



锂离子电池正极材料 LiMn_2O_4 的合成与晶体结构

阮艳莉¹ 唐致远^{*1} 韩恩山² 冯季军¹

(¹天津大学化工学院应用化学系, 天津 300072)

(²河北工业大学化工学院应用化学系, 天津 300130)

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Synthesis and Crystal Structure of LiMn_2O_4 Cathode Material for Li-ion Battery

RUAN Yan-Li¹ TANG Zhi-Yuan^{*1} HAN En-Shan² FENG Ji-Jun¹

(¹Department of Applied Chemistry, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072)

(²Department of Applied Chemistry, School of Chemical Engineering and Technology,
Hebei University of Technology, Tianjin 300130)

Abstract: Spinel LiMn_2O_4 powders were prepared using two-step synthesis method consisting of solid-state reaction method and citrate modified sol-gel method. The effects of the calcination temperature and the Li/Mn ratio of raw materials were studied on the physicochemical and electrochemical properties of the spinel LiMn_2O_4 powders, such as crystallinity, lattice constant and density. The title compound was characterized by powder X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Polycrystalline LiMn_2O_4 powders calcined at 750 °C were found to be composed of very uniformly-sized microcrystal with an average particle size of 300 nm. The improvement in electrochemical properties was mainly attributed to the process of re-grinding by absolute alcohol.

Key words: Li-ion battery; cathode material; LiMn_2O_4 ; crystal structure

0 Introduction

Spinel LiMn_2O_4 has been extensively studied as the most promising cathode material for lithium secondary batteries because of their low cost, easy availability, and nontoxicity. However, its practical application has been limited, in contrast to other cathode candidates such as LiCoO_2 and LiNiO_2 , by a relatively low specific capacity and severe capacity fading with cycling^[1,2]. The quality of the LiMn_2O_4 powders strongly depends on synthetic methods. In previous studies, the title compound has usually been synthesized using

solid-state reactions that involve the mechanical mixing of oxides and/or carbonates followed by high temperature calcination and extended grinding. These synthetic conditions, which require long range diffusion of the reactants, may result in nonhomogeneity, abnormal grain growth and poor control of stoichiometry^[3,4]. There also have been a few reports about low temperature preparation techniques such as sol-gel and precipitation processes^[5,6]. But these synthetic methods are not always effective at maintaining a homogeneous reactant distribution during heating, there-

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*通讯联系人。E-mail: zytang@tju.edu.cn

第一作者: 阮艳莉, 女, 26岁, 博士生; 研究方向: 锂离子电池正极材料。

fore undesirable phase can form at the beginning of calcinations. The relation between structural and electrochemical properties of the spinel LiMn_2O_4 has not been investigated systematically.

In the present study, LiMn_2O_4 powders with different crystallinity were prepared using two-step synthesis method consisting of solid-state reaction method and citrate modified sol-gel method. The effect of the calcination temperatures on the electrochemical properties of the LiMn_2O_4 powders was extensively investigated. The relation between physicochemical and electrochemical properties of the LiMn_2O_4 powders was also studied.

1 Experimental

1.1 Preparation of the spinel LiMn_2O_4

A stoichiometric amount of lithium and manganese acetate salts (cationic ratio of $\text{Li}:\text{Mn}=1.05:2$) was dissolved in distilled water and completely mixed with an aqueous solution of citric acid (CA, $0.3 \text{ mol} \cdot \text{L}^{-1}$). CA was used as a chelating agent in making a gel. The molar ratio of CA to total metal ions was fixed at unity. After adjusting the pH of the solution to 6.5~7.5 with ammonium hydroxides ($3 \text{ mol} \cdot \text{L}^{-1}$), the resultant solution was heated at 70~80 °C while being mechanically stirred with a magnetic stirrer for a few hours until the pink gel precursors were obtained. The resulting gel precursors were decomposed at 400 °C, re-ground (by absolute alcohol or not), and then calcined at 250~850 °C for 10 h in air to obtain the polycrystalline spinel LiMn_2O_4 powders.

