



## Short communication

A study of  $\text{LiMn}_2\text{O}_4$  synthesized from  $\text{Li}_2\text{CO}_3$  and  $\text{MnCO}_3$ X.H. Hu <sup>\*</sup>, X.P. Ai, H.X. Yang, Sh. X. Li*Wuhan University, Wuhan 430072, China*

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**Abstract**

Spinel  $\text{LiMn}_2\text{O}_4$  samples are prepared by heating a  $\text{Li}_2\text{CO}_3/\text{MnCO}_3$  mixture in air at various temperatures, and their structure and chemical performance are studied by using thermal analysis, X-ray diffraction, microelectrode voltammetry, and charge–discharge measurements. It was found that the electrochemical properties of the  $\text{LiMn}_2\text{O}_4$  samples are very sensitive to the synthesis temperature. The  $\text{LiMn}_2\text{O}_4$  powder obtained at  $800^\circ\text{C}$  yields a high initial capacity of  $\sim 115 \text{ mAh g}^{-1}$ , excellent cyclability, and has a good high-rate capability. © 1998 Elsevier Science S.A. All rights reserved.

*Keywords:* Lithium-ion battery; Capacity; Cycle life; Lithium carbonate; Manganous carbonate; Spinel lithiated manganese dioxide

**1. Introduction**

Lithium-ion batteries based on the use of manganese-lithiated oxides,  $\text{LiMn}_2\text{O}_4$ , as the positive electrode have received much attention because of the low cost and natural abundance of manganese oxide materials (e.g., electrolytic manganese oxide, EMD). Compared with  $\text{LiCoO}_2$  [1] or  $\text{LiNiO}_2$  [2,3], however,  $\text{LiMn}_2\text{O}_4$  exhibits a reduced discharge capacity and faster capacity fading, especially at elevated temperatures. These problems severely limit the practical use of  $\text{LiMn}_2\text{O}_4$  in lithium-ion batteries [4,5]. Since it is well-known that the physicochemical properties of spinel compounds are very sensitive to the thermal history of sample preparation, great efforts have been made to optimize the synthesis conditions. In previous work by Hunter [6], a 1:4  $\text{Li}_2\text{CO}_3/\text{EMD}$  mixture was heated at  $850^\circ\text{C}$ ; the product had a capacity of  $\sim 90 \text{ mAh g}^{-1}$ , and limited cyclability. This method was further improved by lowering the heating temperature to  $800^\circ\text{C}$  and resulted in an increased initial capacity of  $\sim 110\text{--}120 \text{ mAh g}^{-1}$ , but the cycle performance and rate capability were still not satisfactory [7]. Momchilov et al. [8] used  $\text{LiNO}_3$  (or  $\text{LiOH}$ ) and CMD as precursors and performed a programmed heating procedure which con-

sisted of a temperature sweep at  $5^\circ\text{C h}^{-1}$  in the range of  $330$  to  $550^\circ\text{C}$ , followed by sintering for  $75\text{--}200 \text{ h}$  at a temperature between  $650$  and  $750^\circ\text{C}$ . The spinel  $\text{LiMn}_2\text{O}_4$  thus prepared exhibited a high capacity of  $\sim 120 \text{ mAh g}^{-1}$  and an excellent rate capability. Later, Jian and Abraham [9] reported a synthesis process that used  $\text{Li}_2\text{CO}_3$  and  $\text{MnCO}_3$  as precursor materials and heating at  $650$  to  $850^\circ\text{C}$  in oxygen. In this paper, we report the synthesis of  $\text{LiMn}_2\text{O}_4$  by heating a mixture of  $\text{Li}_2\text{CO}_3$  and  $\text{MnCO}_3$  in air at  $480\text{--}900^\circ\text{C}$ .

**2. Experimental**

The  $\text{LiMn}_2\text{O}_4$  sample was prepared by mixing stoichiometric amounts of  $\text{Li}_2\text{CO}_3$  and  $\text{MnCO}_3$  (1:4 by mole number). The sample mixture was first ground by ball grinding and then pressed into pellet at about  $1000 \text{ kg cm}^{-2}$ . The pellets were heated at  $480^\circ\text{C}$  for about  $12 \text{ h}$ , and then held at a temperature of  $650\text{--}900^\circ\text{C}$  for about  $12 \text{ h}$ , and finally cooled to room temperature.

