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Efficient microwave hydrothermal synthesis of nanocrystalline orthorhombic $LiMnO_2$ cathodes for lithium batteries

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ABSTRACT

Rod-like orthorhombic $LiMnO_2$ nanocrystals were successfully synthesized using temperature-controlled microwave hydrothermal route (TCMH) in a short time (30 min) at a temperature as low as 160 °C. *o*-$LiMnO_2$ obtained by two different methods was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and electrochemistry test. SEM revealed that the product obtained in case of TCMH was rod-like with a diameter of 40 nm, while the nanoparticles with 200 nm diameter were obtained by traditional hydrothermal route (TH). The dramatic formation of *o*-$LiMnO_2$ in the microwave hydrothermal field influenced the morphology and crystal structure of the final products. The formation and preferred growth orientation mechanism of *o*-$LiMnO_2$ in the microwave irradiation process was discussed. Electrochemistry performance exhibited that the as-synthesized *o*-$LiMnO_2$ nanorods reached the maximum discharge capacity of 194.2 mAh g^{-1} at 0.1 C rate after several cycles between 2.2 and 4.4 V vs. Li^+/Li at room temperature, which was higher than the electrochemical performance of *o*-$LiMnO_2$ obtained by TH. The experimental results showed that the TCMH method provided an effective way for preparing *o*-$LiMnO_2$ cathode material in lithium-ion batteries.

1. Introduction

Since the rechargeable lithium-ion batteries were introduced by SONY Corporation in 1991, they have been widely utilized as power source in electronics revolution, and the technology has also been now vigorously pursued for electric vehicle applications [1]. $LiCoO_2$ cathode was employed for commercial batteries, but it has been prohibited from being used on a large scale because of its high cost, toxicity and chemical instability at deep charge. In this regard, lithium manganese-oxide-based system can fulfill the condition. Among them spinel-type $LiMn_2O_4$ with a three-dimensional framework structure is appealing, but the material has a poor cycle performance mainly due to the collective Jahn-Teller distortion when it cycles below 3 V. In contrast to $LiMn_2O_4$, the trivalent manganese compounds such as $LiMnO_2$ exhibit a better cycle performance even between 2 and 4.5 V vs. Li^+/Li [2,3]. Orthorhombic $LiMnO_2$ (*o*-$LiMnO_2$) should therefore be the best substitute for spinel $LiMn_2O_4$. Meanwhile, $LiMnO_2$ (both in monoclinic and in orthorhombic structure) has a high theoretical capacity of 285 mAh g^{-1}, which is twice as that of spinel $LiMn_2O_4$ within the same Mn^{4+}/Mn^{3+} redox couple [4,5]. Therefore $LiMnO_2$ would be a superior cathode material candidate for lithium-ion battery systems among the lithium manganese oxides.

Tremendous efforts have been made in recent years to synthesize pure *o*-$LiMnO_2$ by different methods such as conventional solid-state synthesis [6–8], reverse micro-emulsion preparation [9], hydrothermal [10–14], etc. The crystal size and structure depends on the synthetic route. The nano-scaled crystals offer short path for lithium ion to migrate, and therefore lead to high capacity and good cyclic behavior. Among the various synthesis approaches pursued in the past few years, hydrothermal method is particularly successful with respect to controlling the chemical composition, crystal size, and particle morphology. However, the conventional hydrothermal process due to its slow kinetics involves a longer reaction time 12–96 h to synthesize $LiMnO_2$ [10–14].

In this regard, microwave hydrothermal synthesis approach owing to its intrinsic heating characteristics shows rapid heating and increases the kinetics of reaction by one to two orders of magnitude. Microwave-assisted synthesis approaches will be attractive because they can control the particle size of the product with a high degree within several minutes and save energy. Manthiram and coworkers have successfully used microwave-solvothermal approach to synthesize olivine $LiMPO_4$ (M = Fe, Mn, Co) for lithium-ion batteries [15–17]. In our previous paper, Yang et al. [18] have reported the crystal growth mechanism and electrochemical properties of $LiFePO_4$ by using temperature-controlled microwave hydrothermal route (TCMH). However, the synthesis of $LiMnO_2$ via TCMH has not been reported yet.

