

## Synthesis and character of spinel $\text{LiMn}_2\text{O}_4$ <sup>①</sup>

XU Cha-qing(徐茶清), TIAN Yan-wen(田彦文), ZHAI Yu-chun(翟玉春),

YU Bing(于冰), GUO Zhao-jing(郭兆靖)

(School of Materials and Metallurgy, Northeastern University, Shenyang 110004, China)

**Abstract:** The spinel  $\text{LiMn}_2\text{O}_4$  was made from  $\text{Li}_2\text{CO}_3$  and  $\text{MnO}_2$  by combining the soft chemical treatment with the solid state reaction. The heating temperature was auto-controlled by program and the two-step treatment was adopted. The synthesis mechanism of the spinel  $\text{LiMn}_2\text{O}_4$  was studied by TGA-DTA analysis. It is found that the reaction of  $\text{Li}_2\text{CO}_3$  and  $\text{MnO}_2$  will occur at the temperature lower than 600 °C and  $\text{MnO}_2$  has self-catalysis function during the reaction. The results of XRD and SEM to the synthesized materials show that the  $\text{LiMn}_2\text{O}_4$  phase is pure, with regular appearance and uniform granularity distribution. The electrochemical tests indicate that the spinel  $\text{LiMn}_2\text{O}_4$  has perfect cycling performances and the cycling capacity still keeps at 109.6 mA·h/g after 5 cycles.

**Key words:** lithium batteries;  $\text{LiMn}_2\text{O}_4$ ; mechanism; combination; soft chemical treatment and solid state reaction

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### 1 INTRODUCTION

The increasing concerns on portable electric elements demand more and more electrochemical energy. Countries all over the world have put large quantity of manual labors, material resources and financial resources on basic research and development on new type of rechargeable batteries<sup>[1,2]</sup>. However, this new type of batteries is based on studying and developing perfect performance of materials, especially on materials of the lithium batteries.  $\text{Li}_x\text{Mn}_2\text{O}_4$  cathode materials have been widely studied over the last two decades as a potential candidate in terms of their lower cost and lower environmental pollution, compared to nickel- and cobalt-based oxides. But these cathode materials have their disadvantages, such as structure and state changes of manganese oxide, difficulty of preparation and significant capacity fading during the cycling process. At present, great efforts have been made to obtain the perfect performance of lithium manganese oxide materials by changing synthesis method and condition, including the solid state reaction<sup>[3-5]</sup> and soft-chemical method<sup>[6-8]</sup>. The researchers were mainly focused on material proportion, atmosphere control and heat-treatment temperature, but less attempt have been taken to the synthesis mechanism. The structure, morphology, special surface area and electrochemical performance are strongly related to the synthesis mechanism. Therefore, study on the mechanism can provide important theoretic basis for the synthesis method.

The solid state reaction to synthesize  $\text{LiMn}_2\text{O}_4$  spinel due to its simplicity was firstly used in the industry. But it needs higher synthesis temperature and the product particle is difficult to control. Furthermore, the soft-chemical method has its disadvantages. In the present paper, the authors combined the solid state reaction with soft-chemical treatment to synthesize  $\text{LiMn}_2\text{O}_4$  spinel, and the authors studied the synthesis mechanism in order to obtain the theoretical foundation for preparing the spinel  $\text{LiMn}_2\text{O}_4$ .

### 2 EXPERIMENTAL

#### 2.1 Material preparation

$\text{LiMn}_2\text{O}_4$  was prepared by combining the solid state reaction with soft-chemical treatment. First, stoichiometric amounts of lithium carbonate and manganese dioxide were ground in the ball mill for a certain time with dispersing solvent of alcohol. Then the mixture was baked in a water box at 70 °C to remove alcohol, so that a well-distributed precursor powder of  $\text{LiMn}_2\text{O}_4$  was obtained. The precursor powder was pressed into blocks and sintered with two-step treatment by auto-controlled temperature program in the air at a certain temperature. During the process of cooling stage, the samples were protected in oxygen and the cooling rate was 3 °C/min.

#### 2.2 Measurements

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**Correspondence:** XU Cha-qing, Tel: + 86-24-81611363; E-mail: xuehaqing@tom.com

The DTA curves of the samples were obtained by means of PERKIN-ELMER 7 series differential thermal analyzer. The samples of 10.00mg were put into a Pt-Au crucible, and measured in a flowing air of 25 mL/min, at a heating rate of 10 °C/min. Powder XRD data were obtained by D/max-A diffractometer. The microstructures of samples were observed with JSM-5800 microscopy operated at 20 kV. The electrochemical properties of the prepared powders were characterized in the Li/ $\text{LiMn}_2\text{O}_4$  cells. The cells were cycled between cut-off voltages of 3.3 - 4.5 V, where the C-rate was 0.1 C.

