

One-step synthesis LiMn_2O_4 cathode by a hydrothermal method

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Abstract

Spinel LiMn_2O_4 powders have been successfully synthesized by a hydrothermal method directly, which is no any pretreatment and following treatment in the process. The structure and morphology of the powders were studied in detail by means of X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM) and thermogravimetric analysis (TGA). The data reveal that the products have well-defined stable spinel structure, and the particles show distinctive crystal faces with 50–300 nm in particle sizes. The electrochemical characteristics of the spinel materials are measured in the coin-type cells in a potential range of 3.2–4.35 V versus Li/Li^+ . The as-synthesized LiMn_2O_4 delivers reversible capacity of about 121 mAh g^{-1} at a current density of 1/10 C. Cycled the cell to 40 cycles, the capacity remains at about 111 mAh g^{-1} at 1/2 C. © 2006 Elsevier B.V. All rights reserved.

Keywords: Spinel LiMn_2O_4 ; Hydrothermal method; Lithium ion batteries; Cathode

1. Introduction

Lithium ion batteries have been studied extensively as power sources for portable electronic devices and electric vehicles. Recently, spinel LiMn_2O_4 has been extensively studied electrochemically due to its potential use as a cathode material. In comparison with the conventional LiCoO_2 positive electrode, it is much safer, cheaper, contains more common elements, and is more in line with environmental standards [1,2].

In general, as for the battery application, LiMn_2O_4 powder should possess single-phase, homogeneity, uniform particle morphology with sub-micron size distribution, and large surface area in order to achieve better electrode properties [3]. However, the preparation of spinel LiMn_2O_4 involves at elevated temperatures as high as 700–900 °C solid-state reactions starting from the raw materials, such as manganese oxides, nitrate or carbonate with lithium hydroxide, nitrate or carbonate. The final products usually contain larger irregular particles, in a broader size distribution, as well as impurity phases. And also, this method could not provide good control on the crystalline growth, compositional homogeneity, morphology and microstructure [4–8]. Recently, some techniques are based on the processes of co-precipitation, ion-exchange, or thermal decomposition at

low temperatures of appropriate organic precursors obtained by sol–gel [9], Pechini [10], freeze-drying [11], melt-impregnation [12], spray-drying [13] methods. These methods lead to homogeneous spinel materials with small particle size, however, these methods also involved high temperature heat treatment, the cost of expensive reagents and process complexity.

The simple methods to synthesize spinel LiMn_2O_4 with excellent electrochemical characteristic have been anticipated at low temperature. Hydrothermal method is considered good for the synthesis of metal oxides at low temperature, which are usually obtained at high temperature by solid-state reaction. This is because the hydrothermal reaction can be carried out at a low temperature, while under high pressure in the aqueous solution. The hydrothermal synthesis of LiMn_2O_4 has been reported by several authors [14–17]. However, among them, some other oxidants or reducers (such as H_2O_2 , glucose and so on) are used for pretreatment of the started reagents, which lead to the process complexity. In a previous work by Feng et al [17], they involved in a very long hydrothermal process of 24 days. In this present work, through adjust the starting materials (manganese and lithium salt), spinel LiMn_2O_4 powders have been synthesized by a hydrothermal method directly without using any pretreatment and completed at a relative much shorter time. This method is so simple, direct, and in effect. The structure, morphology and electrochemical properties of the as-prepared LiMn_2O_4 have been investigated in detail.

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2. Experimental

Spinel LiMn_2O_4 powders were hydrothermally synthesized directly without any additional reagents and other reaction processes. The starting materials, $\text{LiOH}\cdot\text{H}_2\text{O}$ (99% pure), MnO_2 (EMD, $\geq 97.5\%$) and $\text{Mn}(\text{NO}_3)_2$ (50% aqueous solution) were put into an autoclave. The amount of MnO_2 was controlled at 0.075 mol, and $\text{Mn}(\text{NO}_3)_2$ was 0.025 mol. The autoclave were filled with the distilled water to 80% of the capacity (about 150 ml), sealed and kept at 280°C for 36 h, and then cooled to room temperature naturally. After the hydrothermal reaction, the products were washed with distilled water and separated in a centrifuge, and then dried in air at 150°C for overnight.

