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Distinct Copper Electrodeposited Carbon Nanotubes (CNT) Tissues as Anode Current Collectors in Li-ion Battery

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ABSTRACT

A distinct electrodeposition of copper on the external surface of carbon nanotubes (CNT) tissues is demonstrated in two copper electrolytic baths: acid copper sulfate (pH 0.5) and alkaline copper pyrophosphate (pH 8.6). Copper nucleation and growth on the CNT tissue was investigated while applying cathodic polarizations and current transients in a single-step and cost-effective processes. The established copper films are characterized with high uniformity, planarity and excellent adhesion to the densified and bundled CNT tissue substrates, while the surface morphology varies with the chemical composition of the electrolytic bath. Finally, the capability of the copper-coated CNT tissues to function as anode current collectors in a Li-ion battery is shown.

1. INTRODUCTION

The continued interest in miniaturization of electronic devices such as batteries, medical implants and biochemical sensors leads to an increasing demand of their functionality, portability and performance enhancement. With currently scaling down of devices, conventional copper (Cu) and gold (Au), used as conductors, suffer from electro-migration, leading to both decreasing lifetime and performance. Moreover, these conductors are rather expensive and heavy, which is a quite undesirable aspect in the final product. Therefore, new and improved conductive materials are at a great demand. Carbon is a very promising candidate, since it enables better performance and high efficiency, while being light-weight, cost effective, safe and environmentally friendly. In particular, Carbon nanotubes (CNT) are attractive due to their unique characteristics, such as: low density, high electrical and thermal conductivity, high current carrying capacity, high mechanical strength, flexibility and the low cost of large scale production [1].

Materials based on CNT were studied for various purposes, such as interconnect applications in integrated circuits and electrical wiring [1,2]. Yet, their electrical conductivity is lower than copper and aluminum and therefore, other approaches that may enhance the intrinsic lower CNT's conductivity are mandatory. It was reported previously on CNT-copper composite materials presenting 100 times higher current carrying capacity than common electrical conductors, such as Cu and Au [3]. Other researches presented CNT reinforced copper nanocomposites, fabricated by electroless deposition process, presenting homogeneous distribution of the CNTs in the metal matrix that enhances both physical and mechanical properties [4].

We report in this work on a simple single-step electrochemical process, enabling the fabrication of layered CNT-Cu structures, obtaining an electrical conductivity, which is one order of magnitude higher than pristine CNT tissue. In contrast to the conventional approaches that use CNT and metal ions dispersions, electroless deposition or two-stages nucleation-growth electrodeposition processes [3,5–7], we report here on the capabilities to distinctively electrodeposit a thin Cu film on the exterior surface of the CNT tissues. The simple and cost effective process permits a deposition of uniform copper films, particularly over the CNT tissue in acid or alkaline aqueous solutions. Copper nucleation and growth on the CNT tissue is investigated in cathodic polarization and current transient experiments. The study presents the cathodic electrochemical behavior of CNT tissue electrodes in both acid and alkaline aqueous Cu solutions, Cu distinct nucleation and growth on the CNT tissue, as well as the characteristics of the obtained copper thin layer on various CNT tissues possessing different thicknesses and densities. Finally, we demonstrate the ability of the Cu coated CNT tissues to function as Li-ion battery anode current collector. The layered Cu-CNT-Cu structure can

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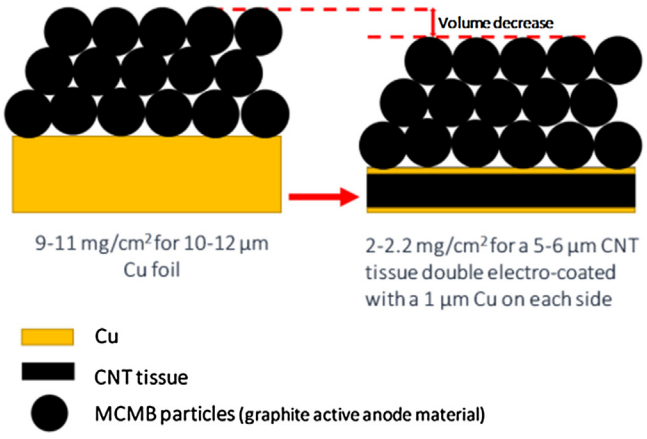
function as a conductive material in various applications. One example is a Li-ion battery as the copper coated CNT tissue may be a fine substitution to the heavy 10–12 μm commercial Cu foil current collector, being used in commercial Li-ion cells. The reader is kindly directed to an excellent and extended review on materials for flexible Li-ion battery's current collectors, recently published by Kim and Cho [8]. Current collectors for flexible Li-ion batteries are of a great interest due to the growing need for shape adaptation and battery flexibility. Additionally, the growing demand for higher performance Li-ion batteries has led to an extensive research on alternative current collectors, replacing the heavy and costly copper and aluminum metals, serving as anode and cathode currents collectors, respectively. Previous innovative studies reported various approaches in the implementation of improved current collectors for Li-ion batteries; honeycomb-patterned Al and Cu current collectors produced by a reactive-ion etching process were reported, suggesting an enhanced adhesion of the active electrode materials as a result of the increased surface area due to the 3D structure [9]. Others, suggested a thin metal layer sputtered onto a porous polymeric membrane (used as the separator, as well). This would provide a lower weight and a rough surface to the current collector [10]. A metallic mesh was also examined, as it provides a relatively low weight and a good electrical conductivity due to the 3D character [11]. Free-standing and flexible film in the form of electrically conducting polymers were also reported; albeit, such films present a rather low specific capacity, requiring an additional active materials loading [12,13]. In addition to all the above, carbon based materials, such as CNT and graphene were suggested as alternative current collectors, owing to their high electrical conductivity and low weight [14–19]. However, the interaction of their high surface area with the highly reactive battery electrolyte, leading to a substantial high irreversible capacities in the first lithiation charge, is a well-known and a recognized challenge. Here, we present Cu-CNT-Cu sandwich tissues that are highly conductive, having substantial lower densities than copper. The thin copper layers deposited on the external (side) surfaces of the CNT tissue would allow higher conductivity, relatively to a bare CNT tissue current collector ($\sim 10^6$ *vs.* $\sim 10^5$ S m^{-1}, respectively), while functioning as a physical barrier, minimizing the contact between the high surface area CNT and the relatively reactive battery electrolyte. The use of this structure, as a replacement to the Cu foil current collector will result in a thinner, lighter and more flexible current collector, which will eventually enable a lower volume of the final electrode structure, as demonstrated in Scheme 1.