The charge–discharge properties of  $\text{LiMn}_2\text{O}_4$  was evaluated in simulated cell. The negative electrode and reference electrode were lithium sheets. The  $\text{LiMn}_2\text{O}_4$  electrode was made by mixing the  $\text{LiMn}_2\text{O}_4$  powder, carbon black and PTFE emulsion with isopropanol solution into a paste. The electrode sheet was obtained by rolling the

<sup>\*</sup> Corresponding author.

paste into a 0.15-mm thick membrane and then pressing on to an aluminum foil. The positive electrode contained 7 wt.% carbon black and 5 wt.% PTFE by weight and had a surface area of 0.64 cm<sup>2</sup> with about 10 mg active material. The electrolyte was 1 M LiClO<sub>4</sub> dissolved in a 1:1 mixture of propylene carbonate (PC) and dimethoxyethane (DME).

The powder microelectrode was prepared by etching the tip of a platinum microdisc electrode (diameter 60 μm) in a hot mixed solution of hydrochloric acid and nitric acid for about 10 min to form a microcavity. The LiMn<sub>2</sub>O<sub>4</sub> powder was filled into the microcavity by the gently grinding in the powder on the surface of flat plate. Cyclic voltammetry (CV) experiments were carried out with a two-electrode configuration. The counter and reference electrodes were pure silver wire covered with Ag<sub>2</sub>O on the surface. The electrolyte was 1 M LiClO<sub>4</sub>/PC + DME (1:1).

The TG and DTA data were obtained using a PRT2 type thermal analyzer made by the Beijing Optical Instrument Factory; the scan rate was 10°C min<sup>-1</sup>. Powder X-ray diffraction of the samples was recorded on a Rigaku Rotaflex RU-200B diffractometer with CuKα radiation.

### 3. Results and discussions

The thermogravimetric curves of pure Li<sub>2</sub>CO<sub>3</sub> and pure MnCO<sub>3</sub>, as well as an 1:4 mixture of the two, are shown in Fig. 1. Pure Li<sub>2</sub>CO<sub>3</sub> displays no significant weight loss until 700°C. When the temperature rises to 600°C, MnCO<sub>3</sub> loses 31.5% of its weight. This corresponds to the decomposition of MnCO<sub>3</sub> completely into Mn<sub>2</sub>O<sub>3</sub> and CO<sub>2</sub>. It is rather puzzling that the mixture of 1:4 Li<sub>2</sub>CO<sub>3</sub>/MnCO<sub>3</sub> undergoes a weight loss earlier than either MnCO<sub>3</sub> or Li<sub>2</sub>CO<sub>3</sub>; it loses 35% of its weight below 460°C. This suggests that an accelerating catalytic decomposition takes place when Li<sub>2</sub>CO<sub>3</sub> and MnCO<sub>3</sub> coexist. By stoichiometric calculation, the decomposition products are most likely

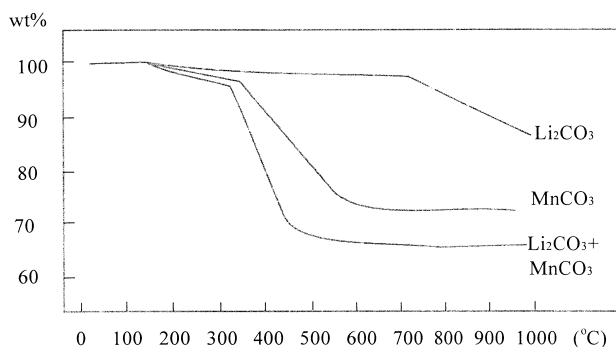


Fig. 1. TG curves of Li<sub>2</sub>CO<sub>3</sub>, MnCO<sub>3</sub> and 1:4 Li<sub>2</sub>CO<sub>3</sub>/MnCO<sub>3</sub>. Scan rate: 10°C min<sup>-1</sup>.

