Carbon 128 (2018) 277–286

Contents lists available at ScienceDirect

Carbon

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

A flexible core-shell carbon layer MnO nanofiber thin film via host-guest interaction: Construction, characterization, and electrochemical performances

Fan Wang [a], Chao Li [b], Jing Zhong [c], Zhenyu Yang [a, b, *]

[a] School of Chemistry, Nanchang University, Nanchang, Jiangxi, 330031, PR China
[b] School of Chemical Engineering and Energy Technology, Dongguan University of Technology, Dongguan, Guangdong, 523808, PR China
[c] School of Civil Engineering, Harbin Institute of Technology, Heilongjiang 150090, PR China

A R T I C L E I N F O

Article history:
Received 22 October 2017
Received in revised form
23 November 2017
Accepted 25 November 2017
Available online 25 November 2017

Keywords:
Flexible thin film
High-voltage electrospining
Dual-carbon layers
Nanofiber
Lithium ion battery

A B S T R A C T

Supermolecular complexation with cyclodextrins by non-covalent host-guest interaction is used for various applications. In this work, we fabricated the freestanding and flexible core-shell MnO/carbon nanofiber (CNF) composite thin films by host-guest interaction and high-voltage electrospining technique. The as-prepared composite thin film with dual carbon layer nanofibers showed smaller MnO particle size, lower electron-transfer resistance, and faster lithium ion migration, which were attributed to intermolecular non-covalent assembling behavior among polyacrylonitrile (PAN), β-cyclodextrin (β-CD) and Mn ion. As expected, the composite film as anode in Li-ion battery showed impressive performance: a high reversible capacity (~1025 mAh g^{-1} at ~0.1 A g^{-1}), excellent rate capability (~376 mAh g^{-1} at ~5 A g^{-1}), and superior cyclability (~844 mAh g^{-1} at the current density of ~1 A g^{-1} after 800 cycles). Such outstanding electrochemical performance endows the MCNFs composites with great potential as anode material for LIBs.

1. Introduction

The development of flexible lithium-ion batteries (LIBs) is very essential for portable electronic devices, including smart communication, wearable devices and so forth. However, it is still a great challenge for fabrication of flexible electrodes with long cycle life and high specific capacity in the commercial applications [1]. Since the pioneering investigation by Poizot et al. the transition metal oxides have caused great attention on M_aO_b (M = Fe, Mn, Co, Ni, Ti, Cu, etc.) and MaX_b (-X = O, N, S, etc.) as anode materials for lithium storage [1–13]. Among these candidates, manganese monoxide (MnO) have received extensive research interest due to their high theoretical capacities (e.g., ~756 mAh g^{-1} for MnO), relatively low electrochemical motivation force (emf) (~1.032 V vs. Li/Li^+), small voltage hysteresis, low cost, environmental friendliness and natural abundance [14–19]. However, like other TMOs, its low electronic conductivity and large volume change during charge-discharge process have limited its commercial applications. Especially, the biggest issue of MnO materials towards LIBs is that they can react with lithium to form metal Mn (dispersed in the Li_2O matrix), resulting in severe agglomeration and repeated volume change during cycling. This could also give rise to drastic pulverization of the entire MnO electrodes and leads to shedding and dissolution of Mn into the electrolyte, leading rapid capacity fading upon cycling [20].

To overcome these issues, carbon coating [21–25], dispersing in carbon matrix [26–31], composting with carbon nanotube [32–35] and graphene [36–38] were often used, because conductive carbon can provide rapid electron transfer channels for MnO, and alleviate the strain caused by the considerable volumetric changes during electrochemical cycling. However, these improvements have also hindered their commercial applications because of limited elasticity and structural stability of composite materials. Recently, the electrospinning technique exerts considerable influence on the Li-ion storage properties, the MnO/C nanowire have been developed for anode materials for LiBs owing to their superior conductivity, large surface area and structural flexibility [39–43]. For example, Zhao et al. [42] have designed and synthesized a porous MnO/C composite material through incorporating MnO_2 nanowires into

---

* Corresponding author. School of Chemistry, Nanchang University, Nanchang, Jiangxi, 330031, PR China. Tel.: +86 0791 83969514.
E-mail address: zyyang@ncu.edu.cn (Z. Yang).

https://doi.org/10.1016/j.carbon.2017.11.075

polymer solution by a facile electrospinning technique. The hybrids consist of isolated MnO nanoparticles beading in the porous carbon and demonstrate superior performance when used as a binder-free anode for lithium-ion batteries. Zhang et al. [43] have prepared a core-shell nanostructure MnO/C composite nanowire via a thermal decomposition followed by a facile in situ interfacial polymerization and carbonization, and the cycling performance is highly improved. Although the above methods have positive influence on prolonging the cycling life of MnO materials, the level of improvement is still very limited. Therefore, it is still necessary to develop a rational and effective strategy to fabricate MnO/C nanocomposite anodes for flexible high-performance LIBs.

Nowadays, supermolecular complexation with cyclodextrins by non-covalent host-guest interaction is used for various applications including modulation of dyes optical properties and sensors for metal ion or pollutants due to noncovalent interactions, e.g. van der Waals, hydrogen bonding, p–p stacking, hydrophobic interactions and host–guest interaction [44]. It is well known that β-cyclodextrin (β-CD) is a kind of natural molecules, which is composed of 7 D-(+)-glucose units linked by 1,4-a-linkages and exhibiting a torus-shaped ring structure. Because of its special architectural conformation, the β-CD can selectively incorporate molecules or metal ion as the guest into its cavity to generate host-guest inclusion complexes.

