

Studies on an Li–Mn–O spinel system (obtained by melt-impregnation) as a cathode for 4 V lithium batteries

Part 1. Synthesis and electrochemical behaviour of $\text{Li}_x\text{Mn}_2\text{O}_4$

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Abstract

An $\text{Li}_x\text{Mn}_2\text{O}_4$ spinel phase is used as a cathode for 4 V lithium batteries and is prepared by the melt-impregnation method, in which melted LiOH or LiNO_3 is impregnated into MnO_2 pores, then reacted with MnO_2 at higher temperature. The effect of synthesis conditions on the electrochemical properties is investigated extensively. For optimum synthesis, the spinel $\text{Li}_x\text{Mn}_2\text{O}_4$ should be prepared in an N_2 atmosphere at a low temperature of less than 750 °C and for a short time of less than 48 h. The optimum LiMn_2O_4 delivers an initial charge capacity of 135 mAh/g, and exhibits good rechargeability. The average specific capacity during first 50 cycles is about 120 mAh/g or more.

Keywords: Lithium; Lithium-ion batteries; Manganese oxides; Lithiated manganese oxides; Spinel

1. Introduction

Secondary lithium batteries have been studied for the past two decades because they exhibit the highest specific energy among the rechargeable batteries. Nevertheless, the safety and rechargeability associated with use of metallic lithium prevent its widespread acceptance in the marketplace. Unsatisfactory results with lithium metal has directed research towards the development of so-called ‘rocking-chair lithium’ or ‘lithium-ion’ rechargeable batteries. These systems were first commercialized by Sony Energytec, Inc. in 1990 [1] and used carbon as an anode. Promising candidate materials for cathodes in ‘lithium-ion’ batteries are LiCoO_2 [1], LiNiO_2 [2], $\text{LiCo}_x\text{Ni}_{1-x}\text{O}_2$ [3] and spinel $\text{Li}_x\text{Mn}_2\text{O}_4$ [4–6].

$\text{Li}_x\text{Mn}_2\text{O}_4$ offers several advantages in terms of low cost, easy preparation and no toxicity [4]. The common method of preparation was first described by Hunter [7], but the resulting compounds prepared by that procedure exhibit low capacity and poor reversibility. A marked improvement in the preparation of spinel $\text{Li}_x\text{Mn}_2\text{O}_4$ with large capacity can be achieved [8] by reacting stoichiometric amounts of Li_2CO_3 and MnO_2 in air with three consecutive anneals at 800 °C (each for 24 h), and then further grounded to obtain a lithiated sample with particles of about 1–2 μm [8].

Although this technique can be carried out in air, it is too complex to apply on industrial scale. More recently, a simple and cheap process route for synthesizing the Li–Mn–O spinel system was reported by Mannev and co-workers [9,10]. This involved a direct synthesis by reacting LiNO_3 or LiOH with chemical manganese oxide (CMD). Optimum results were obtained for a reaction time of 75 to 200 h at a temperature between 650 and 750 °C.

A useful method for producing lithiated compounds may be melt-impregnation process that was suggested initially by Yoshio et al. [11,12]. The principle of this method is as follows. The mixture is first heated at the temperature of the melting point of the selected lithium salt. The molten LiNO_3 (260 °C) or LiOH (460 °C) impregnates the pores on the surface of the metal oxides and, thereby, forms a homogeneous mixture. The final product is obtained from impregnation of the metal oxides with LiNO_3 or LiOH at the desired temperature. One advantage of the compounds produced by this method is the application of a lower final heating temperature, rather than a higher surface area, so that the resulting compounds can practically retain the original pore shape of the metal oxides. The authors have successfully obtained several Li–Mn–O compounds, e.g., $\text{Li}_{0.3}\text{MnO}_2$ and disordered $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$, as cathodes for 3 V and 4 V lithium batteries by this method [12]. It has also been possible to obtain a spinel $\text{Li}_x\text{Mn}_2\text{O}_4$ with a high specific capacity and

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good reversibility in an N_2 atmosphere for a short time and at a low temperature of less than $750^\circ C$. These conditions are closer to industrial practice. This paper reports the synthesis and battery performance of spinel $Li_xMn_2O_4$ prepared from reaction of $LiNO_3$ or $LiOH$ with CMD or electrochemical manganese oxide (EMD).