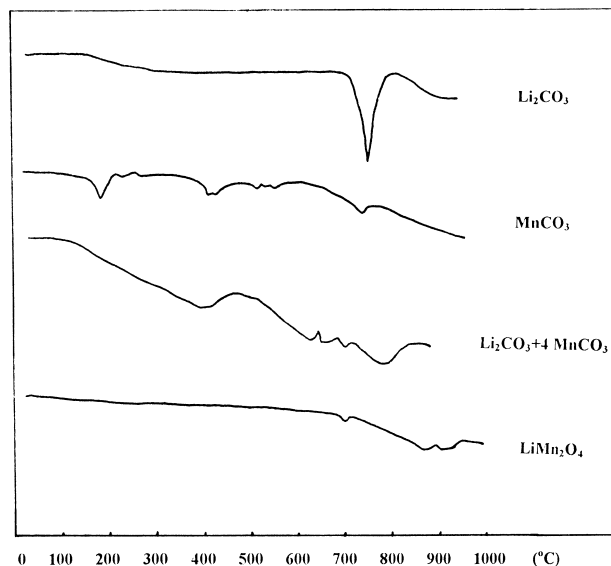


Fig. 2. DTA curves for Li<sub>2</sub>CO<sub>3</sub>, MnCO<sub>3</sub>, 1:4 Li<sub>2</sub>CO<sub>3</sub>/MnCO<sub>3</sub>, and LiMn<sub>2</sub>O<sub>4</sub> obtained at 800°C for 12 h.

Li<sub>2</sub>O and Mn<sub>2</sub>O<sub>3</sub>. The DTA curves of Li<sub>2</sub>CO<sub>3</sub>, MnCO<sub>3</sub>, their 1:4 mixture, and LiMn<sub>2</sub>O<sub>4</sub>, are shown in Fig. 2. The DTA curve of the Li<sub>2</sub>CO<sub>3</sub>/MnCO<sub>3</sub> mixture displays three isothermal peaks at 650, 700 and 780°C. Since there are no

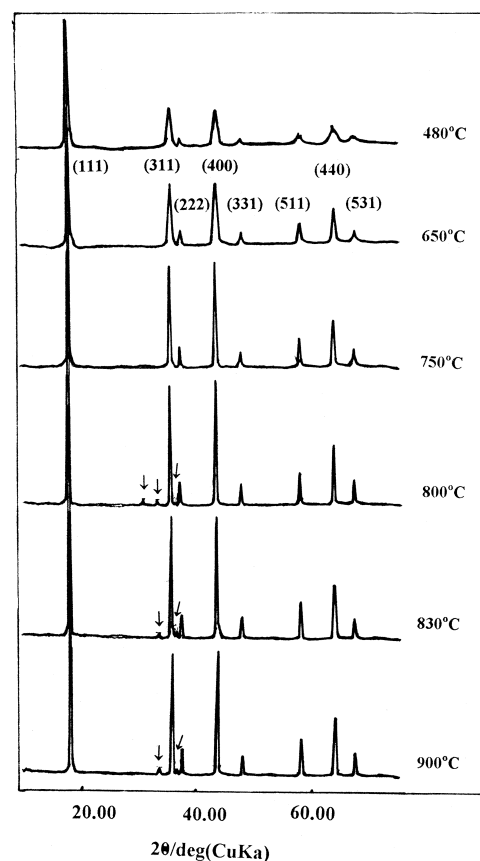


Fig. 3. XRD patterns of LiMn<sub>2</sub>O<sub>4</sub> obtained at different temperatures. ↓: Diffraction lines of Li<sub>2</sub>MnO<sub>3</sub> phase.