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In this study, we present the rapid preparation of nanosized orthorhombic $LiMnO_2$ by using TCMH in a short time (~30 min) at a temperature as low as 160 °C. The as-synthesized o-$LiMnO_2$ reached the maximum discharge capacity of 194.2 mAh g^{-1} at 0.1 C rate after several cycles between 2.2 and 4.4 V vs. Li^+/Li at room temperature, which was higher than the electrochemical performance of o-$LiMnO_2$ obtained by traditional hydrothermal route (TH). The experimental results show that the TCMH method provides an effective way for preparing $LiMnO_2$ cathode material in lithium-ion batteries.

2. Experimental

The sample o-$LiMnO_2$ is prepared as follows: in the mole ratio of Li:Mn of 8:1, 35 mL suspension contained 0.8 g α-Mn_2O_3 (obtained by the calcination of $MnCO_3$ at 700 °C for 3 h in air) and $LiOH{\cdot}H_2O$ stirred for 10 min. The mixture was transferred into a 70 mL polytetrafluoroethylene (PTFE) vessel. TCMH treatment was performed in the Shanghai Sineo microwave digestion system (MDS-6), which was operated at 2.45 GHz frequency and maximum power of 1000 W. The power of this unit can be automatically controlled from 0 to 100% according to the setting temperature and pressure. This system can be operated to a maximum pressure of 750 psi and 250 °C, and both parameters can be controlled by a computer. The automatic temperature and pressure control system allows continuous monitoring and control of the internal temperature (±1 °C) and pressure (0.01 MPa).

The time, pressure/temperature, and power of the reaction system have been controlled by the computer. The pure-phased o-$LiMnO_2$ was produced at 160 °C for 30 min (the obtained sample named as TCMH30m). The traditional hydrothermal synthesis was basically the same with the above-mentioned process, except putting the autoclave in the electric oven at 160 °C for 12 h (named as TH12h). When the vessel was cooled down, a brown precipitate was collected and washed with distilled water several times and finally dried in a vacuum oven at 60 °C for 5 h.

The obtained o-$LiMnO_2$ was characterized by X-ray diffraction (XRD) in reflection mode (Cu Kα radiation) on a Rigaku D/max-2200/PC diffractometer in the 2θ range from 10° to 70°. The scanning electron microscope (SEM) was performed with Hitachi X650 microscope (20 kV).

Electrochemical measurements were carried out with coin cell. The working electrodes were prepared by mixing the obtained o-$LiMnO_2$, acetylene black, and polytetrafluoroethylene in the weight ratio of 80:15:5. Cells were assembled in an argon-filled glove box, using Celgard 2300 membrane as a separator, and a solution of 1 mol/L $LiPF_6$ in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1 ratio in weight) as the electrolyte. The charge and discharge cycling was studied in the voltage range of 2.2–4.4 V at a current density of 0.1 C.

3. Results and discussion

Fig. 1 shows the XRD patterns of the reagent α-Mn_2O_3 and obtained o-$LiMnO_2$ samples TCMH30m and TH12h with their indexing results. Fig. 1(a) shows the pure phase of α-Mn_2O_3 calcinated by $MnCO_3$ at 700 °C for 3 h in air, and all of the reflection peaks could be readily indexed into cubic structure of α-Mn_2O_3 (JCPDS card 78-0390). After treatment in the microwave hydrothermal system for 30 min, a new XRD pattern quite different from that of α-Mn_2O_3 is shown in Fig. 1(b), and indicates that the precursor was transformed to another phase. According to the JCPDS card 35-0749, the peaks labeled in Fig. 1(b) could be indexed as orthorhombic phase of o-$LiMnO_2$ with a space group of *Pmmn*. Fig. 1(c) shows the XRD pattern of $LiMnO_2$ obtained by TH, which was also consistent with the standard o-$LiMnO_2$ diffraction data.

