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Spray-drying technology for the synthesis of nanosized $LiMn_2O_4$ cathode material

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Abstract

Spinel $LiMn_2O_4$ cathode material has been synthesized by a spray-drying method for lithium ion batteries. During the entire process, the as-prepared powders were characterized using TGA/DTA, XRD, FTIR, SEM and TEM. The results showed that this method not only reduces the sintering time to 5 h at 750 °C, but also decreases the average particle size of $LiMn_2O_4$ powders to the order of nanometers. The electrochemical performance of nanosized $LiMn_2O_4$ was investigated by the galvanostatic charge–discharge tests. The data indicate that the nanosized $LiMn_2O_4$ has a specific capacity of about 130 mA h g^{-1} (1/5 C), and at higher rate (1 C), still has good cycling stability.

Keywords: Nanosized $LiMn_2O_4$; Spray-drying method; Lithium ion batteries; Electrochemical characteristics

1. Introduction

In the intense search for high-energy density cathode materials for use in lithium ion rechargeable battery technology, $LiMn_2O_4$ has become one of the most promising alternative materials as compared to $LiCoO_2$ in commercial application [1–3]. It shows many favorable attributes including good capacity, high-energy density, low self-discharge, especially, low cost and low toxicity. So searching for good preparation methods is very significant. But most of the conventional methods require high temperature, or long time, or a complicated process [4–6]. At lower temperature, some Mn_2O_3 may be present as the impurity, which only disappears at 800 °C [7,8].

The spray-drying method [9–11] has been widely used because of its many advantages, including the fact that it is a simple system, its cost effective, and it can be scaled up to tons of quantities. The fabrication of microscale particles via spray-drying has been reported previously. This method for the synthesis of inorganic materials has a number of advantages over more conventional synthetic procedures. For example, high-purity material can be synthesized at a lower temperature. In addition, homogeneous multi-component systems can be obtained by mixing precursor solutions.

The production of nano-structured particles is of interest, because the chemical and physical behavior of the particles is unprecedented and remarkably different from those in bulk form. Nano-structured $LiMn_2O_4$ cathode material with excellent electrochemical characteristics has been reported [12,13]. In this present work, the precursor for $LiMn_2O_4$ cathode material was dried quickly via a spray-drying process. And then, via adjusting the sintering process, nanosized spinel $LiMn_2O_4$ powders were obtained. The structure, morphology and electrochemical properties of those nanosized materials have been investigated in detail.

2. Experimental

Stoichiometric amounts of $CH_3COOLi{\cdot}2H_2O$ and $Mn(CH_3COO)_2{\cdot}4H_2O$ were dissolved in distilled water. The resulting aqueous solution was dried to form a mixed dry precursor via a spray-dryer. The solution was atomized via a sprinkler at an air pressure of 0.2 MPa, and was dried in the spray-dryer by hot air. The inlet air temperature was 220 °C, and the exit air temperature

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was 110 °C. The as-prepared precursor powders were sintered at 500 °C for 6 h in dry air atmosphere, and then to an elevated temperature of 750 °C for 5 h with intermittent grindings.

DTA and TGA were carried out on a TA SQT600 analyzer with a heating rate of 5 °C min^{-1} in the temperature range of 50–900 °C. Fourier transform infrared spectrophotometer (FTIR, Nicolet Nexus670) and powder X-ray diffraction (XRD, Rigaku D/max-rA) were used to analyze the phase of the precursor and sintered powders. The morphology of the powders was observed with a scanning electron microscopy (SEM, Hitachi S-4700) and a transmission electron microscope (TEM, JEM-2010).

A slurry consisting of the sintered powder as active material, conducting agent (acetylene black), and binder (polyvinylidene fluoride) was pasted onto an aluminum foil, with NMP (*n*-methylpyrrolidone) as the solvent. The weight ratio of the active material, conducting agent and binder was 80:10:10 in the working electrode. After drying in air at 80 °C for 4 h, the sheet was pressed under a pressure of 20 MPa to provide increased adherence of the cathode mixture onto the aluminum foil current collector. The weight of the active material in the electrode sheet was about 10.0 mg in a square centimeter of aluminum foil. After drying in a vacuum at 120 °C for 10 h, the electrodes were assembled into the coin-type cells (CR 2025) in an Ar-filled glove box. The metallic lithium sheet was used as the counter electrode. A solution of 50 vol.% ethylene carbonate (EC), 50 vol.% dimethyl carbonate (DMC) and 1 M $LiPF_6$ was used as the electrolyte solution, and a polypropylene (PP) film (Cellgard 2300) as the separator. The galvanostatic charge–discharge tests were conducted on a PCTB-138-8D-A battery program-control test system with the cut-off voltages of 3.2 V and 4.3 V (versus Li/Li^+) under a specific current density (a nominal specific capacity of 120 mA h g^{-1} was assumed to convert the current density into C rate).

