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Enhanced electrochemical performance of an electrospun carbon/MoO_2 composite nanofiber membrane as self-standing anodes for lithium-ion batteries

Jun Xiang[a,*], Zhipeng Wu[a], Xueke Zhang[a], Shanshan Yao[b]

[a] School of Science, Jiangsu University of Science and Technology, Zhenjiang 212003, PR China
[b] Institute of Advanced Materials, Jiangsu University, Zhenjiang 212013, PR China

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ABSTRACT

A flexible carbon nanofiber membrane (NFM) containing uniformly dispersed MoO_2 nanoparticles is facilely fabricated via electrospinning and subsequent controlled reduction-carbonization. This NFM is used directly as a binder-free anode in lithium-ion batteries (LIBs). The self-standing carbon/MoO_2 (C/MoO_2) NFM electrode has a good capacity retention, a satisfactory rate capability and a high reversible capacity of 811 mAh g^{-1} after 100 cycles at a current density of 100 mA g^{-1}, which is superior to most other MoO_2-based anodes. The superior electrochemical properties of the resultant C/MoO_2 NFM are attributed to the cooperative effects from the excellent conductivity of the carbon nanofiber matrix, the high electrochemical performance of MoO_2, the unique one-dimensional nanofiber structure and the three-dimensional porous network structure. The present C/MoO_2 NFM may be an attractive candidate as an anode material for LIBs.

1. Introduction

Rechargeable lithium-ion batteries (LIBs) have been widely used for small-sized portable electronics and electric vehicles due to their high energy capacity and long lifespan [1–9]. Currently, flexible/bendable electronics are a promising and emerging technology for the next generation of electronic devices [10–16]. However, most materials need to be mixed with conductive additives and polymer binders to form film electrodes, which are not flexible enough to adapt to tough environmental situations. Electrospinning has been found to be an effective and facile method for the synthesis of a flexible and freestanding nanofiber membrane (NFM) with a unique network structure and excellent structural stability [17]. Among various anode materials, metal oxides have been identified as promising alternatives to carbon materials because of their higher theoretical capacities. In recent years, some flexible, freestanding, and binder-free carbon nanofiber/metal oxide (e.g., V_2O_5 [18], Fe_2O_3 [19], Fe_3O_4 [20], TiO_2 [21], and SnO_x-ZnO [22]) composites have been successfully prepared by electrospinning and their electrochemical properties as LIB anodes have been investigated. For instance, Wan et al. [20] fabricated Fe_3O_4 nanoparticles anchored on three-dimensional (3D) carbon nanofibers and directly used them as flexible anodes in LIBs without metal collectors, conducting additives or binders. These anodes demonstrated greatly improved electrochemical performance with a stable capacity of 755 mAh g^{-1} for up to 80 cycles in comparison to the bare Fe_3O_4 nanoparticles and most of the carbon/Fe_3O_4 hybrids.

Molybdenum dioxide (MoO_2), as an important semiconductor, has great potential applications in many fields such as chemical sensors, field emission devices, and solar cells due to its efficient charge transport properties [23]. Additionally, MoO_2 has attracted considerable attention as an electrode material for LIBs because of its relatively large theoretical capacity (838 mAh g^{-1}) and high density (6.5 g cm^{-3}) [24]. Various types of carbon/MoO_2 nanohybrids have been developed as anode materials in LIBs [23–31]. Tang et al. [32] synthesized a hybrid consisting of reduced graphene oxide-wrapped MoO_2 porous nanobelts, and reported that the composite exhibited high reversible capacity (974 mAh g^{-1} charging capacity at 60 mA g^{-1}), good cycling stability, and ultrafast rate capability. Although some carbon/metal oxide composite NFMs used in LIB anodes have been reported to date, flexible, freestanding and binder-free C/MoO_2 NFMs have not been investigated previously. In the present work, a flexible C/MoO_2 NFM was synthesized using an electrospinning technique combined with a controlled air-stabilization and reduction-carbonization process, and directly tailored into a coin as a self-standing and bind-free anode for LIBs. The developed NFM exhibits remarkably high capacity retention as well as high reversible and rate capacities in comparison to many previously

* Corresponding author.
E-mail address: junx93@sina.com (J. Xiang).

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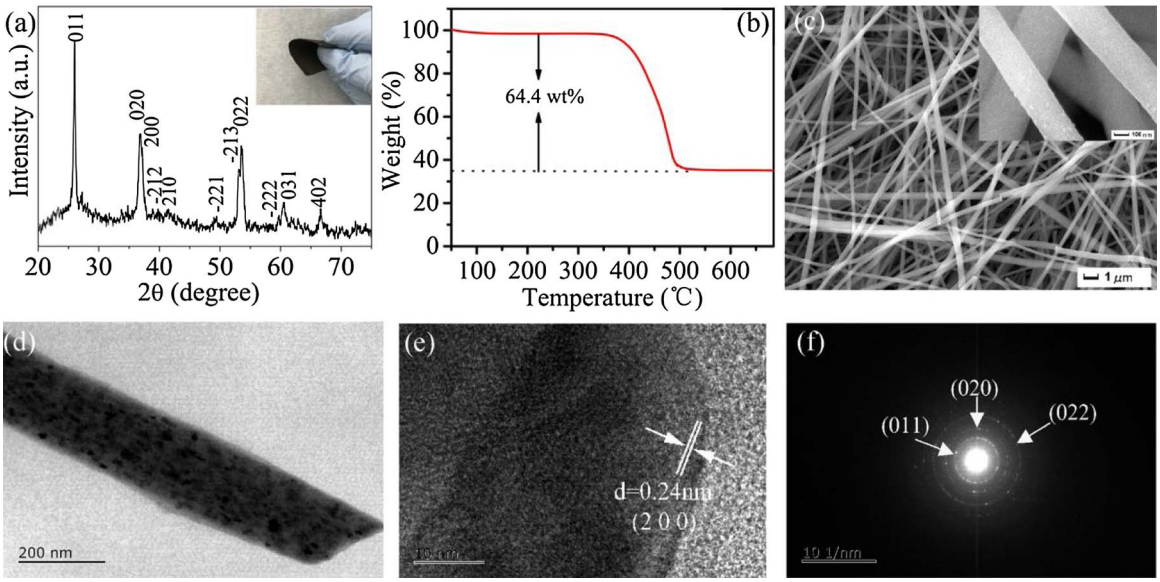

