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Microwave synthesis of $LiMn_2O_4$ cathode material

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Abstract

In order to reduce the cost of cathode materials, microwave synthesis method has been applied in the fast preparation of spinel $LiMn_2O_4$ by using $LiOH \cdot H_2O$ and MnO_2 (CMD) as starting materials. The structure, microstructure and electrochemical performance of the final product have been investigated. For optimum synthesis, the spinel $LiMn_2O_4$ should be prepared at a temperature between 700°C and 750°C. $LiMn_2O_4$ synthesized in optimum conditions delivers an initial charge capacity of 133 mA h/g, and exhibits good rechargeability. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Lithium-ion batteries; Microwave synthesis; $LiMn_2O_4$; Cathode material

1. Introduction

Although lithium-ion batteries have made considerable progress in both quality and quantity, the high price is still an important barrier restricting their applications. In order to make the use of lithium ion batteries more widely applicable, the price should be lowered. At present, the cathode material used currently in commercial lithium-ion batteries is $LiCoO_2$. It has higher energy density (140 mA h/g) and good reversibility, but its price is also very high. As substitution for $LiCoO_2$, spinel $LiMn_2O_4$ is one of the most promising cathode materials. Although its electrochemical capacity (120 mA h/g) is lower than that of $LiCoO_2$, the price of metal Mn is about 1/30 that of metal Co. $LiMn_2O_4$ has obvious advantages in terms of rich natural resources and lower cost. Moreover, the price of $LiMn_2O_4$ can be further reduced if the preparation process is simplified.

In the past 2 years, a new method, the microwave synthesis method, was developed in our laboratory to prepare cathode materials for Li-ion batteries [1,2]. In the microwave field, since the microwave energy is absorbed directly by the bulk of the heated object rather than being conducted from the outside, uniform and rapid heating can be achieved within a short time and at a temperature lower than that normally required. Therefore, energy consumption, processing time and cost as well are reduced significantly. In our previous work, pure and single-phase $LiCoO_2$ with fine and uniform grains can be synthesized in 10 min by microwave calcination. The product has high electrochemical capacity and good cycleability. All the results indicated that the microwave synthesis is a promising method for preparing cathode materials.

The purpose of this work is to investigate the effect of microwave synthesis on the structure and electrochemical properties of $LiMn_2O_4$.

2. Experimental

The microwave synthesis of $LiMn_2O_4$ was conducted in air with a 2.45 GHz multimode microwave oven. $LiOH \cdot H_2O$ and MnO_2 (CMD) were used as the starting materials and were mixed according to nominal composition. After thorough grinding, the material was preheated at 450°C for 10 min in a microwave oven. Then the powders were pressed into pellets and submitted to microwave calcination at a temperature ranging from 600°C to 850°C for 10 min. The temperature was measured with an infrared pyrometer.

The structures of all samples were determined by X-ray diffraction (XRD) analysis. XRD data were obtained from a BD86 powder diffractometer with Fe $K\alpha$ radiation. The microstructure of powder was observed using scanning electron microscopy (SEM).

The electrochemical characteristics of samples were studied using a two-electrode electrochemical cell. The

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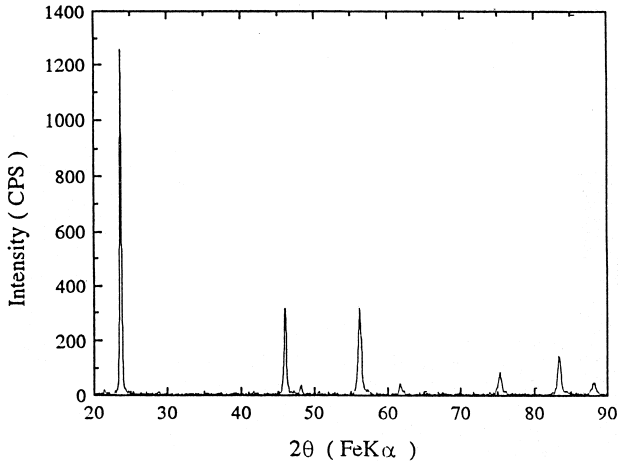

Fig. 1. X-ray diffraction patterns of microwave-synthesized $LiMn_2O_4$ at 700°C for 10 min.

working electrode consisted of 10–20 mg of $LiMn_2O_4$ (80 wt.%) with acetylene black (15 wt.%) and Teflon (5 wt.%). Metal lithium foil is used as the counter electrode. The electrolyte used was 1 M $LiPF_6$ in 1:1 EC/DMC solution. The separator is celgard 2400. The measurements of electrochemical capacity were carried out with an automatic charge/discharge instrument. Cells were charged and discharged at a constant current (0.8 mA/cm^2) in the voltage range between 3.5 and 4.5 V.

