



Three-dimensional carbon nanotubes for high capacity lithium-ion batteries



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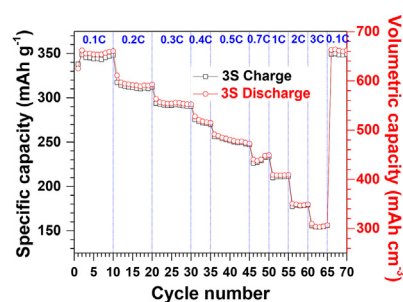
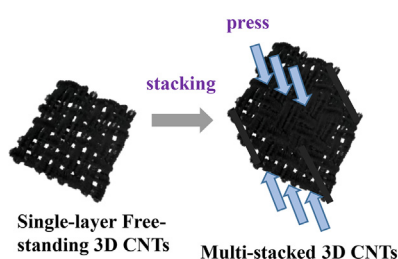
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HIGHLIGHTS

- We show a novel structure of multi-stacked 3D CNTs for a higher loading of CNTs.
- The bulk density of multi-stacked 3D CNTs is twice as high as that of graphites.
- The multi-stacked 3D CNTs yield a stable and high reversible volumetric capacity.

GRAPHICAL ABSTRACT



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ABSTRACT

Carbon nanotubes (CNTs) have been considered as a potential anode material for next generation Lithium-ion batteries (LIBs) due to their high conductivity, flexibility, surface area, and lithium-ion insertion ability. However, the low mass loading and bulk density of carbon nanomaterials hinder their use in large-scale energy storage because their high specific capacity may not scale up linearly with the thickness of the electrode. To address this issue, a novel three-dimensional (3D) architecture is rationally designed by stacking layers of free-standing CNTs with the increased areal density to 34.9 mg cm^{-2} , which is around three-times higher than that of the state-of-the-art graphitic anodes. Furthermore, a thermal compression process renders the bulk density of the multi-stacked 3D CNTs to be increased by 1.85 g cm^{-3} , which yields an excellent volumetric capacity of 465 mAh cm^{-3} at 0.5C. Our proposed strategy involving the stacking of 3D CNT based layers and post-thermal compression provides a powerful platform for the utilization of carbon nanomaterials in the advanced LIB technology.

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1. Introduction

The lithium-ion battery (LIB) has been one of the most commonly used state-of-the-art energy storage systems since it was first commercialized in 1990. The commercial success of the LIB is mainly attributed to the unique features of high operating

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potential (>3.0 V), high energy density (110 – 170 Wh kg^{-1} and 230 – 400 Wh L^{-1}), appropriate cyclability, and cost effectiveness [1,2]. To further enhance the LIB performance, attempts have been made to investigate more efficient anode materials alternative to the conventional graphite anodes offering a theoretical specific capacity of 372 mAh g^{-1} . Among the potential carbon-based materials, the quest for carbon nanotubes (CNTs) has been particularly promising due to their excellent electrochemical and physico-chemical properties [3]. The excellent electrochemical performances of CNTs for LIB are mainly associated with the CNTs' unique characteristics such as high surface area, short diffusion length for lithium-ions, and excellent electrical and mechanical properties [4–6].

Although CNTs have been proven as emerging anode material candidates to yield high specific capacity for LIBs, there are still legitimate limitations to be examined for the application of the CNTs to commercial products [7]. First, the previously reported CNTs with high specific capacity are, in many cases, dimensionally confined in thin film geometries that are not suitable for large-scale LIBs. Second, the specific capacity does not scale proportionally with the thickness of CNTs when the weight of electroactive CNTs is negligibly low relative to the total weight of an LIB cell. Third, CNTs have intrinsically low volumetric capacity that is a critical property for large-scale energy storage systems [8]. As a key property to enhance volumetric capacity, the bulk density (mass divided by total volume of solid matter) of most nanomaterial-based electrodes including CNTs is less than 1 g cm^{-3} , which is a mediocre density compared to that of commercial-grade graphite (0.35 – 0.9 g cm^{-3}) [9,10]. Due to the above-mentioned limitations, there is no clear confirmation that CNTs are indeed pertinent anode nanomaterials for high volumetric capacities to be used in large-scale energy storage systems. To address these challenging issues of the CNT anode, we have introduced a 3D micro-channeled copper (Cu) that has a high surface area to accommodate the large loading amounts of CNTs [11]. In addition, the high porosity of 3D CNTs is suited to facilitate lithium-ion diffusion and electron charge transfer through the electrolyte and bulk electrode into the 3D CNTs as electroactive materials; as a result, the high porosity can enhance cyclic performance and current rate capability of the electrode [12,13]. In recent years, different approaches have been applied to enhance areal density (mass per unit area) and capacity (storage capacity per unit area) as well as bulk density and volumetric capacity. T. Sharifi et al. made the nitrogen-doped CNTs grown on carbon paper substrate by using a catalytic chemical vapor deposition (CVD) method, and the areal density and capacity of the CNTs/carbon paper electrode are 9.6 mg cm^{-2} and 1.95 mAh cm^{-2} at 0.2C , respectively [14], which are comparable to those of commercially available LIBs [15]. D. T. Welna et al. fabricated a free-standing film of vertically aligned multi-wall CNTs on a nickel

substrate using a combined method of catalytic thermal CVD and sputter deposition, and the CNT anode showed the bulk density and volumetric capacity of 0.51 g cm^{-3} and 395 mAh cm^{-3} at 57 mA g^{-1} [16], respectively, which are comparable to those of commercial graphites [10,17,18].