X-ray diffraction (XRD, Rigaku D/max-rA diffractometer with $\text{Cu K}\alpha$ radiation, $\lambda = 1.5406 \text{ \AA}$), field emission scanning electron microscopy (FESEM, FEI SIRION JY/T010-1996) were employed to characterize the as-prepared powders. XRD data were collected at $2\theta = 10^\circ\text{--}70^\circ$. Analysis of Li content in the product was carried out using inductively coupled plasma-mass spectroscopy (ICP-MS) (Thermo Elemental PQ3). The average valence of manganese was determined by the titration method [3]. About 0.06 g of the sample was dissolved in 20 ml of an acidified 0.08 M Fe(II) solution. During dissolution, the higher Mn oxidation states (III) and (IV) were reduced to Mn(II) by the oxidation of Fe(II) to Fe(III). The excess Fe(II) was back titrated with 0.018 M KMnO_4 . Thermogravimetric analysis (TGA) test was carried out on a TA SQT600 analyzer with a heating rate of 5°C min^{-1} in the temperature range of $20\text{--}1000^\circ\text{C}$.

Electrochemical performances of the as-prepared powders were investigated with a two-electrode coin-type cell (CR 2025) with lithium foil as the reference electrode. All the electrodes were obtained by coating the slurry of a mixture (composed of 80 wt.% active material, 10 wt.% conducting agent (acetylene black), and 10 wt.% binder (polyvinylidene fluoride)) onto an aluminum foil current collector (12 mm in diameter). After drying in air at 80°C for 4 h, the electrodes were pressed under 20 MPa for 1 min, and then dried at 120°C for 24 h in vacuum. The weight of active material in the electrode sheet was about 10 mg cm^{-2} . The cells were assembled in an Ar-filled glove box. The electrolyte was 1 M LiPF_6 in the mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) with mass ratio of 1:1. A polypropylene (PP) film (Cellgard 2300) was used as the separator. The galvanostatic charge–discharge tests were conducted on a PCBT-138-8D-A battery program-control test system at $1/2 \text{ C}$ rates (a nominal specific capacity of 120 mAh g^{-1} was assumed to convert the current density into C rate) in the voltage range of 3.20–4.35 V (versus Li/Li^+).

3. Results and discussion

The possible chemical reactions occurring in the synthesis of LiMn_2O_4 could be listed as follows:

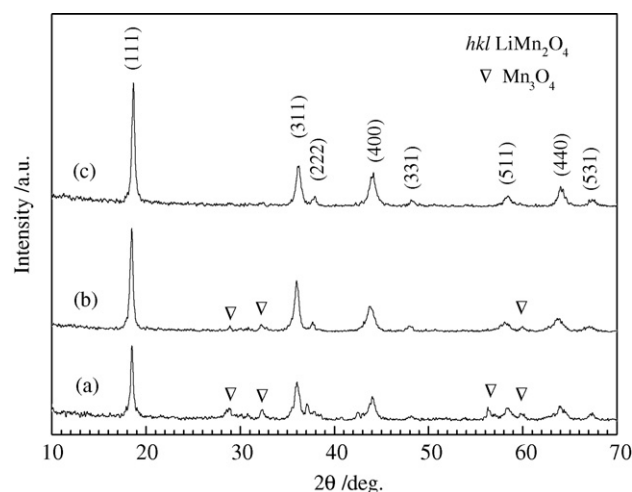
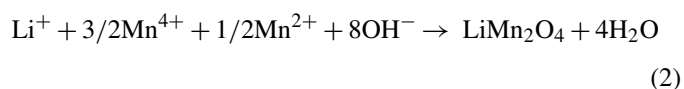
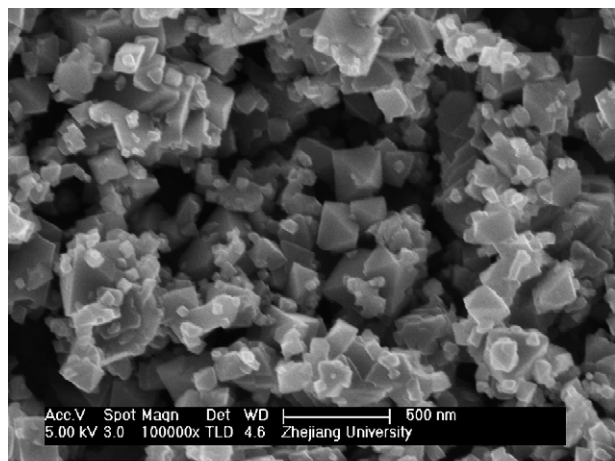


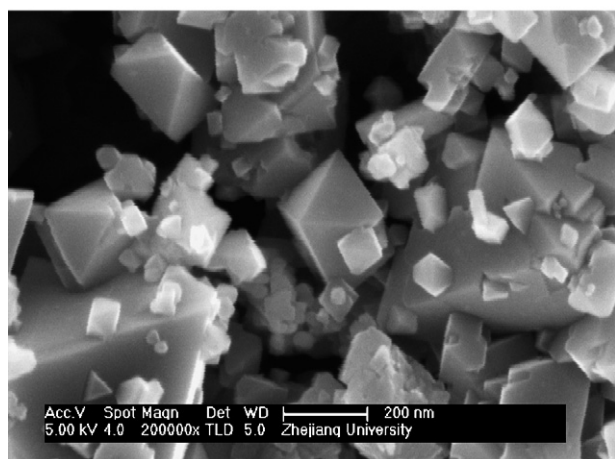
Fig. 1. The XRD patterns of the products prepared by the starting material with (a) stoichiometric amount, (b) stoichiometric amount with addition of ammonia and (c) an excess 20% amount of lithium.