In order to examine the life cycle of $LiMn_2O_4$, an A-size Li-ion battery was prepared in which the cathode material was $LiMn_2O_4$ synthesized by microwave energy, the anode material was graphite and the electrolyte used was the same as above. The voltage range of charge/discharge test was set between 3.0 and 4.25 V.

3. Results and discussion

The results of microwave heating experiments show that the mixture of $LiOH \cdot H_2O$ and CMD can absorb and couple with microwave radiation efficiently. Usually it takes less than 10 min to reach the synthesis temperature from room temperature. Typical XRD pattern of microwave synthesized $LiMn_2O_4$ is given in Fig. 1. All the diffraction lines can be indexed on a cubic unit cell with $a = 8.2395(4)$ Å, which is in very good agreement with $LiMn_2O_4$ obtained from conventional calcination. The result indicates that a single-phase $LiMn_2O_4$ can be obtained by microwave heating at 700°C for 10 min.

Fig. 2 shows the SEM micrograph of the raw material CMD and microwave-synthesized $LiMn_2O_4$. It can be seen that the grain size of CMD is about 10–40 μm. For the $LiMn_2O_4$ synthesized at 700°C for 10 min, the grain size has very little change. The existence of a lot of small broken powders results from grinding. Thus, microwave heating will not cause obvious changes on the shape and size of the raw material grains. The morphology of the product powder is mainly decided by the starting material. This conclusion can be explained according to the character of rapid heating during microwave synthesis. When the heating rate is high, materials will pass through the lower-temperature regime where surface diffusion is more rapid, and the original microstructure will be maintained at higher temperature when grain boundary and lattice diffusion predominate over surface diffusion [3]. Therefore, the time available for grain growth is substantially shortened in this process. Since $LiOH \cdot H_2O$ melts at 460°C and impregnates the pores on the surface of CMD, it has little effect on the shape and size of the final product.