### 3 RESULTS AND DISCUSSION

#### 3.1 Synthesis mechanism of $\text{LiMn}_2\text{O}_4$

The DTA-TGA curves of pure  $\text{Li}_2\text{CO}_3$  at a heating rate of 10 K/min in a flowing air are shown in Fig. 1. From the TGA curve in Fig. 1, it is easily found that the curve below 700 °C was smooth, which suggests that at that temperature the mass changed little. In the DTA curve below 700 °C there is no endothermic peaks and other peaks. Therefore, it can be deduced that these are no decomposition and phase change in  $\text{Li}_2\text{CO}_3$  below 700 °C. Only at about 720 °C, there is an obvious endothermic peak and  $\text{Li}_2\text{CO}_3$  begins to decompose. It is known from Ref. [9],  $\text{MnO}_2$  cannot decompose under 570 °C.

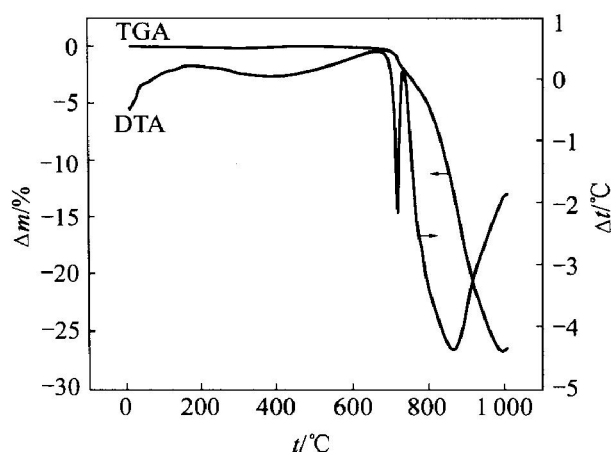
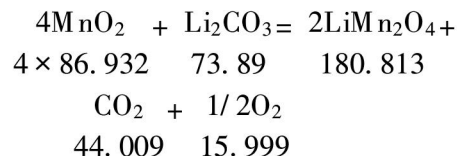


Fig. 1 DTA-TGA curve of  $\text{Li}_2\text{CO}_3$

Fig. 2 is the TGA curve of the precursor powder of the  $\text{LiMn}_2\text{O}_4$ . There is remarkable mass loss above 250 °C. At 600 - 800 °C the TGA curve is nearly linear, which proves that synthesis reaction occurs between 250 and 600 °C. According to the calculation of TGA data, the rate of mass loss is about 2.181% below 200 °C, which can be attributed to the alcohol burning, and 16.13% by 600 °C. Theoretically, for the following reaction:



the synthesis of  $\text{LiMn}_2\text{O}_4$  with  $\text{Li}_2\text{CO}_3$  and  $\text{MnO}_2$  should be

$$(44.009 + 15.999) / (4 \times 86.932 + 73.89) = 14.23\%$$

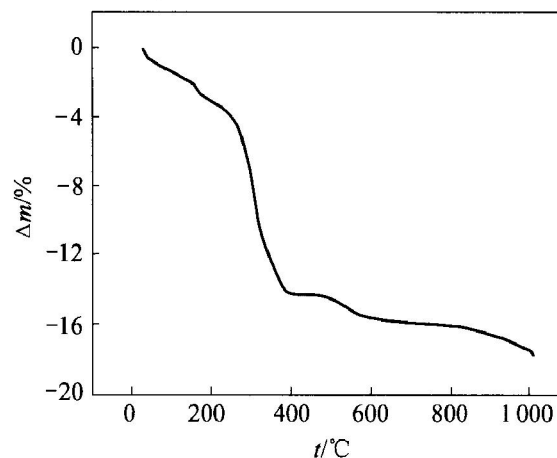


Fig. 2 TGA curve of precursor of  $\text{LiMn}_2\text{O}_4$

This means that the synthesis reaction occurs at 250 - 600 °C and finishes by 600 °C. Owing to decomposition of  $\text{LiMn}_2\text{O}_4$  above 850 °C<sup>[10]</sup>, mass loss occurs once again as shown by TGA curve in Fig. 2.