2. Experimental

The typical procedure for the preparation of $Li_xMn_2O_4$ is as follows: EMD (International common sample No. 17, EMD–Mitsui Metal and Smelting Co., Ltd.) and $LiNO_3$ were mixed with different ratios of Mn and Li (the detail ratio is given below). The $LiNO_3$ was first dried at $120^\circ C$ for more than 5 h to remove adsorbed water. The mixture was ground well in a mortar. After thorough mixing, the material was preheated to $260^\circ C$ for 12 h in air. During this latter process, $LiNO_3$ was melted and impregnated into the EMD pores. The mixture was cooled, reground, and then heated continuously in an N_2 atmosphere at different temperatures for various times. When $LiOH$ was used as the lithium source, the preparation process was the same as that for $LiNO_3$, except for the preheating temperature. The detailed conditions are given below.

The compositions of the samples were determined by atomic adsorption spectroscopy and chemical analysis. The structure was determined by X-ray diffraction (XRD) analysis.

A Gemini 2375 instrument was used for the analysis of specific surface area by the BET method in which N_2 gas adsorption was employed. The samples were heated at $200^\circ C$ for 20 min to remove adsorbed water. Thermogravimetric analysis was performed in order to study the dependence of weight loss from the samples at the heat-treatment temperature; the experiments were conducted in N_2 gas. The sample was heated at $10^\circ C$ per min from room temperature to $800^\circ C$.

The charge and discharge characteristics of the cathode were examined in a laboratory cell. The cell comprised a cathode and a lithium metal anode that were separated by a separator and glass fibre. The cathode consisted of 25 mg active material and 15 mg conducting binder (acetylene black–polytetrafluoroethylene composite). The mixture was pressed on to a stainless screen at 800 kg/cm^2 , and dried at $200^\circ C$ for 24 h. The electrolyte solution was 1 M $LiPF_6/EC$ (ethylene carbonate)–DMC (dimethylcarbonate). The EC and DMC was in a 1:2 volume. Cycling of the test material was performed in CR2032-type button cell. Cell fabrication was carried out in a dry box. Cells were cycled in the range 3.5–4.5 V, and the typical charge and discharge current was 0.4 mA/cm^2 , except where otherwise specified. Other sets of experimental conditions are given below.

3. Results and discussion

3.1. $LiNO_3$ –EMD system

3.1.1. Effect of starting material ratio on the preparation of $Li_xMn_2O_4$ ($1.0 < x < 1.14$)

Mixtures of $LiNO_3$ and EMD (IC-17) with different molar ratios of Li to Mn (from 0.5 to 0.6) were heated at $260^\circ C$ for 12 h and at $650^\circ C$ for 24 h. The structures of all the samples were determined by XRD analysis. Typical XRD patterns are given in Fig. 1. The results indicate that a single spinel phase exists in the range of $1.0 < x < 1.14$ in $Li_xMn_2O_4$. This finding is consistent with other studies [13], in which single spinel phase $Li_xMn_2O_4$ ($0.95 < x < 1.15$) was obtained in air by repeated grinding. The observation here that a single phase compound with the wide range of x values in $Li_xMn_2O_4$ was obtained with only a single grinding is due to the homogeneous distribution of Li in MnO_2 particles during the metalization process of $LiNO_3$. For $x > 1.14$, new peaks that share the signature of Li_2MnO_3 appear. It is reasonable that a high content of Li is effective in forming the rock salt structure Li_2MnO_3 at low temperature. The calculated lattice parameter

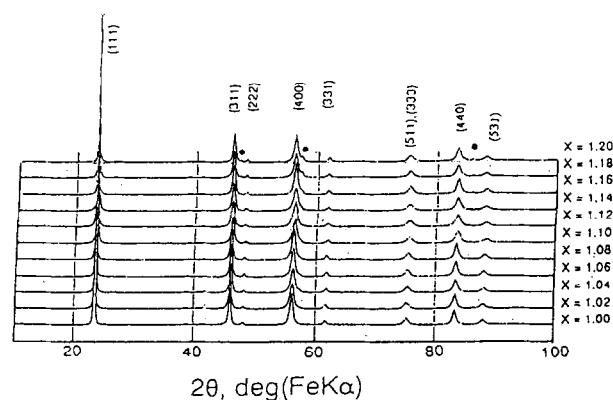


Fig. 1. Powder X-ray diffraction patterns for spinel $Li_xMn_2O_4$ ($1.0 < x < 1.20$) obtained from $LiNO_3$ reacted with EMD with various molar ratios of Li to Mn at $260^\circ C$ for 12 h in air and at $650^\circ C$ for 24 h in N_2 . Peaks corresponding to Li_2MnO_3 phase are marked by solid circles.