Table 1  
Initial capacity and cycle performance of  $\text{LiMn}_2\text{O}_4$  obtained at different temperatures

Heating temperature (°C)	Initial discharge capacity (0.5C rate) ( $\text{mA g}^{-1}$ )	Life performance (cycle number) (discharge capacity) (100% DoD, 1C rate)
480	95	poor
650	115	35 ( $80 \text{ mAh g}^{-1}$ )
750	112.5	75 ( $80 \text{ mAh g}^{-1}$ )
800	115	136 ( $90 \text{ mAh g}^{-1}$ )
830	110	50 ( $80 \text{ mAh g}^{-1}$ )
900	112.5	48 ( $80 \text{ mAh g}^{-1}$ )

corresponding weight losses on the TG curve, phase transformations must exist at 650, 700 and 780°C. On the other hand, the XRD patterns (Fig. 3) of the  $\text{Li}_2\text{CO}_3/\text{MnCO}_3$  mixture at 480°C shows clearly the characteristic peaks of the spinel structure, e.g., the (111), (311) and (400) peaks, though the peaks are relatively broad and some peaks are split into several, smaller peaks. This suggests that the material begins to form a distorted spinel structure. On increasing the heating temperature, peak widths become narrower and the relative intensities of the (311) and (400) peaks increase, indicating crystallization of  $\text{LiMn}_2\text{O}_4$ . When the heating temperature exceeds 800°C, some peaks characteristic of  $\text{Li}_2\text{MnO}_3$  appear and their relative intensity increases with increase in the heating temperature. Given these observations, it be deduced that the mixed  $\text{Li}_2\text{CO}_3/\text{MnCO}_3$  is decomposed completely to  $\text{Li}_2\text{O}$  and  $\text{Mn}_2\text{O}_3$  below 480°C, and this is accompanied by the appearance of a spinel structure. With increasing heating temperature, the crystallites of the spinel  $\text{LiMn}_2\text{O}_4$  grow and become ordered. When the reaction temperature reaches 750°C, a well-ordered spinel structure  $\text{LiMn}_2\text{O}_4$  is produced. When the heating temperature exceeds 800°C however, the spinel tends to rearrange, appearing predominantly as  $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$  ( $x > 0$ ) rather than  $\text{LiMn}_2\text{O}_4$ . This leads to the formation of  $\text{Li}_2\text{MnO}_3$  at higher temperatures.

Table 1 shows the initial capacity and cyclic performance of  $\text{LiMn}_2\text{O}_4$  obtained at different heating tempera-

tures. The data were measured by using a simulated cell at a constant current (1C rate). In the temperature range from 650 to 900°C, all the materials exhibit an initial capacity of 110–115  $\text{mA g}^{-1}$ , but cycling life changes dramatically. For samples obtained below 750°C, and higher than 800°C, the capacities decrease with cycling. In general, after several tens of cycles, the discharge capacity is reduced to 70% of the initial value. For the  $\text{LiMn}_2\text{O}_4$  powder obtained at 800°C however, about 80% of the initial capacity can delivered even after 136 cycles.

The discharge curves of the  $\text{LiMn}_2\text{O}_4$  obtained at 800°C at various current densities are presented in Fig. 4. For a discharge current below 0.5C, the capacity is almost the same about 115  $\text{mA g}^{-1}$ . Even at the 2.0C rate, the capacity is only slightly decreased to 105  $\text{mA g}^{-1}$ . This is a very good rate capability.

CV studies have been performed with a microelectrode technique to calibrate the electrochemical properties of the  $\text{LiMn}_2\text{O}_4$  material. The main feature of the CV curve is two reversible oxidation/reduction peaks, at 4.05 and 4.15 V, that characterize  $\text{Li}^+$  insertion into and de-intercalation from the lattice. On increasing the scan rate [2] from 1 to 50  $\text{mV s}^{-1}$  (Fig. 5), the peak current increases in propor-

