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Controlled synthesis of MnOOH multilayer nanowires as anode materials for lithium-ion batteries

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ABSTRACT

MnOOH multilayer nanowires have been successfully synthesized by a hydrothermal method. It is found that the uniform multilayer structure of nanowires ran through the entire nanowire, which is formed via a layer by layer. The electrochemical properties of MnOOH multilayer nanowires as an anode material for Li-ion batteries (LIB) were investigated, and excellent capacity retention, superior cycling performance, and high rate capability were achieved. Specifically, the reversible capacity of MnOOH multilayer nanowires is 521 mAh/g after 500 cycles at 0.1 C, with excellent electrochemical stability. The multilayer nanowire electrodes exhibit short electron path lengths, high internal dislocation densities and large surface to volume ratio, resulting in increased specific capacity, cycling stability and rate performance in the energy storage devices, which serves as an indication of their potential application in LIBs.

1. Introduction

With growing interests in the development of low-cost, high-power electrochemical energy-storage devices, how to further improve the performance of Lithium-Ion Batteries (LIBs) has emerged as a key technological challenge. LIBs have received significant attention with potential applications in electrical/ hybrid electric vehicles, portable electronic products and other energy storage devices [1,2]. Higher specific capacities, lower charging time, higher rate performance, and longer operating lifetime are necessary in order to meet ever increasing demands on highly efficient electrical energy storage devices [3,4]. Research on active components has been demonstrated to open up prospects for achieving desired features in the nanoscale. As active components, transition metal oxides are among the most promising candidates, due to their unique optics, magnetism, catalysis, and electronics. However, these materials suffer from serious irreversibility (i.e., low coulombic efficiency), poor cycling performance as the anode of LIBs [5–8]. The reason is that the transition metal oxides are commonly subjected to drastic volume variations and degradation of their structure, during the Li^+ insertion/extraction process, followed by the formation of thick solid electrolyte interphase (SEI) films covering the electrode, which consume much of the Li^+ supplied by the cathode [9]. In addition, their low electrical conductivity and high intrinsic resistance also lead to additional performance degradation of metal oxide based electrodes, especially at high current densities. Various nanostructures and morphologies of manganese oxide/hydroxide have been synthesized such as rod, flower-shaped and wire [10,11], and used for a number of electrochemical applications including, supercapacitors, catalysis, especially for increasing the anode performance [12–14]. In particular, compared with particle electrodes, nanowires provide higher surface area, resulting in larger electrolyte-electrode contact area and reducing the charge-discharge time. Moreover, it could better accommodate the volume expansion and restrain the mechanical degradation, enabling better life cycling behaviors [15–17]. Up until now however, it is still a great challenge to synthesis MnOOH with controlled geometry and dimensions, a high reversible capacity, high rate capability, and high cycling stability.

In this paper, we report the facile hydrothermal synthesis of MnOOH multilayer nanowires as an anode material for Li-ion batteries with significantly enhanced capacitive and cycling performance. Rational synthesis of MnOOH with various shapes and morphology was accomplished, and the formation mechanism was investigated and described as a layer by layer process. Furthermore, the electrochemical properties of MnOOH multilayer nanowires as an anode material was studied using charge-discharge measurements, which showed that higher dislocation density between the layers could improve the release volume changes and facilitate repeating Li^+ insertion/extraction during the cycle process, thereby demonstrating the feasibility of practical application of MnOOH multilayer nanowires as an anode material for Li-ion batteries.

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Table 1
Brief summary of the experimental parameters.

Sample	S1	S2	S3	S4	S5	S6	S7
NaOH (g)	0.6	0.6	0.6	0.6	0.05	0.1	0.3
Time (h)	4	8	10	12	12	12	12

2. Experimental section

2.1. Synthesis of MnOOH multilayer nanowires

All reagents were of analytical grade and used as purchased without further purification. MnOOH multilayer nanowires were prepared through hydrothermal treatment in an aqueous solution. First, 0.0845 g of $MnSO_4 \cdot H_2O$ were dissolved in 20 mL of distilled water under magnetic stirring at room temperature. The solution was intensively stirred for 30 min. NaOH was then added to the solution at room temperature under vigorous stirring for another 30 min. The mixtures were stirred vigorously for another 30 min with 5 mL of H_2O_2 added to the solution dropwise and then sealed in a Teflon lined stainless-steel autoclave (30 mL capacity). The experimental details are listed in Table 1. The autoclave was sealed and maintained at 200 °C for 12 h and then cooled to room temperature. The products were washed several times with deionized water and ethanol, and dried in a vacuum oven at 60 °C for 4 h.

2.2. Materials characterization

The phases were identified using X-ray diffraction (XRD) with a Rigaku D/max 2500pc X-ray diffractometer with Cu Kα radiation (λ) 1.54156 (Å) at a scan rate of $0.04^{\circ}s^{-1}$. The morphologies were characterized by a JEOL JSM-6700F field-emission scanning electron microscopy (FESEM) operated at an acceleration voltage of 8.0 kV and equipped with an energy dispersive X-ray spectroscopy (EDS). Transmission electron microscopy (TEM), high-resolution TEM (HRTEM) images and selected area electron diffraction (SAED) patterns were obtained using a JEOL 2100F with an emission voltage of 200 kV.