When the reagents were added into the distilled water, and reaction happened in the autoclave, MnO_2 supported the Mn^{4+} ion due to the hydrolysis (1), and the $\text{Mn}(\text{NO}_3)_2$ supported the Mn^{2+} ion. In LiMn_2O_4 , the oxidation state of manganese is 3.5. According to the previously report [18], the compound can be described as $\text{LiMn}^{3+}\text{Mn}^{4+}\text{O}_4$. All Mn^{2+} ions in the solution were oxidized to Mn^{3+} by Mn^{4+} ions completely. Just as the reaction (2), the LiMn_2O_4 compound was synthesized. In the hydrothermal process, because of Mn^{4+} as oxidant, there is no need any other oxidants.

Fig. 1 shows the XRD patterns of the products. All the samples were synthesized under the same processing condition as described in Section 2 by manipulating the amount of the corresponding starting materials. It is seen that the mainly peaks are attributed to the spinel LiMn_2O_4 . But in the patterns (a) and (b), there are still some other weak peaks, which are the peaks of the impurity (Mn_3O_4). Pattern (a) is corresponding to the starting materials with stoichiometric amount (0.05 mol $\text{LiOH}\cdot\text{H}_2\text{O}$, 0.075 mol MnO_2 , 0.025 mol $\text{Mn}(\text{NO}_3)_2$). Pattern (b) is also stoichiometric starting materials, but adding 15 ml ammonia. The result shows that the spinel LiMn_2O_4 can be synthesized, but there are some impurity in the patterns (a) and (b). Pattern (c) is corresponding to the starting materials with an excess amount of 20% lithium hydroxide. It is gotten that all the diffraction peaks of pattern (c) correspond to a single-phase of cubic spinel structure with a space group $Fd\bar{3}m$. The unit cell parameters and volumes of the spinel structure LiMn_2O_4 materials calculated by the XRD data are $a_0 = 8.239 \text{ \AA}$, $V_0 = 559.27 \text{ \AA}^3$, which are very close to the standard data ($a_0 = 8.247 \text{ \AA}$, $V_0 = 560.90 \text{ \AA}^3$) of JCPDS 35-0782. By the ICP-MS analysis, the Li/Mn ratio of the spinel LiMn_2O_4 under pattern (c) condition was determined to be 1.02/1.98, which can be understood that a little amount of lithium ions hold manganese ions sites (lithium ions occupy the tetrahedral (8a) sites and manganese ions reside at the octahedral (16d) sites in stoichiometric LiMn_2O_4). By the titration method, the average valence of manganese in the spinel LiMn_2O_4 under pattern (c) condition



(a)



(b)

Fig. 2. SEM images of LiMn_2O_4 powder prepared by the hydrothermal method (a) at low and (b) at high magnification.

is determined to be 3.482, which is very close to the nominal manganese valence. These facts indicate that under pattern (c) condition, pure spinel LiMn_2O_4 powder has been synthesized by one-step hydrothermal method, which is only using the excess amount of lithium, no using any other reagents. The following mentioned LiMn_2O_4 were prepared under pattern (c) condition.

The particle morphologies of the pure LiMn_2O_4 powder are shown in Fig. 2. Good crystallization can be clearly seen from the zoomed-out micrograph (Fig. 2b). The distinctive well-defined crystal faces exhibit single spinel crystals of octahedral shape with well-developed [1 1 1] planes. From Fig. 2a, the particle sizes distribute in the range of 50–300 nm. Also, the particles are loosely bound agglomerate.

Typical TGA curve of the LiMn_2O_4 powder prepared by the one-step hydrothermal method is shown in Fig. 3. Up to 1000 °C, it shows that there is only a slight weight loss of 4%. Moreover, from the inset figure of Fig. 3, the most weight loss occurs above 800 °C, which is attributed to the volatilization of lithium at such high temperature. Below 800 °C, there is no distinct weight loss in the TGA curve. It indicates that LiMn_2O_4 powder prepared by the one-step hydrothermal method has a steady structure.

