



Preparation and electrochemical performance of the interconnected LiMn₂O₄ fibers



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ABSTRACT

The interconnected LiMn₂O₄ fibers have been synthesized by using easily accessible cellulose filter paper as template. SEM and TEM images indicate the fibers are porous and constructed by nano grains. Without surface modification, the fibers exhibit superior high-rate capabilities and good cycling stability. The discharge capacities at 0.5 C and 20 C are 123 and 101 mAh g⁻¹ respectively, and about 78.9% of its initial capacity can be retained after 1000 cycles at 5 C. The superior rate performance and excellent cyclability can be attributed to the porous fiber structure, single crystalline and exposed {111} facet.

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1. Introduction

Lithium ion batteries as the energy storage devices have been used widely in portable electric devices. However, to power the newly emerging devices, such as: electric vehicles (EV) and hybrid electric vehicles (HEV), the batteries with higher power density and longer cycling life are needed [1–6]. The battery's performance depends critically on electrode materials. Among various cathode materials possibly to be used in high power batteries, spinel LiMn₂O₄ seems to be the most promising one due to its intrinsic advantages such as low cost, environmental benignity, better safety and high voltage [7–9]. But, its application is usually hindered by problems of large polarization and capacity decay especially under high current densities.

Large polarization is mainly caused by the sluggish Li⁺ diffusion (10⁻¹⁰ ~ 10⁻¹² cm² s⁻¹) in bulk electrode, which can be improved by decreasing the grain size into nano scale [10–12]. Recently, the nano LiMn₂O₄ with special morphologies have been studied, such as: nanorods [13,14], nano porous spheres [15–20], nano hollow spheres [21,22], nanosheets [23], nanowires [24–27] and nanotubes [28,29]. In which, the special architecture can buffer strain from volume variation during Li insertion/extraction; the void spaces benefit for the liquid electrolyte to wet more surface; the constructing nanoblocks can drastically shorten the transport distance of Li⁺ in solid phase, resulting in an improved rate performance. Wang et al. [17] prepared porous LiMn₂O₄ spheres by a facile topochemical route using porous Mn₂O₃ as template, which

revealed a stable high-rate capability, with a specific discharge capacity of 83 mAh g⁻¹ at 20 C. Deng et al. [20] synthesized Porous LiMn₂O₄ microspheres by using porous MnCO₃ microspheres as a self-supporting template, which exhibit a high rate capability and a long-term cyclability, with the specific discharge capacity of 98 mAh g⁻¹ and the corresponding capacity retention of 80% for up to 500 cycles at 20 C. LiMn₂O₄ nanowires can deliver 88 mAh g⁻¹ at the current density of 20 A g⁻¹ in a wide potential range [25].

Capacity decay usually originates from the dissolution of Mn³⁺ in acid electrolytes and structural degradation caused by Jahn-Teller effect [30], which is the main reason hindering LiMn₂O₄ to be used in high power batteries. The dissolution of Mn³⁺ and structural degradation can be effectively ameliorated by the treatments of surface coating [31–34] and cation doping [35–37]. But, these treatments are often required to sacrifice capacity and/or power capability. Extensive studies have revealed the dissolution of Mn³⁺ and structural stability are influenced by the lattice orientation of the surface [38,39], and the (111) plane has the lower Mn dissolution and more stable reconstructed surface structure in comparison with other planes such as (110) and (100) [38,40]. Sun et al. [23] obtained porous LiMn₂O₄ nanosheets with exposed {111} facet, which can deliver 69 mAh g⁻¹ at 25 C, with a capacity retention of 86% up to 500 cycles. Kim [40] synthesized truncated octahedron shape LiMn₂O₄ with the prefer facet of {111}, which not only presented an excellent rate performance with a capacity of 110 mAh g⁻¹ at 20 C, but also had a super cyclability. Although LiMn₂O₄ with preferred facet of {111} has excellent cycling stability at high rate, its preparation is not an easy case especially in large scale.

Herein, a facile way to synthesize LiMn₂O₄ fibers with exposed {111} facet is introduced by using easily accessible cellulose filter

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paper as template. As a template, Filter paper not only can suck solution containing Li^+ and Mn^{2+} into its void space, but also the fiber structure can be maintained not melt or collapse as the temperature increasing, thus facilitating to obtain the fiber structure for electrode materials after calcination. LiMn_2O_4 fibers with exposed {111} facet presented an excellent rate and cycling performance.

2. Experimental

2.1. Synthesis

$\text{LiCH}_3\text{COO}\cdot 2\text{H}_2\text{O}$ (310.3 mg) and $\text{Mn}(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$ (1354.2 mg) were dissolved in 3 ml mixed solvent (2 ml distilled water + 1 ml ethanol) to form a solution. Then, the commercial filter paper (18 pieces, 18×45 cm, about 1300 mg) was mixed into solution. Then the solution was sucked into filter paper completely. The solvent will be fully vaporized at 80°C under constant ultrasonic mixing, and the precursor was obtained. The precursor was calcinated at 400°C for 5 hours, and 700°C for another 10 hours. After cooling down to room temperature, LiMn_2O_4 fibers were fabricated. All the used reagents are from Sinopharm Group Company.