It could be seen from the above analysis that due to the soft-chemical treatment taken in advance,  $\text{LiMn}_2\text{O}_4$  was made from  $\text{MnO}_2$  and  $\text{Li}_2\text{CO}_3$  without single-phase decomposition, so that the synthesis reaction can proceed at lower temperature. Besides, it seems that  $\text{MnO}_2$  possesses catalysis function in the reaction process, which makes the synthesis reaction complete at lower temperature.

Fig. 3 shows the DTA curve of  $\text{LiMn}_2\text{O}_4$  precursor. There is an obvious peak on the curve, which owes to the alcohol loss. Meanwhile, there is a sharp peak at 320 °C, which results from reaction between  $\text{Li}_2\text{CO}_3$  and  $\text{MnO}_2$ . These results are consistent with the above analysis and further prove that the synthesis reaction finishes before 600 °C.

In order to know the reaction of the synthesizing process, XRD patterns of the sample at different temperatures (210, 450 and 600 °C) are shown in Fig. 4. As shown in Fig. 4(a), the outcomes are still  $\text{Li}_2\text{CO}_3$  and  $\text{MnO}_2$ , which further indicates that the peak at about 180 °C is due to the alcohol burning. Fig. 4(b) reveals that there is some spinel  $\text{LiMn}_2\text{O}_4$  at about 450 °C, but the reaction doesn't accomplish. The diffraction peaks in Fig. 4(c) are all  $\text{LiMn}_2\text{O}_4$ .

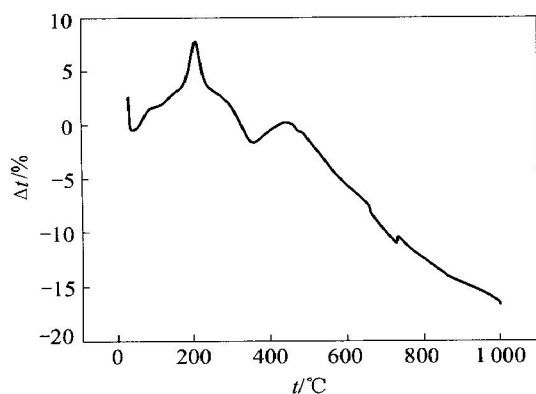


Fig. 3 DTA curve of precursor

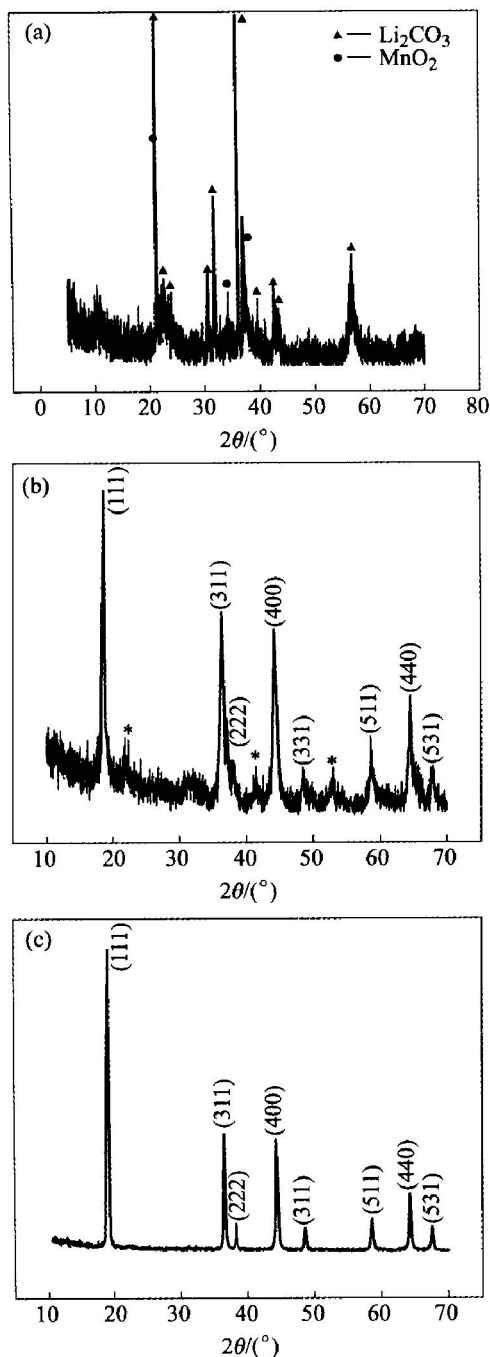


Fig. 4 XRD patterns of samples at different temperatures  
(a)  $-210\text{ }^{\circ}\text{C}$ ; (b)  $-450\text{ }^{\circ}\text{C}$ ; (c)  $-600\text{ }^{\circ}\text{C}$

peaks, which suggests that the prepared product is surely spinel  $\text{LiMn}_2\text{O}_4$ . There are several impurity phase peaks, but their intensities are much less than that of the spinel  $\text{LiMn}_2\text{O}_4$ . This might be caused by the incomplete crystal development. Thus the temperature must be increased to develop the crystal, but it must not be higher than  $850\text{ }^{\circ}\text{C}$ .