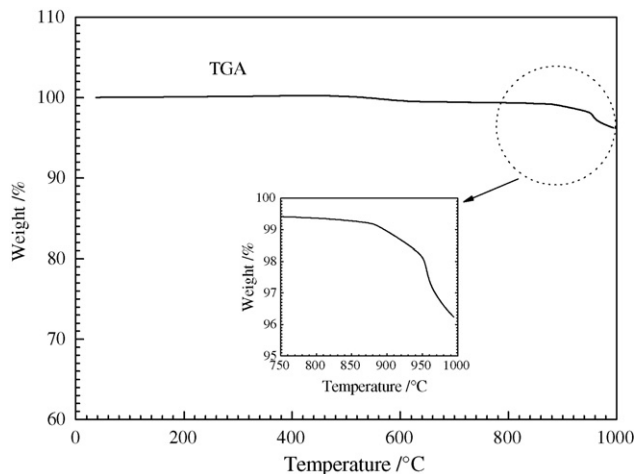


Fig. 3. TGA curve of the as-prepared LiMn_2O_4 powder.

In order to evaluate the electrochemical properties of LiMn_2O_4 compound by the one-step hydrothermal method, the galvanostatical charge/discharge tests are performed at room temperature and shown in Fig. 4. The first charge and discharge test was carried out at a very slow current density of 1/10 C. It delivers an initial charge specific capacity of 131 mAh g^{-1} , followed by a discharge capacity of 121 mAh g^{-1} at room temperature (about 92% of the charge capacity is discharged). On the charge and discharge curves, there are two clear charge/discharge plateaus, which can be proved by the inset figure (the differential specific capacity (dQ/dE) versus voltage). In the inset figure, on the charge/discharge process, there are two pairs of distinctive peaks, which are characteristics of spinel-type lithium manganese oxides with a two-stage mechanism for the electrochemical lithium extraction and insertion. Fig. 5 shows the cycling performance of the spinel LiMn_2O_4 . Its capacity remains to be 111 mAh g^{-1} till to 40 cycles at 1/2 C. The capacity retention is about 95.7% at 40th cycle.

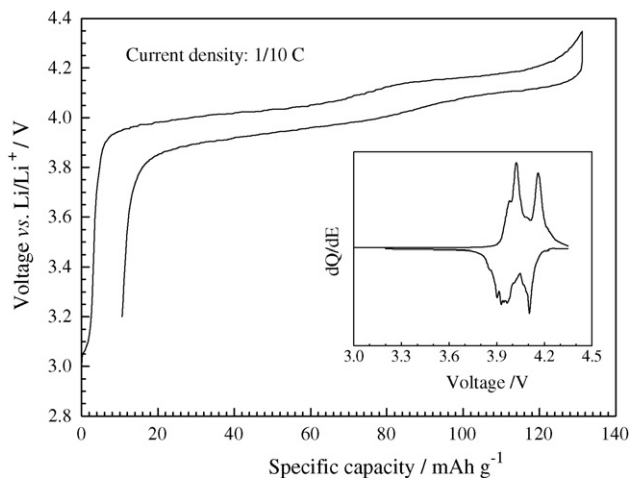


Fig. 4. The initial charge/discharge curves of LiMn_2O_4 prepared by hydrothermal method, the inset is the relationship between dQ/dE and charge/discharge voltage.

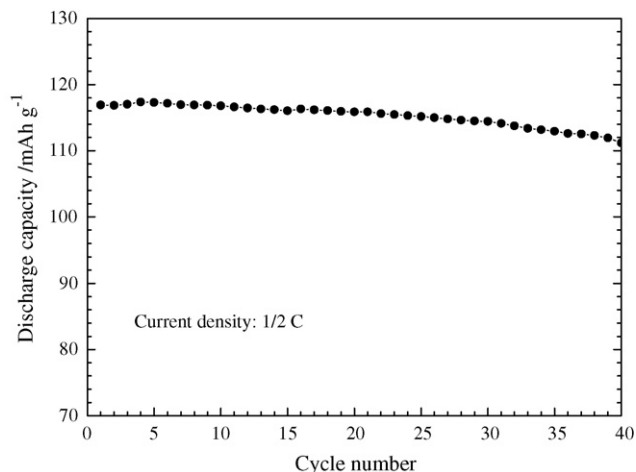


Fig. 5. Cycle ability of LiMn_2O_4 prepared by hydrothermal method.

4. Conclusions

Spinel LiMn_2O_4 powders have been synthesized directly by one-step hydrothermal method without adding any other oxidants. The products show good crystallization and stable structure. The SEM reveals that the synthesized powder distributes in the range of 50–300 nm in sizes. It delivers a high initial discharge capacity of 121 mAh g^{-1} at a current density of $1/10\text{C}$. And after 40 cycles, it still remained 111 mAh g^{-1} at $1/2\text{C}$. So one-step hydrothermal method to make spinel LiMn_2O_4 is simple, direct, and attractive.

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