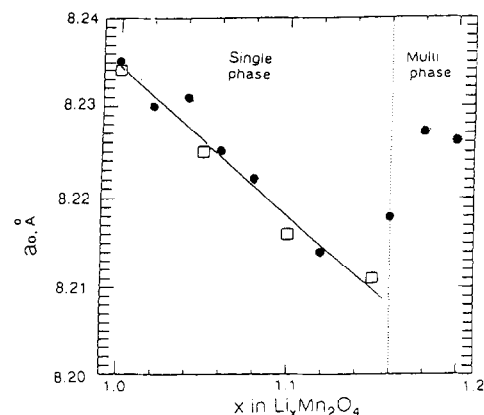


Fig. 2. Variation of cubic lattice parameter a_0 as a function of composition x in $Li_xMn_2O_4$ ($1.0 < x < 1.2$): (●) this work, and (□) Tarascon (Ref. [13]).

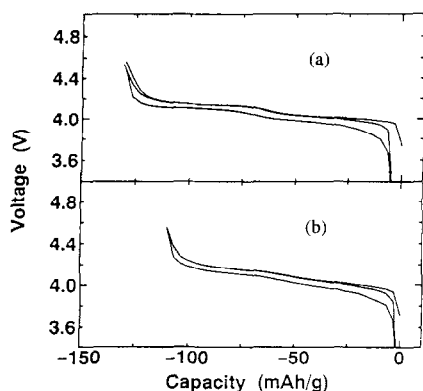


Fig. 3. Charge/discharge curves of (a) LiMn_2O_4 and (b) $\text{Li}_{1.1}\text{Mn}_2\text{O}_4$. Current density = 0.4 mA/cm^2 .

a_0 is plotted in Fig. 2 as a function of composition x . The a_0 -axis of the cubic unit-cell decreases with increasing x . The lattice parameter a_0 lies between 8.234 and 8.214 Å for the single phase spinel. Both the capacity and the rechargeability depend on the value of the cell volume. A small cell volume would lead to low capacity and excellent rechargeability.

Charge/discharge profiles were obtained for all the compounds. Typical curves for various samples of LiMn_2O_4 and $\text{Li}_{1.1}\text{Mn}_2\text{O}_4$ are given in Fig. 3. LiMn_2O_4 yields a voltage profile of a spinel electrode with the characteristic two-step process at 4 V, and delivers an initial charge capacity of 130 mAh/g. On the other hand, a lower initial capacity of 113 mAh/g is given by $\text{Li}_{1.1}\text{Mn}_2\text{O}_4$, which behaves as a quasi-one step process. The initial charge capacity decreases with increase in the molar ratio of Li to Mn. If the compound with excess Li over Mn (reference to stoichiometric spinel LiMn_2O_4) is simply described by the formula $\text{Li}_x\text{Mn}_2\text{O}_4$ ($1 < x < 1.14$), it is easily envisaged that it should deliver a larger initial capacity, but the results show the reverse behaviour. Chemical analysis indicates that the average manganese valence is 3.513 and 3.590 for LiMn_2O_4 and $\text{Li}_{1.1}\text{Mn}_2\text{O}_4$, respectively. It is most probable that the Li-rich spinel $\text{Li}_4\text{Mn}_5\text{O}_{12}$ (manganese valency = 4) is formed together with the LiMn_2O_4 . As shown by several authors [14–16], the XRD pattern of $\text{Li}_4\text{Mn}_5\text{O}_{12}$ cannot be distinguished easily from that of LiMn_2O_4 . Moreover, $\text{Li}_4\text{Mn}_5\text{O}_{12}$ is not an active material for a 4 V cathode, whereas it is used widely as a 3 V cathode for Li batteries.

3.1.2. Effects of heating temperature and time

The dependence of the surface area and initial charge capacity on synthesis duration for the sample $\text{Li}_{1.04}\text{Mn}_2\text{O}_4$ synthesized at 260°C for 12 h in air and at various temperatures for 24 h in N_2 is presented in Fig. 4. The surface area decreases as the temperature is raised, while a plateau between 700 and 800°C is observed. The first charge capacity decreases from a temperature higher than 700°C , which may be attributed to a disturbed structure that results from weight loss by the sample at high temperatures.