1.2 Instruments

Powder X-ray diffraction (XRD, 30W/MPD, Philips) using Ni-filtered Cu $K\alpha$ radiation ($\lambda=0.154\ 064 \text{ nm}$; 40 kV, 10 mA; step size=0.02°, $10^\circ < 2\theta < 80^\circ$) was used to identify the crystalline phase of the materials calcined at various temperatures. The least square method was then performed on the X-ray diffraction data to obtain lattice constants. The morphological change of the materials after the calcinations of gel precursors was examined using scanning electron microscope (SEM, XL-30W/TMP, Philips) and transmission electron microscopy (TEM, TECNAI-20, Philips) performed at 200 kV. Pycnometric density was used to obtain the absolute density of the powders.

1.3 Electrochemical measurement

The electrochemical test cell used two electrodes, an LiMn_2O_4 -based composite as the positive electrode and Li metal as the negative electrode, and $1 \text{ mol} \cdot \text{L}^{-1} \text{ LiPF}_6$ in EC/DMC(1:1) solution as the separator. The positive electrodes were prepared by mixing 85% active material with 10% acetylene black as conductive additives and 5% polytetrafluoroethylene as binder. The mixture was coated onto an aluminum foil and then vacuum dried for 12 h. All cells were fixed in the Ar filled glove box. The galvanostatically charge and discharge experiments were performed at a constant current density with cutoff voltage of 3.0 to 4.3 V (vs Li/Li^+).

2 Results and discussion

2.1 Crystal structure

Fig.1 shows the XRD patterns for the materials calcined at various temperatures for 10 h. The XRD pattern indicates a phase pure material; no peaks attributed to a second phase are observed throughout the calcination range. At 250 °C significant peaks representing spinel LiMn_2O_4 begin to appear. Generally, the higher the calcination temperature is, the sharper and stronger the diffraction peaks are and thus the better is the crystallinity of the LiMn_2O_4 phase. When the calcination was carried out above 650 °C, the peaks were abruptly sharpened, indicating an increase of crystallinity due to the growth of grain size, ordering of local structure, and/or release of lattice strain. However, when the calcination temperature was too

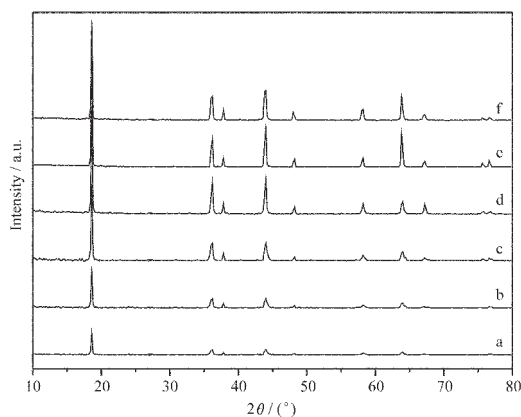


Fig.1 XRD patterns for the sample calcined at different temperatures

a: 250 °C; b: 400 °C; c: 650 °C; d: 700 °C;
e: 750 °C; f: 850 °C

high, parts of peaks became broadened as exemplified in Fig.1f (at 850 °C).

The lattice constant was calculated by the least square method from the XRD data, and the pycnometric density was performed to measure the absolute density of the spinel LiMn_2O_4 powders calcined at different temperatures. These data are given in Table 1. Lower calcination temperatures result in the formation of a more oxidized manganese cation because Mn^{4+} is a/more stable manganese ions at lower temperatures^[7]. The atomic radius of Mn^{4+} (0.067 nm) is smaller than

Table 1 Physicochemical properties of samples calcined at different temperatures

Samples	Temperature / °C	Lattice constant / nm	Density / ($\text{g}\cdot\text{cm}^{-3}$)
A1	250	0.819 9	4.08
A2	400	0.821 1	4.11
A3	650	0.821 8	4.19
A4	700	0.822 5	4.21
A5	750	0.823 1	4.23
A6	850	0.824 3	4.28

that of Mn^{3+} (0.072 nm), so the lattice constant and the density of the powders increase with increasing calcination temperature from 250 to 850 °C as shown in Table 1. The lattice constant of the sample calcined at 750 °C is in agreement with the reported value^[4].