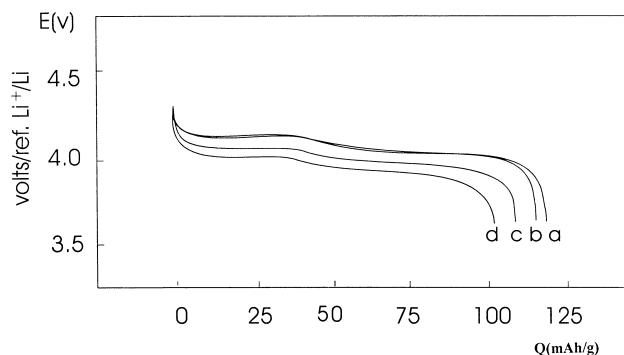


Fig. 4. Discharge curves of  $\text{LiMn}_2\text{O}_4$  (800°C) at different current densities: (a)  $25 \text{ mA g}^{-1}$ ,  $I = 0.365 \text{ mA cm}^{-2}$ ; (b)  $55 \text{ mA g}^{-1}$ ,  $I = 0.8 \text{ mA cm}^{-2}$ ; (c)  $110 \text{ mA g}^{-1}$ ,  $I = 1.6 \text{ mA cm}^{-2}$ ; (d)  $220 \text{ mA g}^{-1}$ ,  $I = 3.2 \text{ mA cm}^{-2}$ .

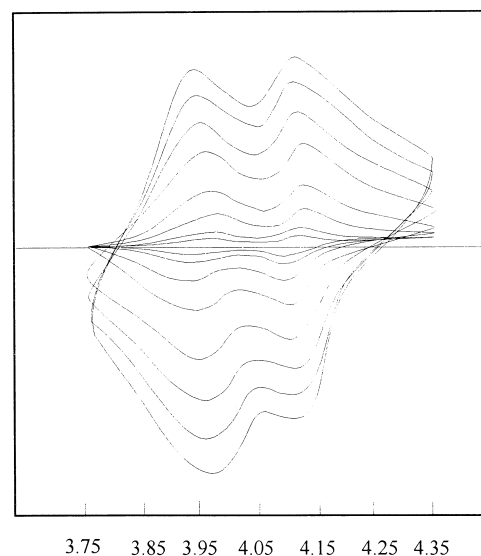


Fig. 5. The CV curves for  $\text{LiMn}_2\text{O}_4$  (800°C) at different scan rate. Scan rate: 1, 2, 5, 10, 20, 30, 40, 50  $\text{mV s}^{-1}$  (from inner to the outer).

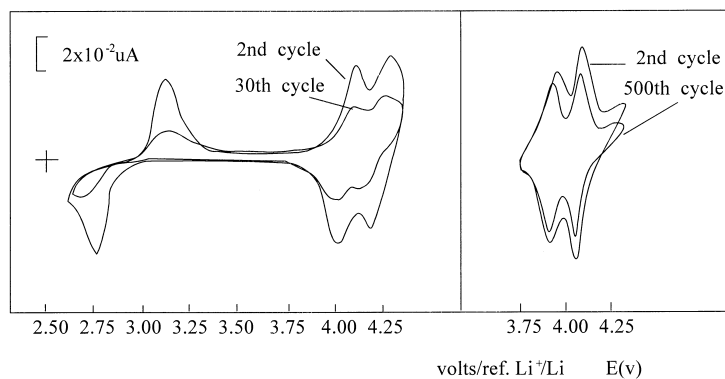


Fig. 6. CV curves for  $\text{LiMn}_2\text{O}_4$  ( $800^\circ\text{C}$ ) over different scan ranges. Scan rate:  $10 \text{ mV s}^{-1}$ .

tion to  $\nu_{1/2}$ . This indicates reversible  $\text{Li}^+$  intercalation and a diffusion-controlled process.

The CV curves for  $\text{LiMn}_2\text{O}_4$  ( $800^\circ\text{C}$ ) over different scan ranges are shown in Fig. 6. In the potential region 3.75–4.35 V vs.  $\text{Li}^+/\text{Li}$ , the electrical quantity of the current peaks after 500 cycles has become slightly decreased and still has 85% of its initial value. When the sweeping potential is extended to 2.6 V, the peak current decays rather rapidly with increasing cycles. This suggests an excellent cyclability for the  $\text{LiMn}_2\text{O}_4$  in normal charge–discharge potential region, but a faster capacity decay in an over-discharged state.

#### 4. Conclusion

$\text{LiMn}_2\text{O}_4$  made from a  $\text{Li}_2\text{CO}_3/\text{MnCO}_3$  mixture at a relatively low temperature has an enhanced discharge capacity, improved cyclability, and good rate capability in

comparison with that synthesized from a  $\text{Li}_2\text{CO}_3/\text{EMD}$  mixture.

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