Scheme 1. A possible replacement of copper current collector in Li-ion batteries via the introduction of copper-coated CNT anode current collector tissues. ***left:*** a commonly used copper foil current collector. ***right:*** a schematic view of a Li-ion battery anode configuration utilizing copper electroplated CNT tissues.

2. EXPERIMENTAL

CNT tissues were obtained from Tortech Nano-Fibers Ldt. (Israel). Prior to any use of them, the tissues were washed with isopropyl alcohol (IPA) followed by an ambient drying. CNT's tissues thickness measurements were conducted with the use of a Mitutoyo digital micro-meter. Two solutions were used for the electrochemical tests and electrodeposition, prepared from the chemicals: copper sulfate ($CuSO_4$, Merck KGaA), sulfuric acid (H_2SO_4, Gadot), potassium pyrophosphate ($K_4P_2O_7$, Carlo Erba Reagents) and copper pyrophosphate ($Cu_2P_2O_7$, Alfa Aeasar) dissolved in de-ionized (DI) water (18MΩ, Millipore). The Chemical composition of the used copper solutions is: a) Acid copper sulfate bath containing 0.13 M Cu^{+2} (8.5 g L^{-1}) and 0.92 M H_2SO_4 (90 g L^{-1}), pH 0.5. b) Alkaline copper pyrophosphate bath containing 0.2 M Cu^{+2} (12 g L^{-1}) and 0.53 M $K_4P_2O_7$ (175 g L^{-1}), pH 8.6. CNT tissue samples (with dimensions of 3 × 1 cm) were used as working electrodes, positioned in an electrochemical cell and pressed by a copper lead, serving as a rigid electrical contact.

The electrochemical measurements related to the copper plating were performed with a PARSTAT 2273a potentiostat (EG&G) in a three-electrode electrochemical cell equipped with a saturated calomel reference electrode (SCE) and a Pt-wire counter electrode. The reference electrode was installed in the solution through a Luggin-Haber capillary tip assembly. All the potentials presented and discussed in the electrochemical measurements are *vs.* SCE. Surface morphology and cross section images of the pristine CNT tissue and with the deposited copper film were obtained by HRSEM (Zeiss Ultra-Plus FEG-SEM) and by SEM (FEI E-SEM Quanta 200). Cross sectional images of the pristine and IPA or Tert-butanol treated CNT tissues were obtained by Dual Beam FIB (FEI Strata 400S). The qualitative evaluation of adhesive characteristic of the deposited copper over the CNT tissue surface (5 × 30 mm) was conducted by bending the coated tissues to 180° and straitening them back to the initial state. Bent surface zones were examined by SEM prior and subsequent to the bending test.

Through plane electrical conductance measurements of the CNT tissues were conducted on 15 × 15 mm samples using a homemade device, consisting of two flat contact electrodes in the form of copper disks, with an applied load of 1 kg, connected to a DC power supply. In the measurement, the CNT electrode is placed and pressed between the copper electrodes and a constant current is passed. The electrical conductivity is calculated from the data of the passed current and the obtained voltage. In-plane electrical conductance measurements were performed using a Signatone Four Point Probe device equipped with SP4 head (having a 1 mm distance between the probes).

The application of the three-layered Cu-CNT-Cu sandwich material structure as a battery current collector was performed by doctur blade ("Dr. Blade") casting a graphite slurry [90% MCMB graphite (Targray):10% polyvinyldene fluoride (PVDF, Aldrich) binder] onto the copper coated CNT or on a 10 μm pure copper foil. The casted film was dried in a vacuum oven at a temperature of 120 °C for 2 hours. The loading of MCMB on the coated CNT tissue and onto the copper foils was ~15 mg cm^{-2}, corresponding to an average capacity of ~5.6 mAh cm^{-2}. Charge-discharge cycles of [CNT-Cu/graphite]/Li metal half-cells were carried out at a current density of 0.1 mA cm^{-2} at room temperature using an Arbin BT2000 battery test system. Slow scan cyclic voltammetry (SSCV) measurements were conducted in a scan rate of 5 μV s^{-1}, with a VersaSTAT (Princeton Applied Research potentiostat/galvanostat) in a three-electrode cell configuration utilizing Li metal as reference and counter electrodes. Potentials in this section of the paper are quoted *vs.* Li/Li$^+$ couple. A detailed description of the cell and anode slurry casting and preparation is reported in our previous work [19].