A series of SEM micrographs (Fig.2) reveals the morphological changes during the calcination of the samples. As the calcination temperature increased, growth kinetics was favored and thus agglomerated spherical particles were changed to larger particulates. The presence of loosely-agglomerated spherical particle with an average grain size of about 100 nm was observed from the powders calcined at 650 °C. For the materials prepared at 750 °C, the particle size abruptly increased to about 600 nm, while the particle size was about 300 nm with a fairly narrow particle-size distribution for the powders re-ground by absolute alcohol. The sample calcined at 850 °C was dispersed in acetone by ultrasonic wave before examination by SEM to prevent from heavy conglomeration.

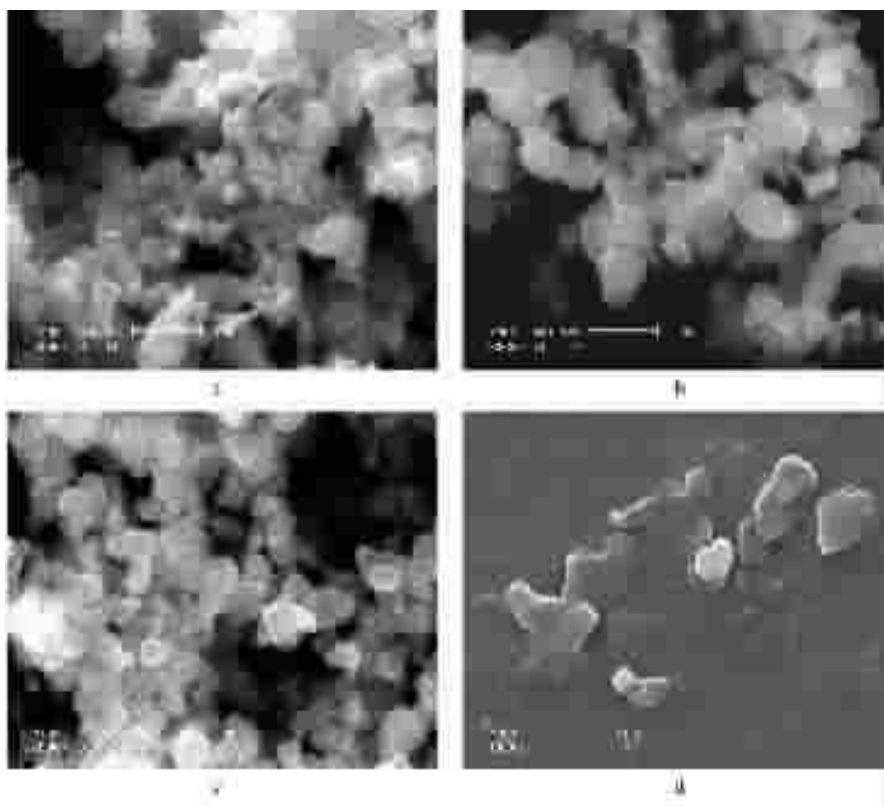


Fig.2 SEM images for the sample calcined at different temperatures
a: 650 °C; b: 750 °C; c: 750 °C (re-ground by absolute alcohol); d: 850 °C

There were visible morphological changes for the two samples calcined at 750 °C. This might be at-

tributed to the re-ground step by absolute alcohol. Absolute alcohol makes the contact of the particles of

the sample closer and more so by the re-ground step. The step helps to crystalline perfection. Transmission electron microscopy (TEM) images are shown in Fig.3 for the powders re-ground by absolute alcohol and then calcined at 750 °C. The last picture is composed of a high-resolution photo and an electronic diffraction

photo for the boundary. It distinctly shows the crystal lattice arrangement of a random particle in the powders. Such regular and perfect crystal lattice arrangement must be some help to the improvement of the electrochemical properties of the sample.

