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Rapid communication

Electrochemical property studies of carbon nanotube films fabricated by CVD method as anode materials for lithium-ion battery applications

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ABSTRACT

Carbon nanotube films (CNT-1 and CNT-2) were fabricated in a vertical CVD gas flow reactor with water sealing. CNT-1 films consist of ordered crystalline carbon nanotubes, while CNT-2 are defective carbon nanotube films. The films are flexible and transferrable and can be used as binder-free anodes for lithium-ion batteries (LIB). Electrochemical measurements show that CNT-2 possess a reversible capacity of 452 mA h g^{-1} under a current density of 30 mA g^{-1}, which is higher than that of CNT-1 (375 mA h g^{-1}) under the same current density. In addition, the CNT-2 shows a reversible capacity of 107.9 mA h g^{-1} after 500 cycles at a current density of 3000 mA g^{-1}, while 82.1 mA h g^{-1} for CNT-1 under the same condition. Good correlations between morphological factors, defective structure and electrochemical performance are observed.

Unbalanced consumption of unsustainable energy resources such as fossil fuel, natural gas or other natural resources leads research interest into renewable energy resources as well as efficient energy storage devices. Lithium-ion batteries (LIBs), being promising as efficient energy storage devices, play an important role in various applications such as portable power sources, electric vehicles (EV) and portable electronics [1–4]. Since commercialized by Sony Corp. in 1991, LIBs have remarkably advanced the rechargeable battery market [5–7]. However, as comparing to mature battery systems such as lead-acid or Ni–Cd, realization of high efficiency lithium batteries needs considerable progress in materials design [1]. Recently, enormous efforts have been focused on fabrication of flexible secondary batteries due to their potential applications in soft portable electronic instruments [8–11]. Bendable lithium-ion batteries depend on the development of free standing electrode materials. Therefore, development of soft electrode-active materials becomes significantly urgent. In terms of LIBs negative electrodes (anodes), carbon nanotubes (CNTs) with one-dimensional lattice structure have received great attention due to their unique structure, low density, high conductivity and excellent mechanical properties [12,13]. It has been reported that the electrochemical performance of CNTs is mostly influenced by their structure and morphology. Further research revealed that multi-wall CNTs based electrodes prepared in different conditions exhibit reversible capacities of 80–640 mA h g^{-1} [14]. Shorter CNTs were reported to exhibit a higher reversible capacity compared to longer CNTs [15]. Thus, it is of great importance to exploit the electrochemical performance of versatile CNTs electrodes for LIB applications.

In this study, electrochemical properties of flexible and binder-free CNT film electrodes were investigated. The use of CNTs as transferable conductive films promises great potential for high performance flexible batteries due to their high electrical conductivity, flexibility and low density [11,16]. At present, many synthesis methods have been reported for the preparation of CNT films or papers such as filtration method [11], rod coating method [17], layer-by-layer method [18] and chemical vapor deposition (CVD) method [19–21]. Comparing to the other methods, the CVD method provides a better controlled mass and overall morphology of CNT films while good cost-efficiency can be maintained. In this study, two forms of CNTs multiple-layer films were synthesized in a vertical CVD gas flow reactor. Resulting films show good correlation

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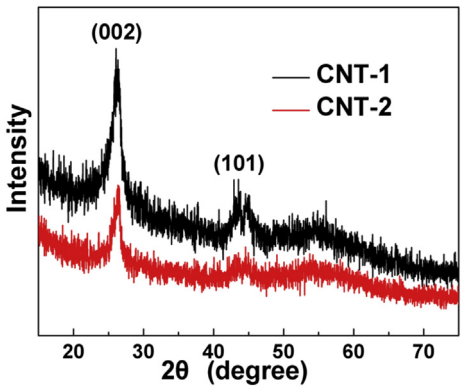

Fig. 1. XRD spectra of CNT-1 and CNT-2.

between morphology and electrochemical performance and can be quite promising for LIB applications.

CNTs films were synthesized using a vertical CVD gas flow system consisting of a quartz tube reactor (60 mm diameter × 1400 mm long) in the center of an electrically-heated furnace. The top of the tube reactor was sealed and connected to the gas inlet, while the bottom was connected to a water tank with gas outlet [20]. Ethanol was used as the carbon precursor. Ferrocene and thiophene were used as catalyst precursor and growth promoter, respectively [22]. All the chemicals were obtained from Tianjin Guangfu. Ferrocene (1.7 wt.%) and thiophene (0.8 wt.%) were dispersed in ethanol (97.5 wt.%) using ultrasonic mixing. The liquid precursors were injected into the top of tube furnace under a H_2 flow (500–800 sccm) at 1100 °C. In the water tank, the continuous CNT film was spooled by a motor driven spindle fixed above the water surface with the axis perpendicular to the gas flow [20]. CNT films with different structure and morphology were synthesized by varying the injection rate of liquid precursors at 6 ml h^{-1} and 9.5 ml h^{-1}, termed as CNT-1 and CNT-2 respectively.

