



Electrochemical performance of new α -MoO₃ nanobelt cathode materials for rechargeable Li-ion batteries



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ABSTRACT

The orthorhombic molybdenum trioxide (α -MoO₃) nanobelts and polyvinyl pyrrolidone (PVP) surfactant MoO₃ nanobelts with high quality were prepared through hydrothermal synthesis. The morphology and microstructure of the samples were investigated by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, field-emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM). The nanobelts with rectangular cross-section have an orthorhombic phase structure, preferentially grow in [001] direction. The results showed that the H atoms in polyvinyl pyrrolidone are H-bonded with the O atoms in the Mo=O bonds of MoO₃ nanobelts. When MoO₃ is modified by the intercalation of PVP, it is effectively shielded against electrostatic interaction between the MoO₃ interlayer and Li⁺ ions. The specific capacity of pure MoO₃ nanobelts battery and (PVP)_{0.2}MoO₃ nanobelts exhibit as 195 mAh g⁻¹ and 237 mAh g⁻¹, respectively after 14 cycles, suggests that the stability of surfactant material is worthy.

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1. Introduction

Lithium-ion battery currently represents the state of the art technology in small rechargeable batteries because of its many merits (e.g., higher voltage, higher energy density and longer cycle life) comparing with traditional rechargeable batteries such as lead acid and Ni–Cd batteries. Typically, a lithium-ion battery consists of a negative electrode (anode, e.g., graphite), a positive electrode (cathode, e.g., LiCoO₂), and a lithium-ion conducting electrolyte. When the cell is charged, Li-ions are extracted from the cathode and inserted into the anode [1–3]. On discharge, the Li-ions are released by anode and taken up again by the cathode. The lithium-ion batteries are commercially successful, especially in small-scale devices. These cells are still objects of intense research to enhance their properties and characteristics. It is largely promoted by an increase of applications such as next-generation wireless communication devices (e.g., 3G mobile phones, MP4).

Molybdenum trioxide (MoO₃) is one of the most important transitional metal oxides (TMOs) due to its rich chemistry associated with multiple valence states, high thermal and chemical

stability. Generally, it exists in three kinds of polymorphs, namely, orthorhombic α -MoO₃, monoclinic β -MoO₃ and hexagonal MoO₃ [4]. Previously, α -MoO₃ has long been used as the lithium storage host materials in view of the thermodynamically stable, intriguing layered structure. They are extensively employed as cathode materials in LIBs to deliver the capacities of 200–300 mAh g⁻¹ between 1.5 and 3.5 V on the basis of an intercalation mechanism [5–13]. Whereas anode materials α -MoO₃ have attracted much less attention because of poor electrochemical properties caused by intrinsic sluggish kinetics for redox conversion reaction and large structure variation upon lithium insertion/extraction, despite that their theoretical capacity can be as high as 1117 mAh g⁻¹. Even for the electrodes composing of various nanostructures (e.g., the nanowires, micro-/nanorods, nanobelts and nanoparticles) [14–21], severe capacity loss still happens at low current rates (often 0.02–0.2 C) despite the observed high initial capacity of 800–1000 mAh g⁻¹. However, the production of truly durable α -MoO₃ electrodes with longer calendar life and improved high-rate performance still remains as a significant challenge at this moment. Hence, molybdenum oxide in the form of micro and nanostructures are promising candidates for electronic and optoelectronic microdevices. Many researchers have modified the MoO₃ with polyaniline (PANI), polymer blends (PVA + PVP) and polyethylene glycol (PEG) [8,22,23]. However, only a limited number of works has been focused on this aspect.

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In this work, we present the synthesis of α -MoO₃ nanobelts by a hydrothermal method. PVP deserves a special attention due to its good electrical properties, easy processability, moderate electrical conductivity and charge transport mechanism [24]. The intercalation of PVP is expected to enhance the mobility of Li⁺ ions in MoO₃ interlayers and improved the reversibility of insertion/extraction of Li⁺ ions. The present study also shows that PVP has great influence on the electrochemical performance of α -MoO₃ nanobelt based electrodes.

2. Experimental section

2.1. Synthesis of PVP surfactant α -MoO₃ nanobelts

Molybdenum powder and polyvinyl pyrrolidone (MW 13×10^5 g mol⁻¹) were purchased from Alfa Aesar Company and used as without further purification. The α -MoO₃ nanobelts were synthesized using simple hydrothermal method, 4 g of molybdenum powder was slowly added to 40 mL of H₂O₂ (30%) under water-cooling until the clear orange peroxomolybdic acid sol was obtained then PVP was added to MoO₃ sols in the proportion of (PVP)_xMoO₃ ($x = 0, 0.1, 0.2$ mol%) to form mixed sols. The feeding rate of Mo powder should be much slower because the reaction of Mo and H₂O₂ is a strong exothermic reaction with the product of MoO₂(OH)(OOH). Finally, the mixed sols were directly transferred into a Teflon-lined stainless steel autoclave and kept at 180 °C for 48 h. After hydrothermal reaction, the autoclave was left to cool and the precipitate was filtered then rinsed with deionized water three times. Then the samples were dried at 80 °C for 12 h.

