



Research paper

Carbon Nanofibers Loaded with Carbon Nanotubes and Iron Oxide as Flexible Freestanding Lithium-Ion Battery Anodes



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ARTICLE INFO

Article history:

Received 17 April 2017

Received in revised form 15 September 2017

Accepted 15 September 2017

Available online 18 September 2017

Keywords:

Electrospinning

Iron oxide

Carbon nanotube

Lithium ion battery

Anode

ABSTRACT

We demonstrate the fabrication of flexible electrospun carbon nanofibers (CNFs) containing uniformly distributed carbon nanotubes (CNTs) and iron oxide (FeO_x) nanoparticles (NPs) as a composite material for lithium-ion battery (LIB) anodes. The uniform incorporation of CNTs and FeO_x NPs within the CNFs was confirmed by transmission electron microscopy. Embedding even a small amount of CNTs (0.1 wt%) in the CNFs increased the LIB performance by a factor of two compared with pure CNFs. The specific capacity was also increased, by 25%, when an iron source (iron (III) acetylacetonate) was added at a concentration of 2 wt%. The FeO_x-CNT/CNF electrode maintained a capacity of 1008 mAh·g⁻¹ at a current density of 100 mA·g⁻¹ after 100 cycles. Further, the high-performance anode material was freestanding, flexible, and lightweight. This makes it suitable for next-generation LIBs, which must deliver high power over long periods while also being light and flexible.

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1. Introduction

Extensive research efforts are focused on producing lithium-ion batteries (LIBs) with higher energy and power densities and longer operational lifetime. Carbon-based materials that have relatively low potential with respect to lithium are usually employed as anode materials in LIBs. However, they fall short in terms of performance due to their limited rate capability and the modest lithium storage capacity of graphite [1]. Although graphene has been widely investigated as a substitute material, it also suffers from the drawback that aggregation of graphene sheets through van der Waals interactions lowers the surface area and reduces the lithium storage capacity [2,3].

Metal oxides such as Fe₂O₃, NiO, Cu₂O, and SnO₂ have shown significant potential for use in batteries and are being studied widely, as they are nontoxic and abundant in nature [4]. Fe₂O₃ as an anode material for LIBs has a high theoretical capacity of 1007 mAh·g⁻¹ [5]. However, disadvantages of Fe₂O₃ include low electrical conductivity and poor capacity retention, owing its

microstructure and/or the tendency of Fe₂O₃ nanoparticles to agglomerate. Efforts have been made to fabricate composite materials by uniformly distributing Fe₂O₃ nanoparticles in a matrix of a carbon material, such as carbon nanotubes (CNTs), carbon nanofibers (CNFs), or carbon black [6,7]. CNTs have been employed to enhance the lithium storage capacity as well as conductivity. Single-walled carbon nanotubes (SWCNTs) and multiwalled carbon nanotubes (MWCNTs) have been reported to have conductivities as high as 10⁶ S·m⁻¹ and 10⁵ S·m⁻¹, respectively [8].

Lithium insertion and storage in MWCNTs occurs at three different potentials: first, at potentials lower than 0.5 V (versus Li/Li⁺), Li is intercalated between the graphene layers; then at 0.5–1.6 V, lithium enters the nanocavities; and finally, at 1.5–3.0 V, lithium reacts with surface oxygen [9]. The inner cores of the CNTs can provide space for lithium storage. However, in the case of pure CNTs, access to the inner parts of the CNTs is highly restricted. To improve access to the inner cores of CNTs, methods such as electron irradiation and chemical oxidation, among others, have been used to form pores in CNTs, increasing the number of sites available for lithium diffusion. Eom et al. reported that the lithium storage capacity of CNTs can be enhanced by etching, while Oktaviano et al. suggested that it could be increased by drilling [10,11]. In addition, Fe₂O₃-CNT hybrid materials have been reported to exhibit enhanced lithium storage capacity [12].

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The use of CNTs and Fe₂O₃ together to form a composite is advantageous because the resilient network of the CNTs can buffer the volume expansion of Fe₂O₃ while also improving the cycling stability. In addition, the conductivity of Fe₂O₃ is improved upon combination with CNTs. This also ensures stable electrochemical kinetics. The CNTs may prevent the drifting or agglomeration of metal oxide nanoparticles, thus ensuring that the active reaction sites are maintained. Adding Fe₂O₃ onto or into a carbon nanofiber matrix was reported to enhance the charge storage capacity [13]. The use of CNTs with CNFs was shown to enhance the mechanical properties of CNF [14]. Electrospun CNFs are easy to prepare and can be directly used as a conductive electrode material after carbonization [15]. The prior reports described above led us to expect that adding both Fe₂O₃ and CNTs into CNFs could produce a composite material with a high capacity and stability and good capacity retention properties.

Zhou et al. [6] prepared a composite consisting of 5–10 nm diameter Fe₂O₃ nanoparticles anchored on flexible SWCNT membranes for use as a LIB anode. The material showed a specific capacitance of 1243 mAh·g⁻¹ at a current density of 50 mA·g⁻¹. Filling of CNTs with Fe₂O₃ has also been attempted. Yu et al. [16] tried to fill CNTs with Fe₂O₃ nanoparticles via a chemical vapor deposition process. Further, Gao et al. [17] reported the fabrication of hybrid Fe₂O₃/CNT composites by a hydrothermal process. Zhao et al. [18] used a hydrothermal method to produce Fe₂O₃-decorated SWCNTs with a “nanohorn” morphology. Yan et al. produced Fe₂O₃ encapsulated within MWCNTs [19]. Bak et al. [20] deposited Fe₂O₃ nanoparticles on functionalized CNTs through a two-step process. However, their capacity decreased from 272 to 182 mAh·g⁻¹ after 50 cycles at a current density of 100 mA·g⁻¹.