### 3.2 Structural analysis

In order to obtain the well-developed crystal of the spinel  $\text{LiMn}_2\text{O}_4$ , the sample were heated up to  $600\text{ }^{\circ}\text{C}$  with a heating rate of about  $5\text{ }^{\circ}\text{C}/\text{min}$  and kept for a certain time, and then heated at  $750\text{ }^{\circ}\text{C}$  for a certain time. The XRD pattern of  $\text{LiMn}_2\text{O}_4$  at  $750\text{ }^{\circ}\text{C}$  is shown in Fig. 5.

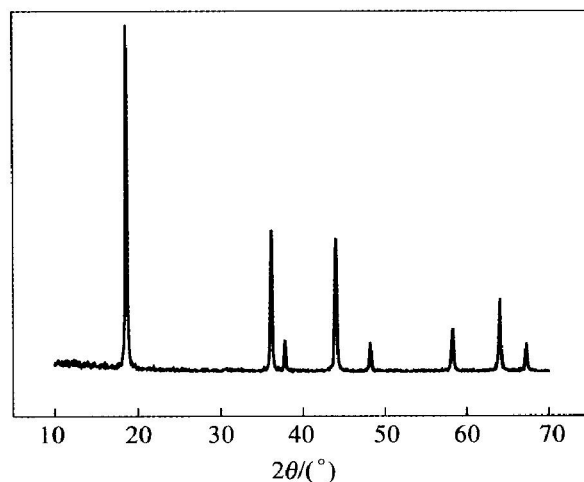


Fig. 5 XRD pattern of  $\text{LiMn}_2\text{O}_4$  at  $750\text{ }^{\circ}\text{C}$

There are no impurity phase peaks found but more sharper peaks compared to the samples at  $600\text{ }^{\circ}\text{C}$ . The spinel structure belongs to cubic structure with space group  $\text{Fd}3\text{m}$ . The lattice constant  $a$  can be calculated by the formula of cubic crystal gap and Bragg equation<sup>[11]</sup>

$$\alpha = \frac{\lambda}{2\sin\theta} \sqrt{H^2 + K^2 + L^2}$$

where  $\lambda$ —wavelength;  $\theta$ —diffraction angle;  $H$ ,  $K$ ,  $L$ —crystal index.

The calculated results are listed in Table 1.

Table 1 Lattice parameters of synthesized and standard  $\text{LiMn}_2\text{O}_4$

Parameter	Synthesized samples	Standard $\text{LiMn}_2\text{O}_4$
$I/I_{0[111]}$	100	100
$I/I_{0[311]}$	41	38
$I/I_{0[400]}$	39	33
$I/I_{0[440]}$	20	16
$d_{111}/\text{\AA}$	4.762 1	4.764 8
$a/\text{\AA}$	8.237 0	8.247 6

It can be known from the data listed in Table 1 that the three most intensive peaks (111), (311) and (400) for the synthesized samples are more intensive than that of standard spinel, are sharpen in peak shape, smaller in crystal gap and in crystal parameter  $a$ .

Thus, the higher temperature is beneficial to forming the perfect crystal of spinel  $\text{LiMn}_2\text{O}_4$ . However, the temperature cannot be too high because the formed  $\text{LiMn}_2\text{O}_4$  would be decomposed into the oxygen-deficient  $\text{LiMn}$  spinel oxide and release out oxygen<sup>[12]</sup>. This would bring about the oxygen deficiency and larger crystal units, and result in the poor performance.

Fig. 6 gives the SEM image of  $\text{LiMn}_2\text{O}_4$  at 750 °C. The spinel  $\text{LiMn}_2\text{O}_4$  is of regular appearance and a uniform granularity distribution.