2.3. Electrochemical properties of as-prepared MnOOH

The electrochemical experiments were performed via CR2025 cointype test cells assembled in a dry argon-filled glove box with both moisture and oxygen contents below 1 ppm. The test cell consisted of a working electrode and lithium foil which were separated by a Celgard 2400 membrane. The electrolyte solution was prepared by dissolving 1 M LiPF6 in ethyl carbonate and diethyl carbonate (1:1, wt/wt). The working electrodes were prepared by casting slurry containing 80% active material, 10% acetylene black and 10% polyvinylidene fluoride (PVDF) onto a copper foil. After vacuum drying at 80 °C for about 12 h, the electrode disks (d = 12 mm) were punched and weighed. Each electrode has approximately 1–3 mg of active material. Galvanostatic charge-discharge cycling tests were performed using an LAND CT2001A multi-channel battery testing system in the voltage range between 0.01 and 3.0 V at room temperature.

3. Results and discussion

3.1. Synthesis and characterization of MnOOH multilayer nanowires

MnOOH multilayer nanowires (S4) were successfully fabricated and the morphologies and structures in Fig. 1. Fig. 1(a) and (b) give the morphology of the S4 product by FESEM, which shows that nanowires with diameters about 50 nm (Fig. 1(b)) formed at 200 °C for 12 h. TEM was used to further elucidate the nanowires structure (Fig. 1(c), (d)). The corresponding high magnified TEM images indicate that the nanowires exhibit a uniform multilayer structure over the entire surface of each nanowire. In addition, HRTEM image (Fig. 1(e)) was recorded on the interface fringe of S4. From Fig. 1(e), the lattice interplanar spacing is measured to be 0.34 nm, corresponding to the $(\bar{1}11)$ plane. Meanwhile, it is shown the preferred orientation is along $[\bar{1}11]$ direction, which is also proved that preferred orientation of $[\bar{1}11]$ direction. Fig. 1e inset is the corresponding SAED pattern which shows the imperfect single crystal nature of the product. The character of SAED spots illustrate that the nanowires should be a multilayer nanowire structure, because of the superposition of the different multilayer nanowire crystals. Fig. 2 shows

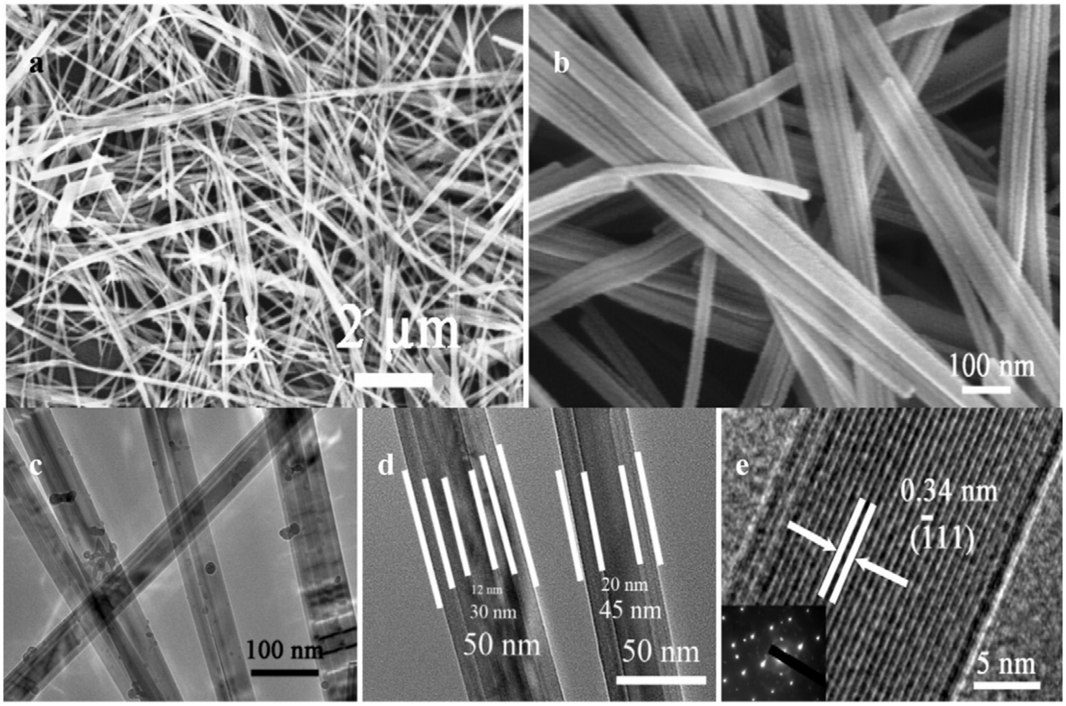

Fig. 1. (a) Low and (b) high magnification FESEM image of S4; (c), (d) TEM image (e) HRTEM of S4.