Herein, we fabricated a freestanding and flexible core-shell MnO composite nanofiber thin films by host-guest interaction and high-voltage electrospining technique. Due to intermolecular non-covalent assembling behavior in the precursor solution among polyacrylonitrile (PAN), β-cyclodextrin (β-CD) and Mn ion, the as-prepared composite materials showed the core-shell carbon layer structure, the smaller MnO particle size, lower electron-transfer resistance, and faster lithium ion migration, which improve lithium ion transfer in the thin film anode. In addition, this strategy can make sure that most of the crystalline grains and grain boundaries of MnO are homogeneously embedded in the core-shell carbon layer matrix, in which the inner carbon layer has been enhanced the electrical conductivity and improve the robustness and stability of 3D frame film; and the outer carbon layer has been enhanced the flexibility and specific surface area due to torus-shaped ring structure of β-CD. Thus, such thin film not only provides abundant carbon double layer to allow Li^+ intercalation/deintercalation, stabilizes the electrode surface, and hinders shedding and dissolution of Mn into the electrolyte, but also creates an interconnected 3D film network for continuous electron transport. The thin film anode exhibits excellent electrochemical performances: a high reversible capacity (~1025 mAh g^{-1} at ~0.1 A g^{-1}), excellent rate capability (~376 mAh g^{-1} at ~5 A g^{-1}), and superior cyclability (~844 mAh g^{-1} at the current density of ~1 A g^{-1} after 800 cycles), demonstrating great potentials of Mn-based materials for LIBs.

2. Experimental

2.1. Materials

Polyacrylonitrile (PAN, Mw = 150,000) and Manganese (II) acetate tetra hydrate ($MnAc_2.4H_2O$, 99.9%) were purchased from J&K Chemical. N, *N*-dimethyl- formamide (DMF, AR) and β-cyclodextrin (β-CD) were purchased from Sino pharm Chemical Reagent Co, Ltd. All these reagents were used without further purification.

2.2. Preparation of β-CD/PAN@MnO

Precursor solutions were prepared by dissolving a certain quantity of PAN, β-cyclodextrin (β-CD) and $MnAc_2.4H_2O$ with ~10 ml dimethylformamide (DMF) under magnetic stirring at ~60°Cfor ~6 h. Then, precursor solution was charged into a plastic syringe having a stainless-steel nozzle. An applied voltage and the distance between the electrospinning jet and the collector is ~16 kV and ~15 cm, respectively, and the flow rate of the syringe pump is ~1 mL h^{-1}. Then the β-CD/PAN @$MnAc_2.4H_2O$ nanofiber membranes were obtained.

The β-CD/PAN@$MnAc_2.4H_2O$ were firstly heated at ~260 °C in air for ~2 h to promote stabilization. Then, the MCNFs was obtained by a simple carbonization treatment process. To optimize the formula ratio of β-CD/PAN, the four samples were added at β-CD/PAN weight ratios of ~2/8, ~3/7, ~4/6 and ~5/5, and the total mass of the two carbon sources is ~1 g. Then these four different samples were carbonized at ~800 °C for 3 h in argon atmosphere with a heating rate of ~5C°min^{-1}, which were denoted as MCNFs-1, MCNFs-2, MCNFs-3, MCNFs-4, respectively. In order to investigate the influence of temperature, the precursor solution of MCNFs-2 sample was electrospun and carbonized at different temperature (~700, ~800, ~900 °C). The obtained sample were named as MCNFs-5, MCNFs-2, and MCNFs-6, respectively. For comparison in control experiment, the MnO/CNFs samples and the pure MnO sample was obtained by sintering $MnAc_2.4H_2O$/PAN and under the sintering temperature of ~800 °C.

2.3. Characterization

The crystal structures of the obtained samples were determined by X-ray diffraction (XRD, Bruker D8 Focus X-ray diffractometer) using Cu Ka radiation over the range of 2θ = ~5-80°. The morphology and structure of samples were examined using a Scanning electron microscopy (SEM, FEI Quanta200F) and transmission electron microscopy (TEM) and high-resolution TEM (HRTEM, FEI Tecnai G2 F20, 200 kV). X-ray photoelectron spectra (XPS) were recorded using an X-ray photoelectron spectrometer (K-Alpha 1063) with a monochromatic Al Ka X-ray source. Raman spectroscopy were performed with a laser micro-Raman spectrometer (Renishaw inVia, Renishaw, 532 nm excitation wavelength). The Brunauer-Emmett-Teller (BET) surface area and the pore size of the samples were determined by N_2 adsorption/desorption isotherms using Bei Shi De 3H-2000PS1 apparatus.

2.4. Cell fabrication and electrochemical measurements

Electrochemical experiments of the half-cell was carried out on CR 2025 coin cells, which were assembled in an Ar-filled MBraun glove box. Li metal was used as counter and reference electrode, and celgard 2400 as the separator. The as-obtained flexible nanofiber films were tailored into freestanding discs with a diameter of 10 mm and a mass loading of ~0.4 mg/cm^2, which were directly used as the working electrode without any binder and conductive additive. The electrolyte was 1 M LiPF6 dissolved in a mixture of ethylene carbonate/dimethyl carbonate/diethyl carbonate (EC/DMC/DEC = ~1:1:1, v/v). Cyclic voltammogram (CV) experiment was performed in the potential window of ~0.02–3.0 V at a scanning rate of ~0.1 mVs^{-1}. The coin cells were Galvano statically cycled between ~3.0 and ~0.02 V (vs. Li/Li+) using a NEWARE battery measurement system at room temperature. Electrochemical impedance spectroscopy (EIS) tests were measured in the frequency range from 100 kHz to 0.1 Hz on a electrochemical workstation (PARSTAT 2273, Princeton, USA).