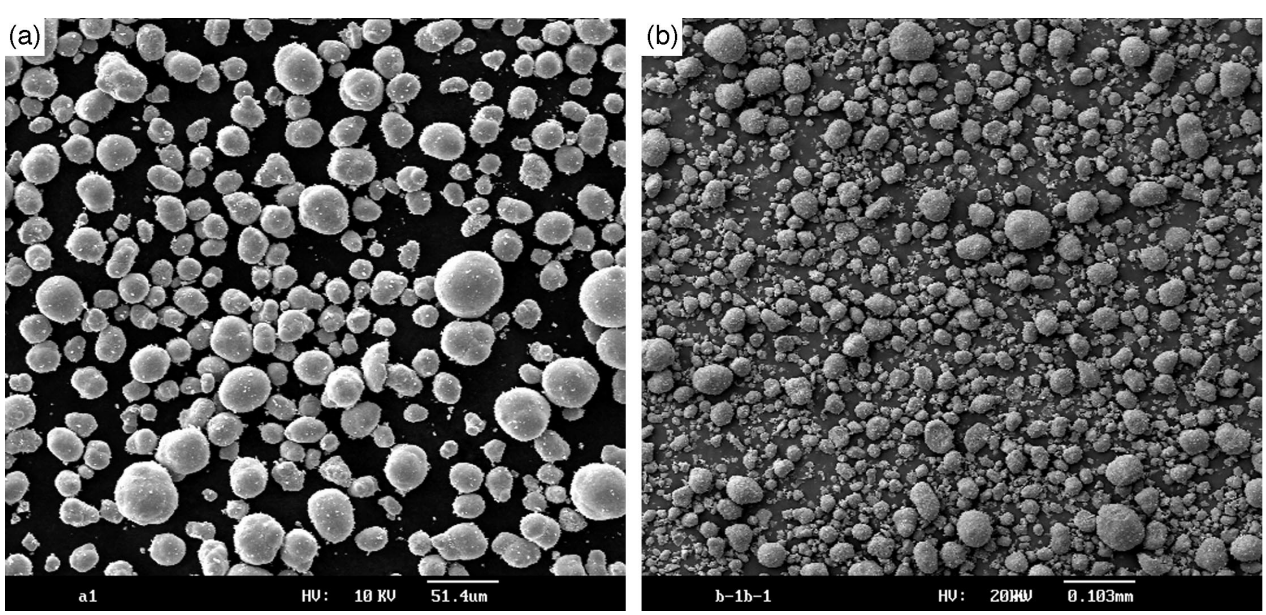

Fig. 2. Morphology of starting material CMD and microwave-synthesized $LiMn_2O_4$. (a) CMD; (b) microwave-synthesized $LiMn_2O_4$ at 700°C for 10 min.

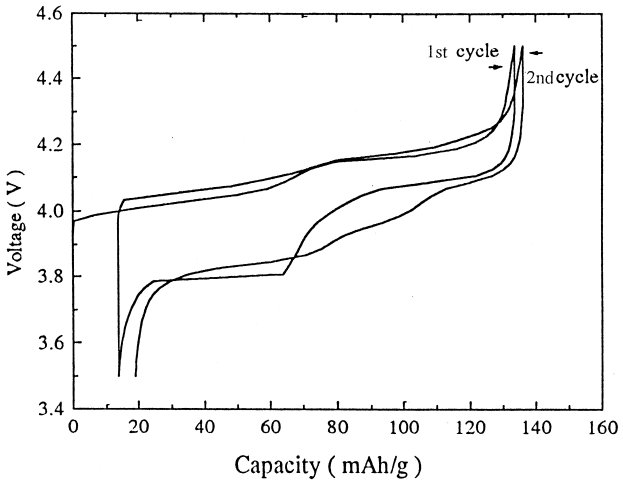

Fig. 3. Charge and discharge curves of $Li/LiMn_2O_4$ synthesized by microwave heating at 700°C for 10 min.

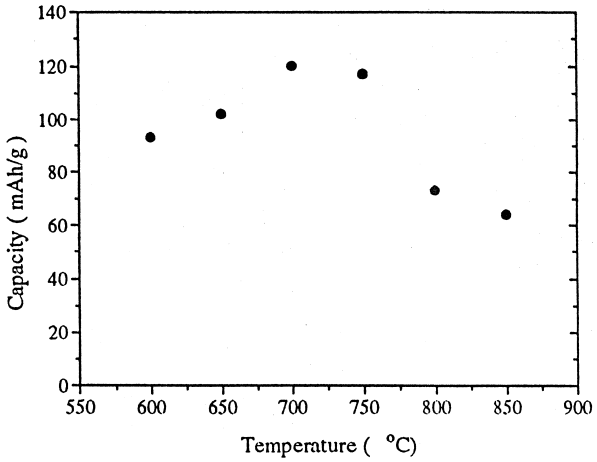

Fig. 5. Dependence of specific capacity on heat-treatment temperature for $LiMn_2O_4$ synthesized by microwave calcination for 10 min.

The lithium de-intercalation and intercalation behavior of microwave-synthesized $LiMn_2O_4$ were studied. Fig. 3 shows charge and discharge curves of cell $Li/LiMn_3O_4$ synthesized by microwave heating at 700°C for 10 min. It can be seen that its initial charge capacity is 133 mA h/g and discharge capacity is 120 mA h/g, which is a rather good result for $LiMn_2O_4$.

In order to optimize the structure and capacity of microwave synthesized $LiMn_2O_4$, effects of heating temperature on the structure was investigated. Fig. 4 shows XRD patterns of $LiMn_2O_4$ synthesized at 450°C for 10 min and at other temperatures for 10 min as well. The results indicated that a single-phase structure exists at a temperature lower than 800°C. For temperatures higher than or equal to 800°C, new peaks corresponding to Mn_3O_4 and Li_2MnO_3 appear due to the decomposition reaction of $LiMn_2O_4$. According to Tarascon et al. [4], when the spinel phase is heated to 900°C in air, it transforms to $LiMnO_2$:

$$3LiMn_2O_4 \rightarrow 3LiMnO_2 + Mn_3O_4 + O_2$$

$LiMnO_2$ is unstable in air below 900°C and will be oxidized according to the reaction:

$$3LiMnO_2 + 0.5O_2 \rightarrow LiMn_2O_4 + Li_2MnO_3$$

The decomposition temperature of $LiMn_2O_4$ observed in this study is lower than 900°C because the temperature of the inner part of the sample is higher than the surface temperature which was measured by an infrared pyrometer for the microwave heating. Therefore, the synthesis of $LiMn_2O_4$ by microwave energy should be carried out at a temperature lower than 800°C. Electrochemical capacity results of these samples have proven above viewpoint. As can be seen in Fig. 5, the discharge capacity of $LiMn_2O_4$ synthesized at 800°C or higher is lower than 80 mA h/g. While the synthesis temperature is in the range between

