Electrochimica Acta 222 (2016) 856–861

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Self-assembly of one-dimensional nitrogen-doped hollow carbon nanoparticle chains derived from zinc hexacyanoferrate coordination polymer for lithium-ion capacitors

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ARTICLE INFO

Article history:
Received 28 September 2016
Received in revised form 5 November 2016
Accepted 8 November 2016
Available online 11 November 2016

Keywords:
1D carbon nanostructures
mesoporous materials
energy storage
metal hexacyanoferrate
supercapacitors

ABSTRACT

One-dimensional nitrogen-doped hollow carbon nanoparticle chains (CNCs) featuring bimodal pore size distribution were obtained by direct thermal pyrolysis of a three-dimensional cyanide-bridged coordination polymer precursor (zinc hexacyanoferrate) without the need for additional carbon, nitrogen, and catalyst sources. Nitrogen doping turned out to play the key role in the formation of mesoporous compartment layers and structural defects in the CNCs. Small mesopores in the walls provided high surface area for charge storage and allowed the migration of electrolyte into the compartments. Large mesopores in the hollow compartments accommodated electrolyte for easy transport of lithium ions. The commercial multiwalled carbon nanotube (CNT) electrode stored lithium ions primarily through the intercalation process, while the CNC electrode stored lithium ions through both the intercalation and adsorption processes. Thus, the CNC electrode exhibited superior supercapacitive performance than the CNT electrode. The CNC electrode with low internal resistance could deliver a high capacitance of 680 $F g^{-1}$ at 1 $A g^{-1}$ in the working potential range of 0.01-3.50 V *vs.* Li/Li^+, which was much better than the commercial CNT electrode (252 $F g^{-1}$).

1. Introduction

Lithium-ion capacitor (LIC) has gained increasing attention in the field of energy-storage devices on account of its high energy density compared with traditional electric double-layer capacitor (EDLC). More importantly, LIC has superior power density and cycle stability comparable to the EDLC [1–3]. Activated carbon materials are frequently adopted as the active materials for LIC because they exhibit high surface area and tunable pore geometry for accommodating large amounts of lithium ions [4–6]. Some carbon materials such as graphene, graphite, graphdiyne, carbon nanotube (CNT), hard carbon, and soft carbon materials have been reported as the promising materials for LICs [7–20]. Hybrid LICs using lithiated metal oxides as cathode and carbon materials as anode have received considerable interest since they have fairly higher energy density than traditional EDLCs [21–26]. Among the anode materials, carbonaceous material is particularly attractive because of its natural abundance, high chemical stability, and relatively low cost. The unique properties of CNTs such as one-dimensional (1D) structure and electrical conductivity make them a promising material for high-performance LIC and supercapacitors [27]. The co-doping of carbon materials with heteroatoms including nitrogen, sulfur, boron, and phosphorous has become one of the most straightforward strategies to improve the electrochemical and physicochemical properties of carbon materials. Nitrogen-doped carbon materials turn out to exhibit beneficial effects on the supercapacitive performance of the carbon electrodes owing to the significant improvements in wettability and electrical conductivity of electrodes [28–30].

LICs represent a vital strategy for energy storage, but they are typically restricted by relatively low energy density as compared with conventional rechargeable batteries, especially the lithium-ion batteries [19,31]. Carbon cuboids derived from three-dimensional (3D) MOF (metal-organic framework) materials have been reported as highly prospective materials for high-performance LIC in view of their extremely high surface area [32]. Previous report indicated that the titanate nanotubes display unique pseudocapacitive features owing to their intrinsic characteristics, such as the high surface area, multiwalled structure, thin wall, as well as large interlayer space [33]. In addition to high surface area, an appropriate pore distribution may play the crucial role in the success of the LIC. Bimodal porous carbon materials containing

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http://dx.doi.org/10.1016/j.electacta.2016.11.047

both small and large mesopores are highly promising active materials for LIC. The small mesopores (or micropores) offer a large number of electroactive sites for storage of lithium ions, while the large mesopores (or macropores) provide wide channels for facilitating the ion diffusion [30]. In this work, 1D nitrogen-doped hollow carbon nanoparticle chains (CNCs) with bimodal pore distribution (small and large mesopores) are self-assembled by direct thermal pyrolysis of zinc hexacyanoferrate (ZnHCF, a 3D cyanide-bridged coordination polymer) particles as an active material for advanced LIC. Supercapacitive performance of the CNC electrode is investigated and compared with a commercial CNT electrode.

2. Experimental

ZnHCF powder was synthesized by dropwise adding 50 mL of potassium hexacyanoferrate solution (0.02 M) into 50 mL of zinc nitrate solution (0.04 M) under continuous stirring at 70 °C. The precipitate (ZnHCF) was centrifuged and cleaned with de-ionized (DI) water several times. CNC sample was prepared by thermal pyrolysis of ZnHCF powder at 700 °C for 5 h in the flow of argon gas. To remove the metal nanoparticles that were not fully embedded in CNCs, the collected CNC powder was treated by hydrochloric acid solution (1 M) under ultrasonic irradiation for 1 h and then washed by DI water several times till a neutral pH state was reached. CNC film was deposited on stainless steel (SS, 1 cm x 1 cm) sheet by electrophoretic deposition (EPD). In typical, EPD process was performed in a colloidal suspension comprising 50 mg of CNC material, charging agent (0.1 mM zinc nitrate), and isopropyl alcohol (50 mL). A potential difference of -40 V was applied between working (SS) and counter (Pt sheet) electrodes with a separation of 1 cm. After deposition, the working electrode was heated at 300 °C in air for 1 h. For comparison, a commercial multiwalled CNT sample with a diameter of 20–40 nm and a length of 0.5–200 μm (ECHO Chemical Co. Ltd., Taiwan) was deposited on SS sheet using the same procedure as the CNC electrode. Prior to EPD, the commercial CNT sample was etched with boiling concentrated nitric acid solution for 2 h under reflux to increase the surface area without severe damage of the nanotube structure. The loading amounts of CNC and CNT on SS sheets were kept almost the same (0.3 mg) by varying the deposition time.