2.2. Material characterization

X-ray diffraction (XRD) was recorded on a Bruker D8 advanced diffractometer with Cu K α radiation. The morphology of LiMn_2O_4 fibers was characterized by scanning electron microscopy (SEM) (JEOL JSM-6360LV). TEM and HRTEM investigations were carried out using a JEOL JEM-2100F transmission electron microscopy operated at an accelerating voltage of 200 kV. The Thermogravimetry Analysis (TGA) and Differential Thermal Analysis (DTA) of LiMn_2O_4 precursor were performed by Analysis Equipment (HCT) (Beijin Henven Scientific Instrument Factory) in the temperature range of 30 to 800°C in air atmosphere, and the scanning rate was 5°C min^{-1} .

2.3. Electrochemical investigation

Electrochemical measurements were performed using a 2016 coin-cell composed of a LiMn_2O_4 cathode and a lithium metal anode separated by a microporous polyethylene film. The cathode was prepared by mixing the active material with conductive carbon black and PTFE in a weight ration of 80:15:5. The mixture was pressed onto aluminum foil ($20\ \mu\text{m}$) and then dried under vacuum at 363 K for 10 h. The active material loading of the electrodes is about $10\ \text{mg/cm}^2$ for all the electrochemical tests. The coin-cell was assembled in an argon-filled glove box, and the electrolyte is 1 M $\text{LiPF}_6\text{-EC/DMC}$ (1:1, v/v). The charge-discharge cycling test was carried out galvanostatically at different current densities on the electrochemical equipment of Land (Wuhan Land electro-chemical equipment company, China). The cut-off voltages for charge and discharge processes are 4.4 and 3.0 V respectively. The cyclic voltammogram (CV) test was performed on CHI600B (ShangHai, China) electrochemistry workstation between 3.0 and 4.4 V vs. Li^+/Li . Experiments were carried out at room temperature.

3. Results and Discussion

Fig. 1 shows the SEM images of filter paper template (a and b) and the precursor of LiMn_2O_4 (c and d). Many fibers can be observed clearly in template, and many pores can be found among the fibers as shown in Fig. 1a. From Fig. 1c, the precursor of LiMn_2O_4 also shows fiber structure, but the fibers' surface became smoother in comparison with template, indicating LiCH_3COO and $\text{Mn}(\text{CH}_3\text{COO})_2$ were homogeneously deposited on the template fibers' surface. Fig. 2 presents the TG-DTA curves of LiMn_2O_4 precursor, a decrease in weight between 200 to 300°C is related to the decomposition of the template fibers and the loss of the crystallized water in $\text{Mn}(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$ and $\text{LiCH}_3\text{COO}\cdot 2\text{H}_2\text{O}$; the second weight loss between 330 to 380°C is possibly associated with the decomposition of $\text{Mn}(\text{CH}_3\text{COO})_2$ and LiCH_3COO , which correspond to the endothermic peaks in DTA curve at about 295°C .

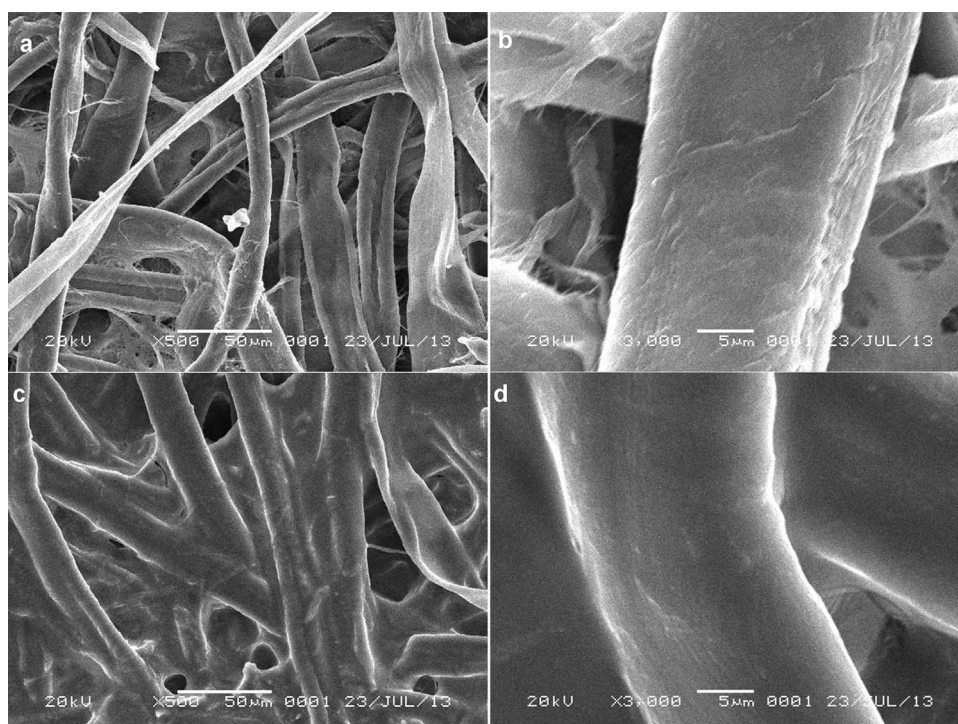


Fig. 1. SEM images of filter paper template (a) and (b), and precursor of LiMn_2O_4 (c) and (d).

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