In this study, we report that multi-stacked 3D CNTs demonstrate a stable and reversible volumetric capacity higher than that of the state-of-the-art graphitic anode used in an LIB. The structure of multi-stacked 3D CNTs provides one of the most pragmatic approaches towards the enhanced LIB performance of CNTs as promising anode nanomaterials for advanced large-scale LIBs.

2. Experimental

2.1. Fabrication of multi-stacked 3D CNT anode

In this work, a multi-stacked 3D CNT-based anode was prepared through the following key steps: (1) 3D CNTs were directly grown on a Cu mesh ($>99\%$ purity) with 50 μm thickness and 65 μm hole size (TWP Inc.) as a substrate by using a thermal catalytic CVD method; (2) The Cu substrate was removed by ferric chloride (FeCl_3) etching solution (Transene Company, Inc.) to obtain 3D free-standing CNT layers; and (3) The 3D free-standing CNT layers were stacked through the vacuum annealing and thermal compression methods to fabricate multi-stacked 3D CNTs with a high bulk density. Fig. 1 schematically represents the process for the formation of the multi-stacked 3D CNT-based anode. In Fig. 1(a), CNTs were directly grown on Cu mesh by a CVD method, where nickel (Ni) and titanium (Ti) were deposited onto Cu, using a radio frequency (RF)-direct current (DC) magnetron-sputtering system, which served as a catalyst for CNT growth and a barrier layer against carbon diffusion into Cu during CNT growth, respectively. The Ni/Ti deposited Cu mesh was placed in a CVD system, and the mixture gas of H_2 and C_2H_4 with a volume ratio of $1:2$ flowed into the furnace for 50 min at the growth temperature of 750 $^\circ\text{C}$. The weights of each sample before and after CNT growth were measured to calculate the net weight of CNT as an electroactive material for a LIB. After 4 h of Cu etching, Cu mesh was completely dissolved into the concentrated FeCl_3 solution, and the solution was left with 3D free-standing CNT structures (see Fig. 1(b)). The free-standing structures were thoroughly washed with de-ionized water and dried in a vacuum oven (Thermo Scientific Lindberg) at 120 $^\circ\text{C}$ for 4 h as presented in Fig. 1(c). To prepare a highly dense multi-stacked 3D CNT anode, we employed polyvinylidene fluoride (PVDF, Sigma–Aldrich) as a binder dissolved into *N*-Methyl-2-pyrrolidone (NMP) solvent. The solution is composed of 1.4 wt% of PVDF and 98.6 wt% of NMP (the weight ratio of CNTs to PVDF is $8:2$). Two pieces of free-standing CNT layers were sandwiched within the solution and subsequently heated at 120 $^\circ\text{C}$ under a

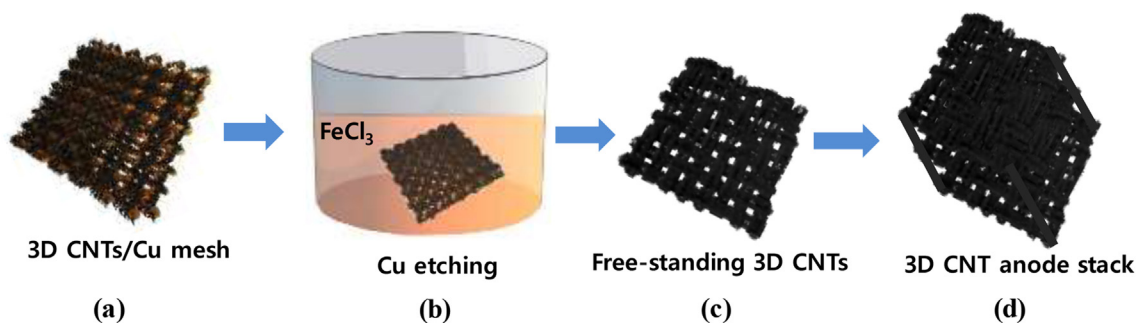


Fig. 1. Process flow for the fabrication of multi-stacked 3D CNT anode. (a) CVD grown 3D CNTs on Cu mesh. (b) Chemical etching process of the Cu mesh via the FeCl_3 etching solution. (c) 3D free-standing CNT structure after the etching process. (d) The multi-stacked 3D CNT anode fabricated by pressing the layers of 3D CNTs with the aid of PVDF binder.

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