Fig. 6 SEM image of  $\text{LiMn}_2\text{O}_4$  at 750 °C

### 3.3 Electrochemical properties of $\text{LiMn}_2\text{O}_4$

The initial charging/discharging curves of the spinel  $\text{LiMn}_2\text{O}_4$  prepared at 750 °C are shown in Fig. 7. The two charging plateaus of the synthesized samples are not very clear and nearly overlapped. Moret et al<sup>[13]</sup> found two charging plateaus (4.05 V and 4.15 V), and Chen et al<sup>[14]</sup> also found the similar phenomenon. However, the  $\text{LiMn}_2\text{O}_4$  prepared in this paper has only one charging plateau (about 4.09 V), which indicates that the materials in this method are more stable in structure and have perfect charging performance. But there are two obscure discharging plateaus, at about 4.05 V and 3.95 V, which is in agreement with the references. Fig. 8 presents the charging/discharging curves of the  $\text{LiMn}_2\text{O}_4$  in the first 5 cycles. During the cycles, the charging curves can overlap only two times, and then voltages increase, two charging plateaus occur. The reason is probably that the polarity increase causes voltage increase. On the other hand, the discharging curve was very stable, and almost overlapped at 5th cycle. The initial discharging capacity was 108.6  $\text{mA}\cdot\text{h/g}$ , and it was 109.6  $\text{mA}\cdot\text{h/g}$  after 5 cycles, which reveals that the material has a very good discharging performance. It is worth to mention that during discharg-

ing the initial capacity is not the highest, but the second highest is 111.7  $\text{mA}\cdot\text{h/g}$ . This is probably due to activation of the spinel  $\text{LiMn}_2\text{O}_4$  during charging/discharging process<sup>[15]</sup>.

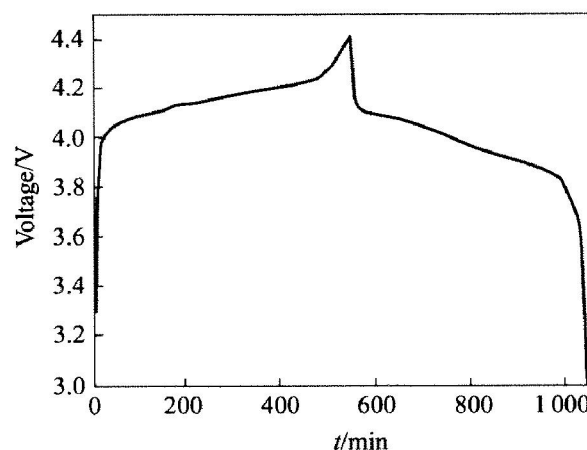


Fig. 7 Initial charging/discharging curve of sample

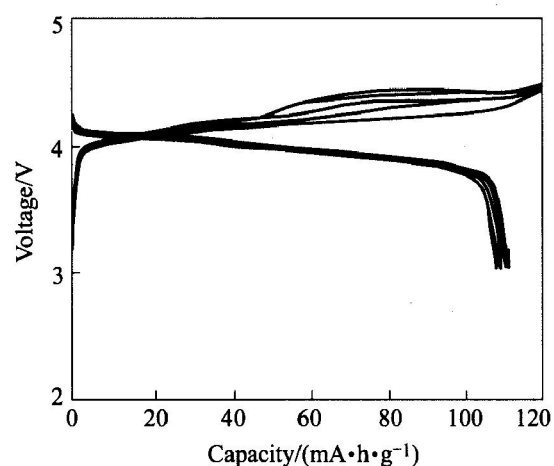


Fig. 8 First 5 cycles charging/discharging curves of  $\text{LiMn}_2\text{O}_4$

## 4 CONCLUSIONS

1) Before the decomposition of the pure  $\text{Li}_2\text{CO}_3$ ,  $\text{Li}_2\text{CO}_3$  and  $\text{MnO}_2$  react to form the spinel  $\text{LiMn}_2\text{O}_4$  directly, and the reaction can finish at a low temperature. The reaction is



2) Based on the mechanism, by combining the solid state reaction with soft-chemical treatment, the spinel  $\text{LiMn}_2\text{O}_4$  is prepared at 750 °C in the air. The XRD patterns of the samples show that the high temperature makes the spinel  $\text{LiMn}_2\text{O}_4$  more perfect in crystal, more compact in structure and more stable in properties.

3) The results of electrochemical test demonstrate that the spinel  $\text{LiMn}_2\text{O}_4$  prepared has only one charging plateau and two obscure discharging plateaus. A value of 109.6  $\text{mA}\cdot\text{h/g}$  of the discharging capacity retains after 5 cycles, expressing the mar-

terial possesses a perfect charging/ discharging performance.

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