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1D porous MnO@N-doped carbon nanotubes with improved Li-storage properties as advanced anode material for lithium-ion batteries

Dao-Sheng Liu [1], Dai-Huo Liu [1], Bao-Hua Hou, Ying-Ying Wang, Jin-Zhi Guo, Qiu-Li Ning, Xing-Long Wu*

National & Local United Engineering Laboratory for Power Batteries, Faculty of Chemistry, Northeast Normal University, Changchun, Jilin 130024, PR China

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ABSTRACT

As a promising anode candidate for lithium ion batteries (LIBs), MnO has attracted wide attentions owing to its theoretically high Li-storage capacity, lower working voltage and polarization than other oxides, low cost, environmental friendliness, and abundant resources. Herein, we develop a facile and low-cost strategy to fabricate a unique porous MnO@N-doped carbon (MnO@N-C) nanotube and demonstrate its outstanding Li-storage properties as anode material for LIBs. Benefiting from its unique 1D porous features, the prepared MnO@N-C electrodes exhibit high reversible specific capacity (971.8 mAh g^{-1} at 0.1 A g^{-1}), superb high-rate capability (359.5 mAh g^{-1} at 30 A g^{-1}) and remarkable cycling stability (441.5 mA h g^{-1} after 3500 cycles at 10 A g^{-1}). Such superior electrochemical performance should be due to the high conductivity and protection effects of N-doped carbon layer, and adequate internal voids in the MnO@N-C to effectively accommodate the volume changes of MnO during cycling. In addition, it is also disclosed that the high capacity contribution arises from the pseudocapacitive charge storage.

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1. Introduction

In recent years, environmental deterioration and energy shortage have become two foci of world attentions. An effective method of resolving the issues of environment pollution and energy crisis is to develop and use the clean power and renewable energy resources [1–5]. During the processes of utilizing the usually unstable and discontinuous energies, energy storage is becoming significant increasingly. With the development of energy storage technologies, Lithium ion batteries (LIBs) are widely employed in various energy storage fields [2,6,7]. To meet the ever-growing requirements of energy storage performance, LIBs need constant innovation and development, including high safety, longer cycle life, smaller volume, lighter weight, higher energy and power densities, as well as lower price [1,2,7,8]. For the traditional anode of graphite, it cannot meet the needs of next-generation high-energy LIBs because of the low theoretical Li-storage capacity (372 mAh g^{-1}), poor rate and cycling performance and high sensitivity to electrolyte [9–11].

As a highly promising anode for LIBs, the silicon-based materials has attracted great interests and widely studied in the past few years [12–14], because of its low pollution, abundant resources, low lithiation potential and high theoretical Li-storage capacity [15]. Furthermore, transition metal oxides (abbreviated as TMOs, e.g., MnO, NiO, Co_3O_4, Fe_3O_4, and MoO_2, etc) also have been extensively investigated as promising anode candidates for LIBs owing to their high theoretical capacity and low cost [16–23]. Among various TMOs, MnO-based anode materials have a lot of advantages such as low conversion potential with high theoretical capacity of 756 mAh g^{-1}, environmental friendliness, low cost, and abundant resources [10,24,25]. Nevertheless, like other TMOs, the drastic volume changes during the successive de-/lithiation processes and low electrical conductivity easily lead to the pulverization of pure MnO based electrodes, resulting in poor rate capability and cycling stability [16,26,27]. Up to now, huge efforts have been made to settle these issues [16,28,29]. Currently, the commonly employed approaches include: (1) preparing MnO nanoparticles to shorten the diffusion path of Li-ions and electrons [30–32]; (2) designing the MnO/carbonaceous matrix nanocomposites, which can greatly enhance the conductivity of MnO-based electrodes and

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* Corresponding author.
E-mail address: xinglong@nenu.edu.cn (X.-L. Wu).
[1] Equal contribution.

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effectively buffer the strain caused by the volume change during Li-insertion/extraction [9,33–35]; (3) fabricating porous or hollow structures, which can accommodate large volume changes during cycling to hence improve the cycle life [10,11]. It is proposed that, the electrochemical performance of MnO-based anodes can be more effectively enhanced by combining the aforementioned methods.

Herein, we develop a simple and effective approach to construct a novel advanced anode material composed of one-dimensional (1D) nanotubes, in which porous MnO (p-MnO) nanoparticles are well encapsulated into N-doped carbon (N-C) nanotubes (NTs), forming the composite abbreviated as p-MnO@N-C NTs. Contrast studies demonstrates that the prepared p-MnO@N-C NTs exhibit much better electrochemical performance compared with the control of peapod-like MnO@N-C NTs (abbreviated as pl-MnO@N-C NTs) prepared at the similar procedures for p-MnO@N-C NTs. As a result, the p-MnO@N-C electrodes deliver a high Li-storage capacity of 971.8 mAh g^{-1} at 0.1 A g^{-1}, outstanding dis-/charge rate capability (359.5 mAh g^{-1} at 30 A g^{-1}), and ultralong cycle life (a remaining capacity of 441.5 mA h g^{-1} with the capacity decay of 89.8% after 3500 cycles at 10 A g^{-1}), demonstrating that the p-MnO@N-C NTs are a highly potential anode candidate for LIBs. It is also disclosed that such superior electrochemical performances should be owing to the high pseudocapacitive contribution in charge storage, as well as high conductivity and protection effects of N-C layer, and adequate internal voids in p-MnO@N-C NTs to accommodate the volume changes of MnO during cycling.