The effect of heating time on the surface area and specific capacity was also investigated. The samples were heat treated

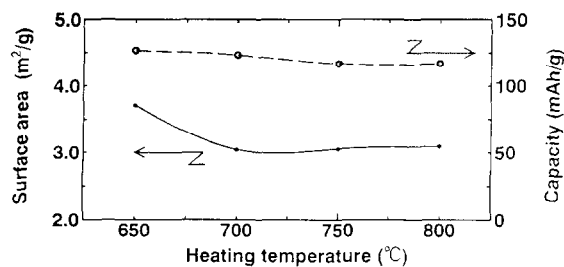


Fig. 4. Dependence of surface area and specific capacity on heat-treatment temperature for $\text{Li}_{1.04}\text{Mn}_2\text{O}_4$ obtained from LiNO_3 on reaction with EMD at 260°C for 12 h in air and at different temperatures for 24 h in N_2 .

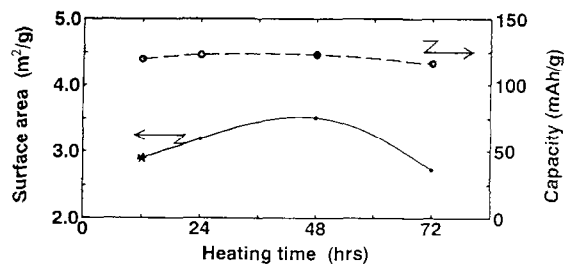


Fig. 5. Effect of synthesis duration on surface area and specific capacity of $\text{Li}_{1.04}\text{Mn}_2\text{O}_4$ produced from LiNO_3 on reaction with EMD at 260°C for 12 h in air and at 700°C for various times in N_2 . The point indicating heating at 700°C for 12 h twice is marked by an asterisk.

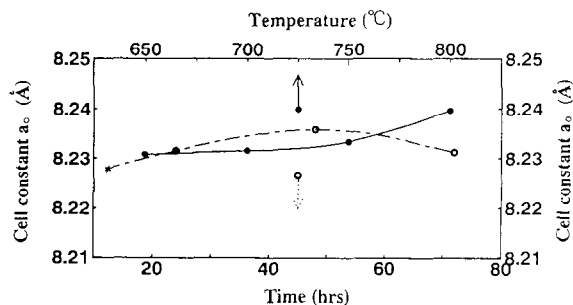


Fig. 6. Dependence of cubic unit-cell constant a_0 on heat-treatment temperature and time for spinel $\text{Li}_{1.04}\text{Mn}_2\text{O}_4$. The point indicating heating at 700°C for 12 h twice is marked by an asterisk.

initially at 260°C for 12 h, and then heated continuously at 700°C for two periods of 12, 24, 48 and 72 h. The effect on the surface area and first charge capacity is displayed in Fig. 5. The surface area increases with time, and a well-defined maximum between 24 and 48 h, is observed; further heating at 72 h reduces the surface area. The specific capacity is consistent with the distribution tendency of the BET surface area.

The dependence of the cubic unit-cell constant, a_0 , on heat-treatment temperature and time for $\text{Li}_{1.04}\text{Mn}_2\text{O}_4$ is demonstrated in Fig. 6. The a_0 parameter increases with rise in temperature. In contradiction with this, the first charge specific capacity decreases, as shown in Fig. 5. This is interpreted in terms of O_2 loss: the O_2 loss increases with an increase in the heating temperature, as shown in Fig. 7. The weight loss starts at 600°C , and reaches a value of 3% at 800°C . Such changes in O_2 must affect the composition and structure of

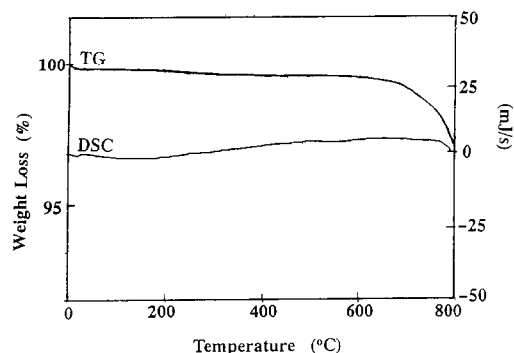
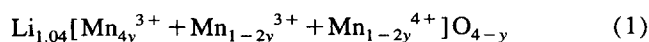


Fig. 7. Thermal analysis (thermal gravity and differential scanning calorimetry) for $\text{Li}_{1.04}\text{Mn}_2\text{O}_4$ obtained from LiNO_3 and EMD heated in N_2 at rate of 10°C per min from room temperature to 800°C .