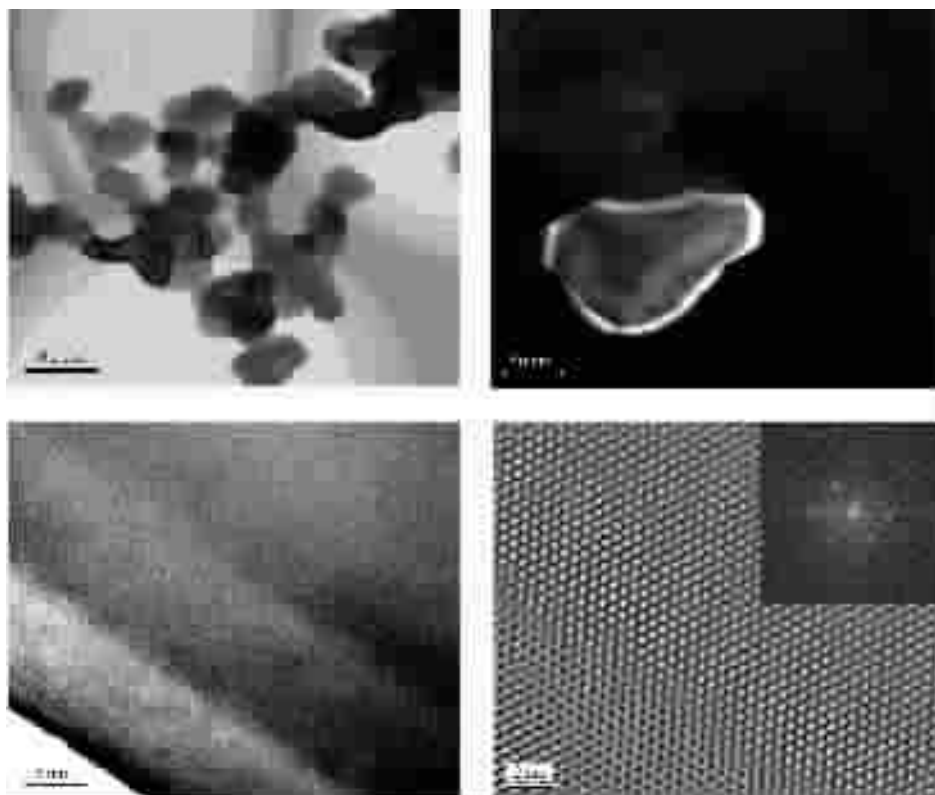


Fig.3 TEM photos of the powders re-ground by absolute alcohol and calcined at 750 °C

2.2 Electrochemical properties

Fig.4 shows comparisons of the discharge capacities with the number of cycles for the spinel LiMn_2O_4 powders calcined at different temperatures. It can be easily seen that the LiMn_2O_4 sample calcined at 750 °C and re-ground by absolute alcohol has the maximal specific capacity and the most excellent cycle ability among all the samples. This may be explained by its higher crystallinity and better retention ability of the spinel structure, and thus higher lithium ion diffusion coefficient^[4]. It should be specially pointed out that the powders prepared at 650 °C, which deliver the lowest initial capacity, have excellent cycling behavior with 6.64% loss from the initial discharge capacity at the 20 cycles. It is due to much more defects in sample's crystal structure favoring the lithium ion intercalation/deintercalation. The sample calcined at 850

°C, which conglomerated heavily, faded most seriously as cycling.

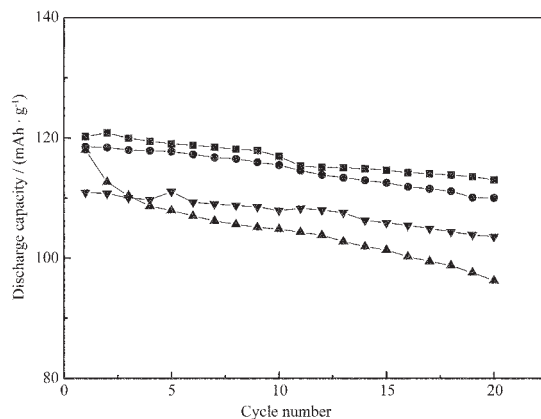


Fig.4 Electrochemical cyclic performances of spinel LiMn_2O_4 powders calcined at different temperatures
▼: 650 °C; ●: 750 °C; ■: 750 °C (re-ground by absolute alcohol); ▲: 850 °C

3 Conclusions

The spinel LiMn_2O_4 powders were prepared using two-step synthesis method consisting of solid-state reaction and citrate sol-gel methods. The compound is a phase pure material and $750\text{ }^\circ\text{C}$ is the best temperature for the preparation. SEM, TEM and electrochemical tests confirm that the powders re-ground by absolute alcohol have higher crystallinity and thus a good capacity retention with cycling. The electrochemical behavior of the title compounds depends strongly on crystallinity and local crystal structure, which can be altered by different calcination temperatures and synthetic methods.

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