2. Experimental section

2.1. Preparation of MnO@N-C composites

The precursor of α-MnO_2 NTs were prepared according to the previous report by Xing et al. [36] with a minor modification. In detail, 0.658 g of $KMnO_4$ was dissolved in 75 mL deionized (DI) water, and then magnetically stirred at room temperature for 40 min, followed by the addition of 2.5 mL of HCl (36 wt%). After another vigorous stirring of 20 min, the resulting solution was transferred into a Teflon-lined stainless steel autoclave (100 mL), which was sealed and maintained at 140 °C for 10 h, and then allowed to cool to room temperature. The generating α-MnO_2 NTs could be collected by centrifugation, washed with DI water and ethanol several times, and finally dried in air at 80 °C overnight.

In order to prepare the p-MnO@N-C NTs, 240 mg of α-MnO_2 NTs were dispersed into Tris-buffer solution (300 mL, 10 mM) followed by a sonication of 10 min. Subsequently, 120 mg of dopamine was added with vigorous magnetic stirring of 5 h. The resulting sediment of MnO_2@polydopamine (MnO_2@PDA) NTs could be easily collected after centrifugation, washing of several times by DI water and ethanol, and drying at 70 °C for 10 h. Finally, the obtained MnO_2@PDA NTs were annealing at 500 °C for 2 h in the Ar/H_2 (Ar:H_2 = 95%:5% in volume) mixing atmosphere to generate the p-MnO@N-C NTs. In contrast, pl-MnO@N-C NTs was prepared by calcining MnO_2@PDA NTs at 800 °C for 2 h under the Ar/H_2 (Ar:H_2 = 95%:5%, volume) mixing atmosphere.

2.2. Material characterization

The electronic states and surface element composition of products were analyzed through X-ray photoelectron spectroscopy (XPS, ESCALABMKLL, VG Instruments). Power X-ray diffraction (XRD) tests were carried out on a Rigaku SmartLab X-ray diffractometer (Cu-Kα radiation, λ = 1.5418 Å, current: 30 mA, voltage: 40 kV). Morphology and microstructure features of the prepared materials were observed by scanning electron microscopy (SEM, HITACHI SU8000, current: 5 mA, accelerated voltage: 3 kV) and high-resolution transmission electron microscopy (TEM, JEOL-2100 F). N_2 adsorption/desorption tests were performed using a Brunauer-Emmett-Teller analyzer (BET, ASAP 2020 M). Specific surface area and pore size distribution was calculated from the isothermal N_2 adsorption/desorption curves by the MultiPoint BET and Barrett-Joyner-Halenda (BJH) method, respectively. The carbon contents were obtained by thermogravimetric analysis (TGA) from room temperature to 600 °C in an air flow at a heating rate 10 °C min^{-1}.

2.3. Electrochemical measurements

The working electrodes were prepared by mixing active MnO@N-C NTs (70 wt %), carbon black (20 wt %), and carboxymethyl cellulose (CMC, 10 wt %) binder in distilled water to make a slurry, which was coated onto the washed Cu foil and dried overnight at 60 °C in vacuum oven. The mass loading of the active material was controlled at 1–1.5 mg cm^{-2}. Half cells of CR2032 were assembled in an argon-filled glovebox. Electrolyte is 1 mol L^{-1} $LiPF_6$ in a mixed solvent of ethylene carbonate and diethyl carbonate (EC/DEC, 1:1 in volume). Fresh metallic lithium foils were used as counter electrodes. Galvanostatic charge/discharge measurements were performed on LAND battery testing system (LAND CT2001A) within the voltage window of 0.005–3 V (*vs.* Li/Li^+) at room temperature. VersaSTAT 3 electrochemical workstation (Princeton Applied Research) was employed to test the cyclic voltammetry (CV) curves in the potential window of 0.005–3 V (*vs.* Li/Li^+) at varied scan rates. Electrochemical impedance spectroscopy (EIS) patterns were collected on the P4000 electrochemical workstation (Princeton Applied Research) with amplitude of 5 mV and frequency between 1 MHz and 100 mHz. Note that, all the electrochemical tests were performed at room temperature.

3. Results and discussion

The MnO_2 NTs precursor was prepared by hydrothermal method (Fig. S1, Supporting Information). The synthesis process of the MnO@C-N NTs hybrid involves two steps as illustrated in Fig. 1. First, the MnO_2@PDA (Fig. S1a) was obtained by coating MnO_2 NTs with PDA. Subsequently, the obtained MnO_2@PDA was carbonized

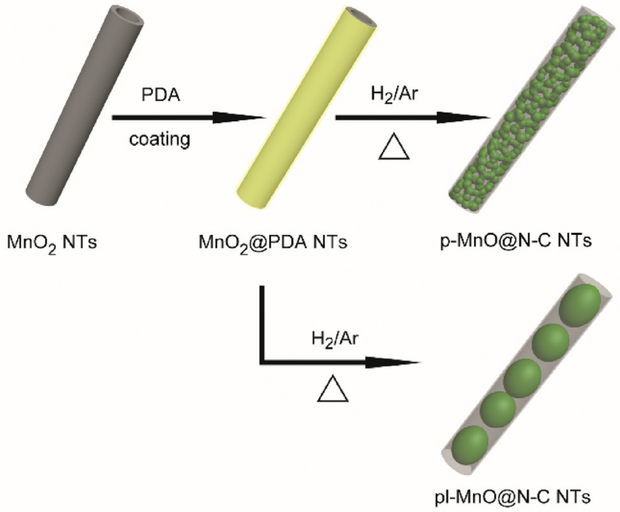

Fig. 1. Schematic illustration of the formation of p-MnO@N-C NTs and pl-MnO@N-C NTs.

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