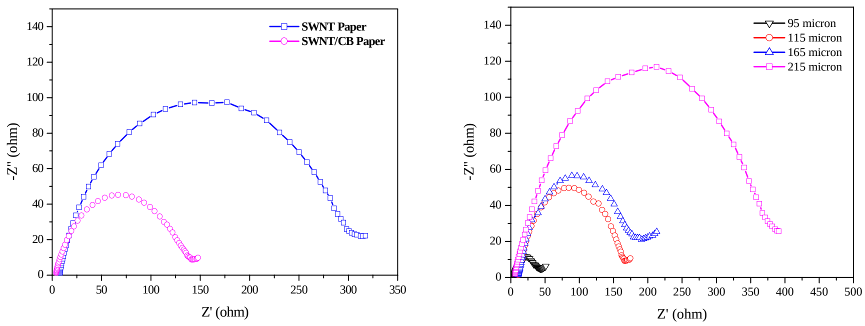


Fig. 2. (a) TEM image of SWNTs precursors; and (b) typical SEM image of SWNT paper.

3.2 Electrochemical characteristics of SWNT composite papers

Electrochemical impedance spectroscopy measurements were carried out using an EG&G Model 6310 Electrochemical Impedance Analyzer (Princeton Applied Research) within a frequency sweep range of 100.00 kHz to 0.01Hz. Fig. 3(a) shows the impedance results obtained for the cells using SWNT paper and SWNT paper with 10 wt.% carbon black. The results indicate that the electrical impedance of the cell using SWNT paper with carbon black as electrode is lower than that of the SWNT paper without carbon black. It is obvious that the cell conductivity was improved by carbon black addition. The impedance of the cells also increased as the thickness of the SWNT papers increased (Fig. 3(b)).

(a)



(b)

Fig. 3. Nyquist plots for (a) SWNT paper and SWNT/CB composite paper, and (b) SWNT paper with different thicknesses.

The cells were galvanostatically charged and discharged in the range of 0.01-2.00 V at a current density of 0.08 mA cm^{-2}. Fig. 4 shows the reversible capacity versus cycle number for cells made from the SWNT paper electrodes (for both the thin and thick paper) and the SWNT/CB composite paper electrode. It can be seen that the capacity improved with the addition of carbon black in the SWNT composite paper electrodes due to the improved electrical conductivity (See Fig. 3(a)). Besides the thickness of the bucky paper also played a crucial role in determining the cyclability of the cell. Thin bucky paper shows superior cyclability performance when compared with thick bucky paper. The SWNT/CB composite paper anode demonstrated a reversible capacity of 200 mAh g^{-1} beyond 100 cycles.

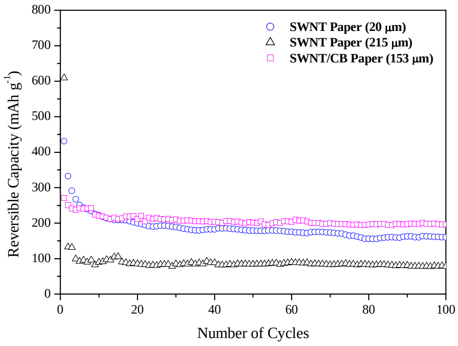


Fig. 4. Reversible capacities vs. cycle number. The current density was 0.08 mA cm^{-2}.

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