the spinel compound. In order to maintain the charge balance in $\text{Li}_{1.04}\text{Mn}_2\text{O}_4$, O_2 loss causes Mn^{4+} reduction to Mn^{3+} . For this partially-reduced spinel, the chemical formulation can be represented by [9,17]:



Here, y is not the molar fraction of lost O_2 . Mn_{4y}^{3+} cannot be transformed to Mn^{4+} during the de-intercalation of Li ions, and this causes the specific capacity to decrease. Furthermore, O_2 loss produces a decrease in the attraction force between the Mn and O ions and, therefore, an expansion of cell-unit volume. It can be concluded that the proper heating temperature for synthesis of spinel $\text{Li}_x\text{Mn}_2\text{O}_4$ may lie in the range 650 to 750°C .

The dependence of heating time on the a_0 -axis of the cubic unit-cell of $\text{Li}_{1.04}\text{Mn}_2\text{O}_4$ is given in Fig. 6. The maximum value of the cell constant a_0 was obtained for a heating time of between 24 and 48 h; the resulting compounds yield large capacity. This suggests that the optimum value of the a_0 -axis parameter lies in the range 8.23 – 8.24 \AA . It should be noted, however, that the value of a_0 of compounds that deliver low capacity and better rechargeability is less than 8.23 \AA .

As a general conclusion, the optimum synthesis conditions for spinel $\text{Li}_x\text{Mn}_2\text{O}_4$ ($1.0 < x < 1.14$) prepared by LiNO_3 reaction with EMD are: 650 – 750°C for less than 48 h in N_2 atmosphere, combined with preheating at 260°C in air. A high heating temperature and a long process time will lead to a decrease in specific capacity. The latter results from a decrease in surface area and a disturbed stoichiometry.

On the basis of environmental acceptability, the toxicity of nitrogen oxides, the co-product of the synthesis process, cannot be ignored. This is considered to a disadvantage of the LiNO_3 –EMD system. To ameliorate this problem, LiOH has been used instead of LiNO_3 as a Li source. It is well known that LiNO_3 is more easily melted and adsorbed by MnO_2 than LiOH. Therefore, EMD was replaced with CMD (IC No. 12, Sedema, Belgium) since the latter has a higher porosity and a greater mean pore radius than EMD. The results are discussed in the next section.

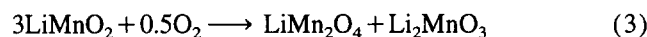
3.2. LiOH–CMD system

3.2.1. Effect of heating temperature

Powder XRD data for samples synthesized from LiOH and CMD at 470°C for 12 h in air and at various temperatures for 24 h in N_2 are shown in Fig. 8. The characteristic XRD pattern of spinel was observed at temperatures below 700°C . As the temperature is raised, however, the cubic- LiMn_2O_4 phase gradually transforms to an orthorhombic- LiMnO_2 phase. The formation of LiMnO_2 also takes place with the intergrowth of Mn_3O_4 . When the spinel phase is heated to 900°C in air, it transforms to LiMnO_2 ; this behaviour has been observed by Tarascon et al. [13]. The decomposition reaction of LiMn_2O_4 is as follows:



It is evident that an N_2 atmosphere encourages this reaction to occur. In fact, the transformation of LiMn_2O_4 to LiMnO_2 can proceed at a low temperature, but LiMnO_2 is unstable in air below 900°C ; it is oxidized and eventually disproportionates according to the reaction [14]:



The transformation reaction should proceed easily in an N_2 atmosphere, however, due to the fact that reaction (3) will be inhibited in a reducing atmosphere. This indicates that preparation of spinel from LiOH and CMD should be carried out at a temperature lower than 700°C in an N_2 atmosphere.

The continuous charge/discharge performance of LiMn_2O_4 and $\text{Li}_{1.04}\text{Mn}_2\text{O}_4$, synthesized at 470°C for 12 h in air and 700°C for 24 h in N_2 , is displayed in Fig. 9. The electrode has an initial charge capacity of 135 mAh/g for sample (a) and 123 mAh/g for sample (b), and then delivers a corresponding rechargeable capacity of 127 and 120 mAh/g with extremely low electrode polarization.