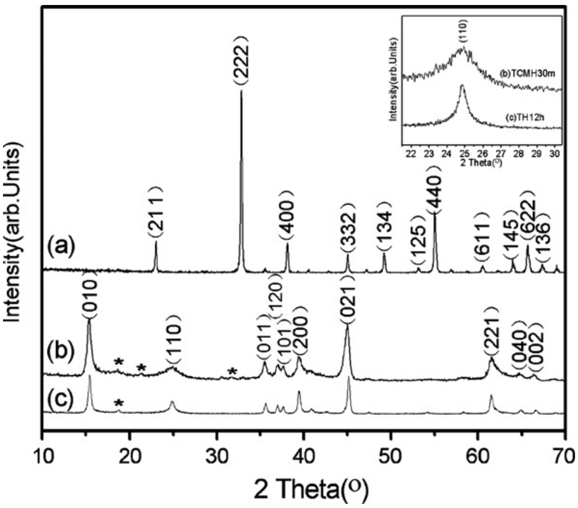

Fig. 1. XRD patterns of the precursor (a) α-Mn_2O_3, and the product o-$LiMnO_2$ (b) TCMH30m synthesized for 30 min by temperature-controlled microwave hydrothermal method, and (c) TH12h synthesized for 12 h by traditional hydrothermal method. In inset, patterns enlarged over the (1 1 0) for o-$LiMnO_2$. The peaks noted with asterisk were Li_2MnO_3.

Compared with TH method that always operated for dozens of hours, TCMH-produced pure phase o-$LiMnO_2$ showed a great decrease in the reaction time (dozens of minutes). However, an impurity phase appeared in the samples TCMH30m and TH12h, demonstrating very weak peaks notated as asterisks which were assigned to Li_2MnO_3 phase (as shown in Fig. 1). Such weak peaks implied that the amount of Li_2MnO_3 obtained in both TCMH and TH was trace, especially in the sample of TH12h. This impurity phase might have originated from oxidation by the remaining air in hydrothermal vessel (filled degree is 50%) during the hydrothermal process.

A careful indexing of the patterns of Fig. 1(b) and (c) indicated that the full width at half-maximum (FWHM) of the characteristic peaks of TCMH30m was larger than that of TH12h. It might be due to the fact that the dramatic formation of $LiMnO_2$ in dozens of minutes resulted in the mismatching of ionic transfer and the growth of $LiMnO_2$ crystal structure in microwave field, and the following SEM images demonstrated the relative crystal morphology. The crystal theory shows that the FWHM depends on the size and stacking faults of the crystals. Both the size and the stacking faults of the crystal have some effect on the electrochemical performance of the products. The detailed crystal growth mechanism and the electrochemical properties of $LiMnO_2$ in microwave hydrothermal condition will be discussed in the following work.

The SEM images presented in Fig. 2 describe the size and the shape of the as-obtained products. Fig. 2(a) shows that the products synthesized by TCMH had rod-like shape with a diameter of about 40 nm. However, the products obtained by hydrothermal method were discrete nanoparticles with a diameter of about 200 nm as shown in Fig. 2(b). SEM images indicated that the diameter of the sample TCMH30m was smaller than that of the sample TH12h, which may be due to the very short heating time in microwave system. Meanwhile, microwave owing to its special crystal growth mechanism, such as preferred growth orientation along different lattice axis and preferred growth on some crystal plane, influenced the size and morphology of as-obtained $LiMnO_2$ in microwave hydrothermal field. The particular crystal growth structure of $LiMnO_2$ presented in SEM results also could be analysed in the lattice parameters by using Rietveld refined process. The detailed description of how the microwave hydrothermal system controls the growth of nano-scaled crystals is under investigation.