The coupling of CNFs with CNTs has also been attempted previously [21,22]. However, to the best of our knowledge, there has been no report on the coupling of iron oxide with a CNT/CNF composite, which is the focus of this study. CNTs and iron oxide can be readily incorporated into or onto CNFs by electrospinning. A post-spinning annealing treatment removes the binder from the CNFs, producing a freestanding film that can itself act as the current collector, reducing the overall mass of the system by eliminating the need for a separate current collector [23].

2. Materials and Methods

2.1. Fabrication of FeO_x-CNT/CNF composite

First, 0.05 g and 0.75 g of polyacrylonitrile (PAN, *M_w* = 150 kDa, Sigma-Aldrich) were each separately dissolved in 4.5 g of *N,N*-dimethylformamide (DMF, 99.8%, Sigma-Aldrich) by stirring at 60 °C for 24 hours, to make concentrations of 1 wt% and 9 wt% PAN/DMF. Then, 0.1 wt% of MWCNTs (purity >90%, XNM-HP-1500, XinNano Materials Inc. Taiwan) was added to the 1 wt% PAN solution, and the solution was stirred for an additional 24 h to ensure that the CNTs were dispersed uniformly. Higher PAN concentrations hampered the dispersion of CNT. Thus, the additional 9 wt% PAN is added after dispersing the CNT in 1 wt% PAN solution. The 0.1 wt% of CNT was observed to be optimal for maintaining a stable dispersion; higher CNT concentrations led to agglomeration. Note that the CNT used here is in as received form without any further treatment to improve the dispersibility of the CNT. Then, iron (III) acetylacetonate ((FeAcAc), Fe(C₅H₇O₂)₃, Sigma-Aldrich) was added to the CNT/PAN-DMF solution, and the mixture was stirred for 12 h at 25 °C to completely dissolve the FeAcAc. The mixture was then tip-sonicated for 30 s to ensure homogenous dispersion of the CNTs in the solution. The CNT and FeAcAc weight percents stated here are relative to PAN/DMF solution. The proportion of the CNTs in all the solutions was kept constant by varying the metal concentration, as shown in Table 1, to determine

Table 1
Precursor composition.

Case No.	CNT/FeAcAc [wt%]
1	0.0: 0
2	0.1: 0
3	0.1: 2
4	0.1:4

the optimized concentrations of FeAcAc and CNT for ensuring good electrochemical performance, in terms of capacity, stability, and capacity retention.

Next, NFs were produced by the electrospinning process [24]. The setup used consisted of a syringe, needle, grounded collector, and high-voltage power supply. The precursor solution (Fig. 1a) was delivered using a syringe (Fig. 1b) at an optimized flow rate of 250 μL·h⁻¹, which yielded a stable Taylor cone at the end of the needle. The electrospun NFs were collected on a drum collector held 15 cm away from the needle. Mats of different colors were formed, depending on the concentration of the FeAcAc salt (Fig. 1c). The synthesized mats were stabilized by heating in air at a rate of 5 °C min⁻¹ to 280 °C and holding them at that temperature for 30 min. The stabilized mats were annealed again in a tube furnace at a temperature of 700 °C for 2 h in flowing argon. The temperature of the furnace was raised from room temperature to 700 °C at a rate of 3 °C min⁻¹ in order to carbonize the stabilized NFs. After carbonization, the mats turned black (Fig. 2) and became highly conductive.

2.2. Characterization

The surface morphologies of the composite mats were analyzed by field-emission scanning electron microscopy (FE-SEM, S-5000, Hitachi, Ltd.), transmission electron microscopy (TEM, JEM 2100F, JEOL Inc.) and elemental mapping by energy-dispersive X-ray spectroscopy (EDX) within the TEM. The structural properties of the mats were characterized by X-ray diffraction (XRD) analysis (SmartLab, Rigaku). A confocal Raman spectrometer (Jasco, NRS-3100) was used to analyze the defects in the CNFs in the mats. Finally, X-ray photoelectron spectroscopy (XPS) measurements (Theta Probe Base System, Thermo Fisher Scientific Co.) were performed to evaluate the chemical states of the constituent elements on the surfaces of the composite mats. N₂ adsorption and desorption isotherms were measured to determine the surface area of composites using a volumetric adsorption apparatus (Tristar 3000, Micromeritics). The sample was pretreated at 70 °C for 48 h under high vacuum (< 10⁻⁶ Torr) before commencing adsorption studies.

2.3. Electrochemical tests

The carbonized mats were highly flexible and freestanding and could be punched to directly produce working electrodes. The mats showed good flexibility and could be bent without breaking, as shown in Fig. 2. The punched electrodes (14 mm in diameter) were used to form CR2032 coin-type half-cells, which were subjected to electrochemical tests. A metallic Li sheet was used as the reference electrode, and a microporous polymer separator (Celgard 2400, Celgard, Chungbuk, South Korea) was placed between the two electrodes. A solution of 1 M LiPF₆ in a mixture of ethylene carbonate, dimethyl carbonate, and ethyl methyl carbonate (1:1:1 by volume) (PuriEL, Soulbrain, Seongnam, South Korea) was used as the electrolyte. Galvanostatic discharging/charging was performed between 0.005 and 3 V at 25 °C using a WBCS3000 battery cycling system (WonATech, Seoul, South Korea). The cells were subjected to rate tests at different current densities (10 cycles each

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