2.2. Preparation of Li batteries

The electrochemical properties were investigated by CR 2025 coin-type cell with Li metal as anode electrode. The cells were assembled in an argon-filled glove box at room temperature, 1 M solution of LiPF₆ in ethylene carbonate/dimethyl carbonate as electrolyte and pellets were made from the obtained products, acetylene black and PTFE are in the ratio of 6:4:1 as positive electrode.

2.3. Characterization

The X-ray powder diffraction measurement was performed on a PANalytical, Netherlands equipped with Cu-K α radiation ($\lambda = 1.5418$ Å). Fourier-transform infrared absorption spectra of samples were recorded using a 60-SXB IR spectrometer with a resolution of 4 cm⁻¹ in the wavelength range 400–4000 cm⁻¹. Field-emission scanning electron microscopy (FESEM) images were obtained using a JSM-6700F scanning electron microscope at 20 kV. Transmission electron microscopy (TEM) images were taken in a JEOL JEM-2100 FEF microscope operated at 200 kV. The electrochemical performance was analyzed by an Autolab model PGSTAT 30 System with scan rate of 1 mV s⁻¹ at 1.5–4.0 V vs. Li/Li⁺ potential range. The discharge characteristics were analyzed by battery testing system (CT-3008W 5 V/5 mA) operated at constant current density 30 mA g⁻¹ with 1.5–4.0 V vs. Li/Li⁺ potential range.

3. Results and discussion

The X-ray diffraction patterns of pure α -MoO₃ nanobelts and 0.2 mol% PVP surfactant MoO₃ nanobelts are shown in Fig. 1. All the diffraction peaks are indexed to orthorhombic α -MoO₃, with cell parameters $a = 0.3966$ nm, $b = 1.3858$ nm and $c = 0.3693$ nm, which is consistent with the standard values of bulk MoO₃ (JCPDS card No. 76-1003), no impurity phase has been detected by XRD.

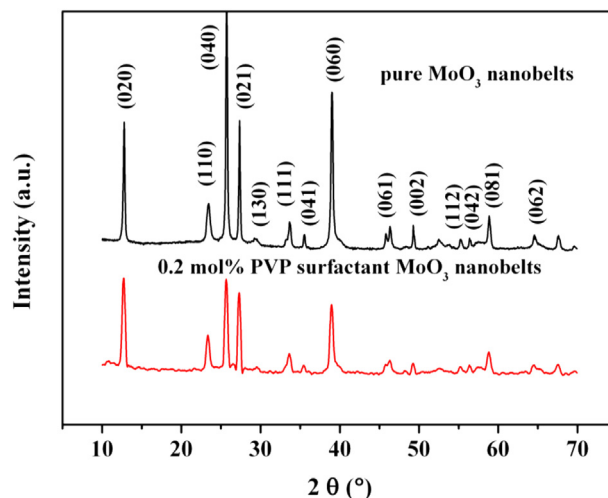


Fig. 1. X-ray diffraction patterns of MoO₃ nanobelts and PVP surfactant MoO₃ nanobelts.

The XRD patterns also showed the intercalation of PVP does not change the crystal structure of orthorhombic MoO₃. The sharp diffraction peaks indicate the prepared α -MoO₃ nanobelts have excellent crystallinity. The XRD patterns also show the diffraction peaks of (020), (040), (060) crystal faces are much stronger than the rest, which means the products are significant anisotropy and a preferential growth occurred in a direction at the crystal formation process. According to Bravais law, actual crystal faces are often parallel to the crystal planes with the largest atom density [25]. The interplanar spacing is larger, and the force of crystal faces attracting external particles in the vertical direction is weak. Consequently the crystal faces are grown slowly. Then the lattice planes expand in horizontal direction and grow in a preferential direction. In orthorhombic phase α -MoO₃ (010) crystal planes are the largest atom density planes. Hence the synthesized samples grew in the [001] direction and formed as α -MoO₃ nanobelts.

The FTIR spectra of MoO₃ nanobelts and PVP surfactant MoO₃ nanobelts are shown in Fig. 2. The MoO₃ nanobelts exhibit three main vibrational modes in the range of 400–1000 cm⁻¹. The terminal oxygen symmetry stretching mode (ν_s) of Mo=O and the bridge oxygen asymmetry and symmetry stretching modes (ν_{as} and ν_s) of Mo–O–Mo are at 973, 723 and 583 cm⁻¹ respectively [9,26].

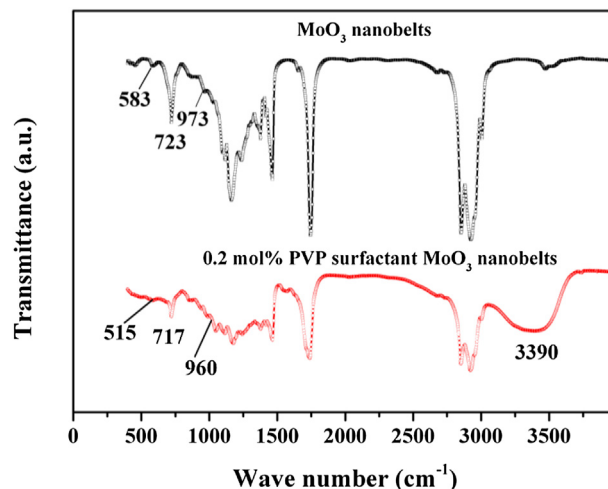


Fig. 2. FTIR spectra of MoO₃ nanobelts and PVP surfactant MoO₃ nanobelts.

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