3. Results and discussion

The results of TGA and DTA analysis are shown in Fig. 1. For the precursor powders obtained by the spray-drying method, two distinct steps of weight loss are observed on the TGA curve. The first step is obviously due to vaporization of water, which corresponds to a sharp endothermic peak around 130 °C on the DTA curve. The weight loss is about 20% in this reaction step. From 200 °C, up to 380 °C, on the DTA curve, there are more than three strong endothermic and exothermic peaks, and on the TGA curve, the weight loss reaches about 40%. This step corresponds to the decomposition of the metal acetate and the formation of $LiMn_2O_4$ gradually. From 400 °C to 700 °C, the weight of the sample hardly changes. It is mainly associated with $LiMn_2O_4$ crystallization. Above 700 °C, the weight loss is due to the loss of lithium in the compound. Therefore, the selected heating treatment process is that, first, at relative low temperature, spinel $LiMn_2O_4$ powders are synthesized, and next, temperature is elevated to gain good crystallization.

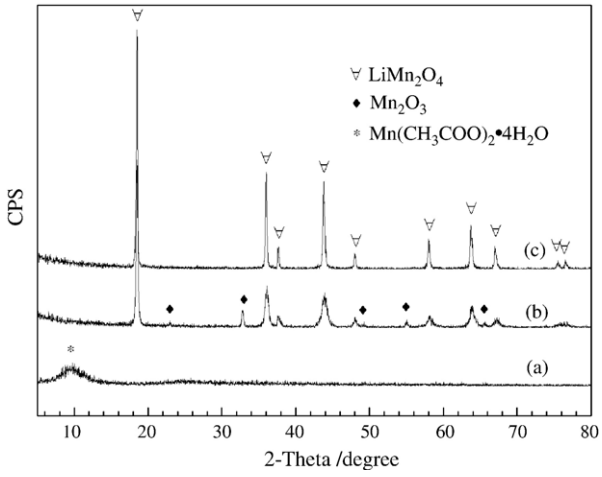

Fig. 2. XRD patterns of the as-prepared powders. a: Precursor; b: after being sintered at 500 °C for 6 h; c: after being sintered at 750 °C for 5 h.

Fig. 2 shows the XRD patterns of the precursor and synthesized materials sintered at different temperatures. The precursor is basically amorphous (Fig. 2a). Besides a broad $Mn(CH_3COO)_2·4H_2O$ peak at 10°, there is no other Bragg reflection visible in the pattern originating from the precursor. In this spray-drying method, the quick dry rate and low dry temperature lead to the precursor powder low crystallization. When heated at 500 °C, however, there are a lot of obviously diffraction lines on the XRD pattern (Fig. 2b), and most are attributed to spinel $LiMn_2O_4$, the others are Mn_2O_3. Compared with Fig. 2a and corresponding to Fig. 1, no peaks of salt acetate can be found in Fig. 2b,

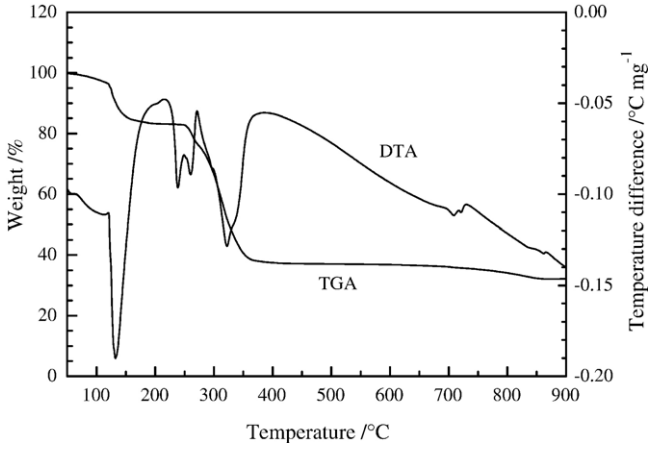

Fig. 1. DTA/TGA curves of the precursor powder prepared by the spray-drying method.

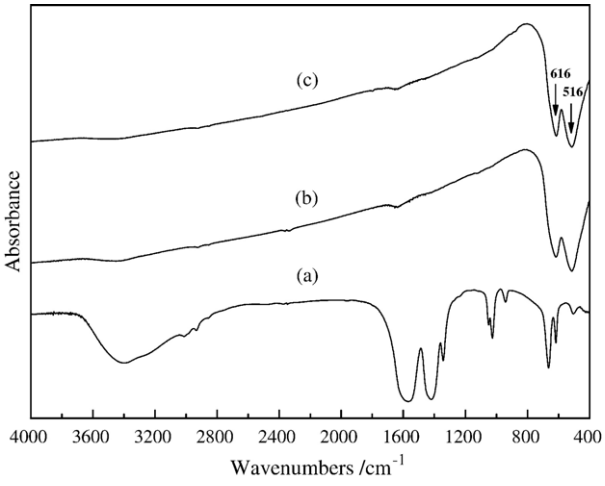

Fig. 3. FTIR spectra of the as-prepared powders. a: Precursor; b: after being sintered at 500 °C for 6 h; c: after being sintered at 750 °C for 5 h.