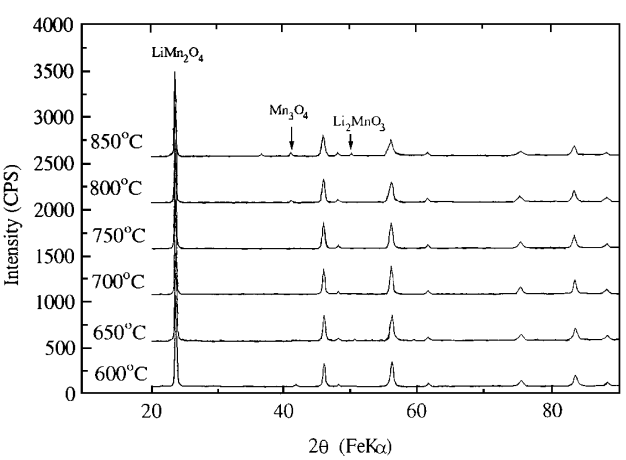

Fig. 4. XRD patterns of $LiMn_2O_4$ synthesized at 450°C for 10 min and at other temperatures (600°, 650°, 700°, 750°, 800° and 850°C) for 10 min.

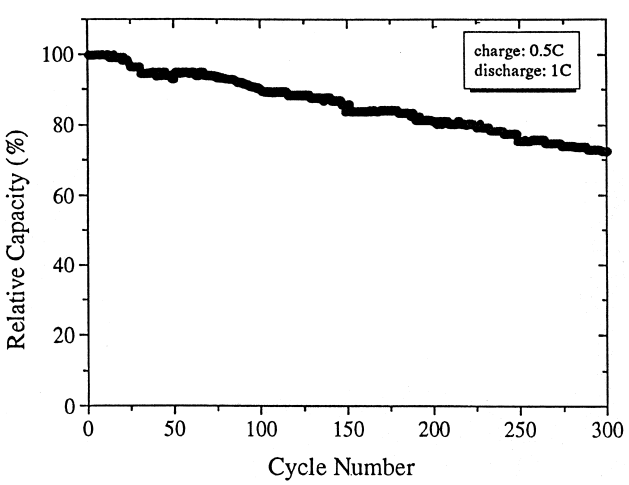

Fig. 6. Relative capacity vs. cycle number for A-size lithium-ion battery with $C/LiMn_2O_4$ synthesized by microwave energy according to optimum conditions. The first discharge capacity with 0.2 C rate was used as initial capacity and marked as 100%.

700° and 750°C, microwave-synthesized $LiMn_2O_4$ displays the highest capacity (120 mA h/g).

The rechargeability test of $LiMn_2O_4$ synthesized by microwave energy according to optimum conditions was performed by using an A-size C/$LiMn_2O_4$ Li-ion battery. First, it was charged and discharged with 0.2 C rate. The obtained capacity was regarded as the initial capacity and marked as 100%. Then the Li-ion battery was charged with 0.5 C rate and discharged with 1.0 C rate. The results are shown in Fig. 6. It can be seen that $LiMn_2O_4$ exhibits good reversibility. After 300 cycles the discharge capacity is still 72% of its initial capacity. When 0.2 C charge/discharge was used again, the remaining discharge capacity reached to 90% of its initial capacity.

4. Conclusions

Single-phase spinel $LiMn_2O_4$ can be synthesized quickly by microwave calcination. The shape and size of the produced powder are decided by the starting material, MnO_2. For optimum synthesis, the preparation of $LiMn_2O_4$ should be carried out at a temperature between 700° and 750°C. The obtained $LiMn_2O_4$ has high electrochemical capacity and good cycleability. The results indicate that microwave synthesis is a promising method for preparing $LiMn_2O_4$ cathode materials.

Acknowledgements

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