Fig. 1. The C/MoO_2 NFM: (a) XRD pattern, (b) TG curve, (c) SEM image, (d) TEM image, (e) HRTEM image, and (f) SAED pattern. The inset in (a) is an optical image of C/MoO_2 NFM.

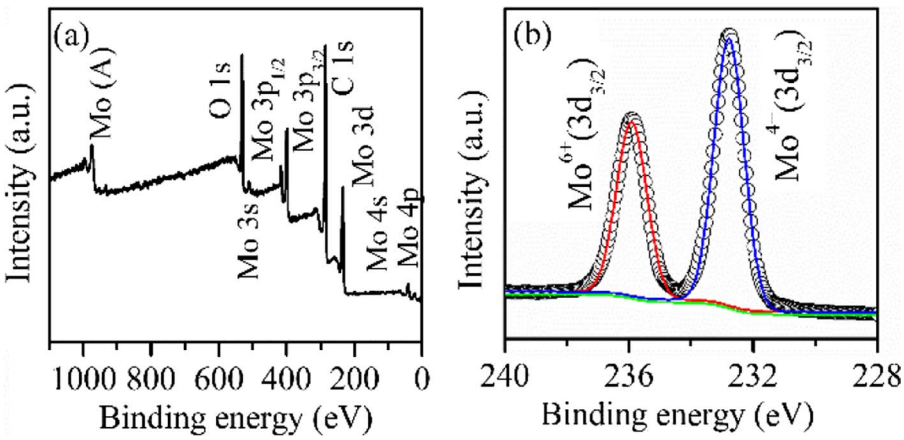

Fig. 2. XPS results of the C/MoO_2 NFM: (a) survey spectrum and (b) high-resolution spectrum of Mo 3d.

reported MoO_2-based materials as LIB anodes, highlighting its good prospect for applications as an anode material in LIBs.

2. Experimental

2.1. Preparation of C/MoO_2 NFM

First, 4.4 g of polyacrylonitrile (PAN, Mw = 150 KDa, Sigma-Aldrich) was dissolved in 33.6 g of *N*,*N*-dimethylformamide (DMF, 99.5%, Sinopharm Chemical Reagent Co., Ltd. China) by stirring at 60 °C for 4 h. Then, 2 g of molybdenum pentachloride ($MoCl_5$, 99.6%, Shanghai Aladdin Bio-Chem Technology Co., Ltd.) was added into the above PAN/DMF solution and continuously stirred for approximately 12 h to form a homogeneous spinning solution. The obtained solution was electrospun at room temperature on a TL-01 electrospinning apparatus (Shenzhen Tongli Micro/Nano Technology Ltd.) with an applied voltage of 20 kV, a feeding rate of 0.3 mL h^{-1} and a receiving distance of 18 cm between the needle and the collector. After the electrospinning process was completed, the collected mats were annealed in air at 220 °C for 2 h at a heating rate of 1 °C min^{-1}, and then the stabilized mats were further carbonized in a tube furnace at 600 °C for 5 h under an Ar/H_2 (5:1 by volume) atmosphere at a rate of 2 °C min^{-1} to yield the flexible and freestanding C/MoO_2 NFM.

2.2. Characterization

The phase structure of the product was identified by X-ray diffraction (XRD, Rigaku D/max-2500PC, Cu Kα radiation, λ = 0.154056 nm). The surface morphology and microstructure of the fabricated NFM electrode were analyzed using field emission scanning electron microscope (FE-SEM, JEOL JSM-7001F) and transmission electron microscope (TEM, JEOL JEM-2001). Thermogravimetric analysis (TGA) was performed using a Shimadzu DTG-60H thermal analyzer under atmospheric conditions to evaluate the thermal stability of the NFM and the MoO_2 content. X-ray photoelectron spectroscopy (XPS) spectra were measured on a Thermo Fisher Scientific ESCALAB 250Xi XPS System with a monochromatic aluminum anode X-ray source.

2.3. Electrochemical measurements

The electrochemical performance was measured using a CR2025 coin-type half-cell, in which the obtained flexible C/MoO_2 NFM was punched into small discs (12 mm in diameter and approximately 3 mg in weight) and directly applied as the anodes without mechanical milling or a slurry-coating process. No current collectors or binders were used in these electrodes. A metallic Li sheet was utilized as the counter electrode. A Celgard 2400 microporous polypropylene membrane was used as the separator. The electrolyte in the cell was 1 M $LiPF_6$ in a solvent mixture of ethylene carbonate (EC), ethyl methyl