Internal structure and surface morphology of CNCs were observed by a transmission electron microscopy (TEM, Jeol JEM-1400) as well as scanning electron microscopy (SEM, Auriga), respectively. Raman spectrum and elemental composition of CNCs were measured by a Raman microscopy and XPS (X-ray photoelectron spectroscopy), respectively. Specific surface area and pore size distribution of CNC powder were analyzed by means of BET (Brunauer-Emmett-Teller) and BJH (Barrett-Joyner-Halenda) techniques, respectively, using nitrogen adsorption/desorption isotherms (Micromeritics, ASAP 2020). The coin cell (type CR2032) was assembled in a glove box filled with argon atmosphere using CNC (or CNT) electrode as working electrode and lithium foil as the reference and counter electrodes. A polypropylene separator (Celgard 2400, 25 μm in thickness) was inserted between the working and counter electrodes. Supercapacitive performance of electrodes was evaluated in a ternary organic mixture of propylene carbonate/diethyl carbonate/ethylene carbonate (1/2/1, by volume) containing 1 M $LiPF_6$ by cyclic voltammetry and charge/discharge measurements (Keithley, 2400) in a potential window of 0.01-3.50 V *vs.* Li/Li$^+$. Electrochemical impedance spectroscopy of CNT and CNC electrodes was performed by a potentiostat/galvanostat (Autolab, PGSTAT 302 N) by applying a sinusoidal bias of 10 mV *vs.* open-circuit potential in a frequency range of $0.01 - 1 \times 10^6$ Hz.

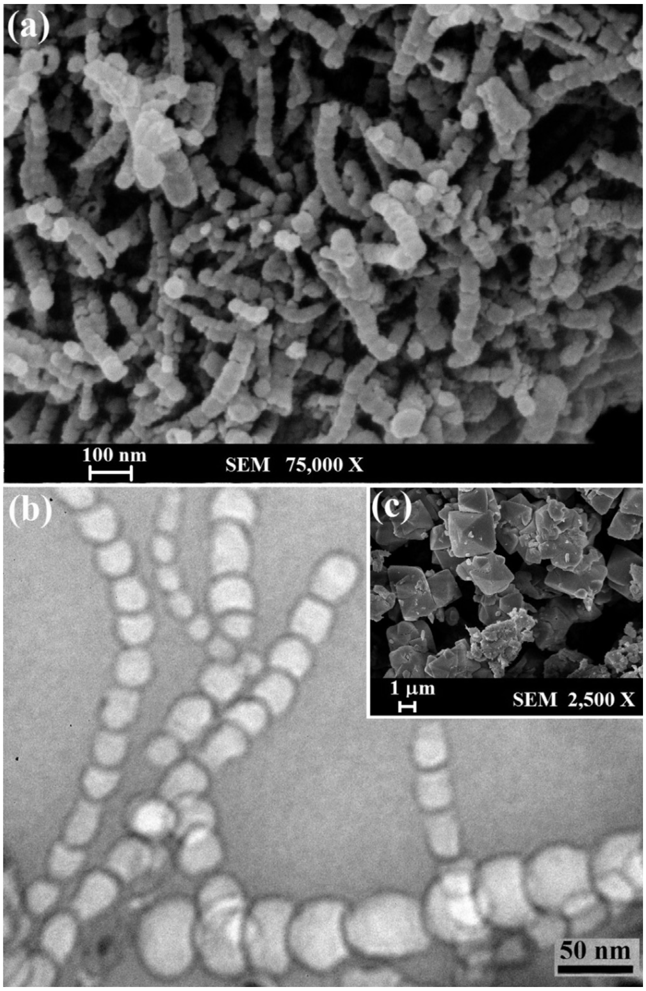

Fig. 1. (a) SEM and (b) TEM images of CNCs. (c) SEM image of pristine ZnHCF powder.

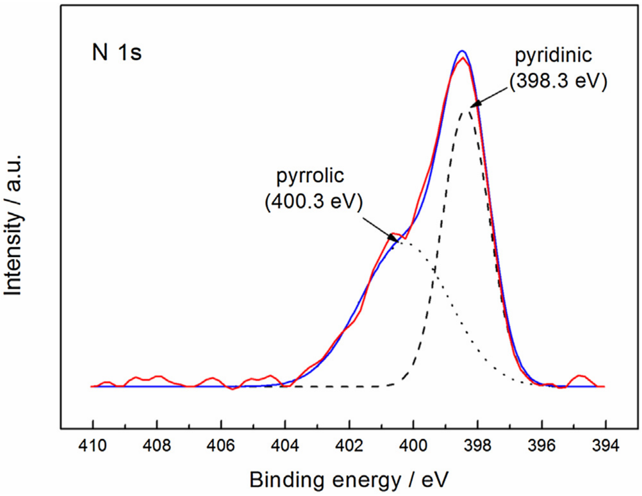

Fig. 2. Deconvoluted N 1 s XPS spectrum of CNC powder.