XRD patterns of as-prepared films were obtained using a Rigaku D/Max 2500 V/PC with CuKα radiation at an accelerating voltage of 40 kV and an emission current of 40 mA, from 10° to 90°. Raman spectroscopy was performed using Renishaw Lab RAM HR800 with a diode laser of 632.8 nm wavelength. The morphologies of the films were characterized by field emission scanning electron microscope (FE-SEM, JEOL, JSM-6700F) and transmission electron microscope (TEM, FEI, Tecnai G2F20). Electrochemical performance for both CNT films was conducted using a half cell (CR 2032) with lithium foil as the counter electrode and a porous polypropylene film (Celgard) as separator. The electrolyte solution was prepared by dissolving 1 mol L^{-1} $LiPF_6$ in ethylene carbonate/dimethyl carbonate (EC/DMC) (volume ratio = 1:1) mixture. As-prepared CNT films were dried in vacuum oven at 120 °C for 12 h, and then pressed into 12 mm diameter binder-free electrodes with applied pressure of 3 MPa. The weight and thickness of as-prepared electrodes are ~1 mg

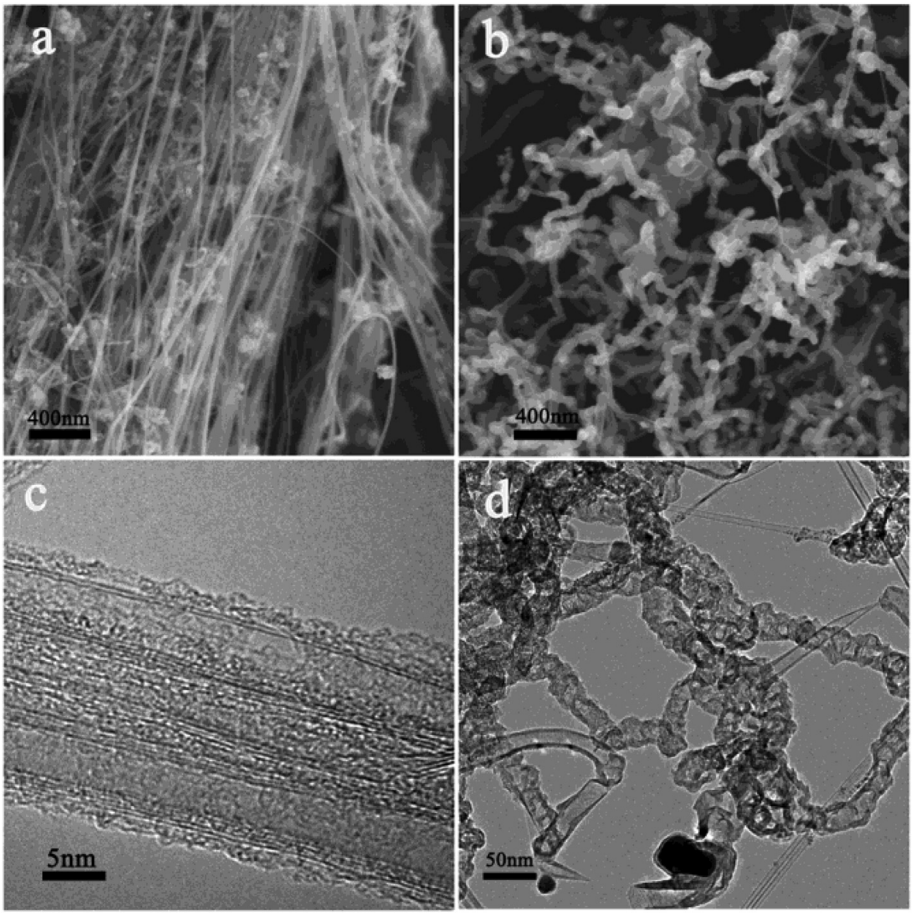

Fig. 2. FE-SEM images of (a) CNT-1 and (b) CNT-2; TEM images of (c) CNT-1 and (d) CNT-2.