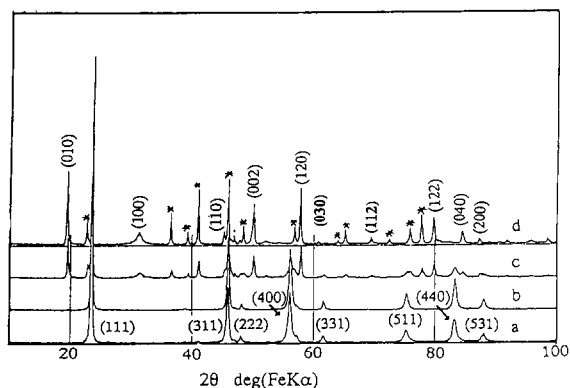


Fig. 8. XRD patterns of samples obtained from LiOH on reaction with CMD at 470°C for 12 h in air and at different temperatures for 24 h in N_2 atmosphere: (a) 650°C ; (b) 700°C ; (c) 750°C , and (d) 800°C . Miller indexes of LiMn_2O_4 (in curve (a)) and LiMnO_2 (in curve (d)) are given for peaks. Peaks corresponding to Mn_3O_4 phase are marked by an asterisk.

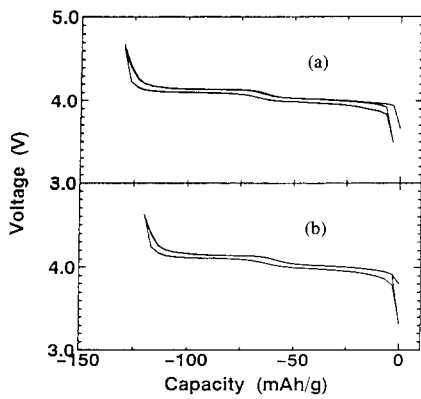


Fig. 9. Continuous charge/discharge curves of (a) LiMn_2O_4 ; (b) $\text{Li}_{1.04}\text{Mn}_2\text{O}_4$ obtained from LiOH and CMD at 470°C for 12 h in air and 700°C for 24 h in N_2 .

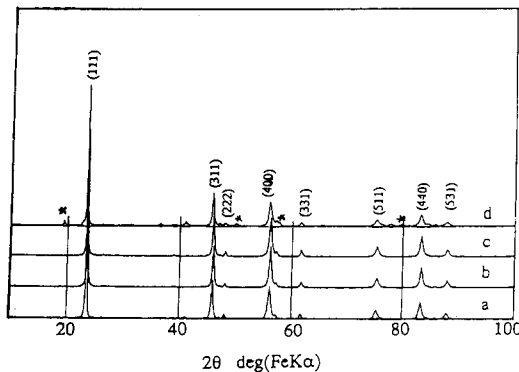


Fig. 10. XRD pattern for LiMn_2O_4 prepared at 470°C for 12 h in air and 700°C for different times in N_2 atmosphere. (a) 24 h (only at 700°C); (b) 24 h; (c) 48 h; (d) 72 h. Peaks corresponding to LiMnO_2 phase are marked by an asterisk (*).

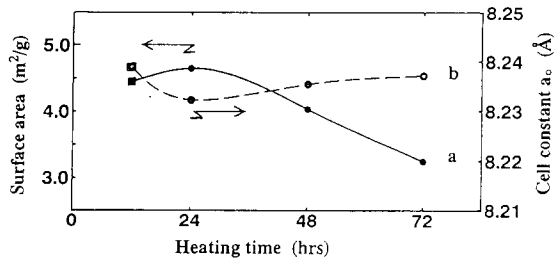


Fig. 11. BET surface area and a_0 -axis parameter vs. heat-treatment time for LiMn_2O_4 obtained from LiOH on reaction with CMD at 700°C in N_2 . The first point indicates treatment at 700°C for 24 h without preheating at 470°C for 12 h in air.

3.2.2. Dependence of heating time

The effect of heating time on the properties of the resulting compounds was also studied. For example, Fig. 10 gives the XRD pattern for LiMn_2O_4 prepared at 470°C for 12 h in air and 700°C for different times in a N_2 atmosphere. Long heating times cause a significant chemical reduction of LiMn_2O_4 to LiMnO_2 , and lower the surface area, as illustrated in Fig. 11. As expected, the sample with preheating at 470°C for 12 h has a larger surface area than a sample without preheating. It is likely that this results from the different formation route for the two processes. LiOH was melted and

impregnated into the MnO_2 pores together with the formation of a distorted spinel structure, LiMn_2O_4 , on preheating at 470°C . A stoichiometric LiMn_2O_4 can be synthesized through the distorted spinel, instead of the Mn_2O_3 phase, as an intermediate product in a one-step synthesis process. Preheating treatment improves the surface area of the final product. The results of effects of heating time on first discharge capacity and rechargeability for the compounds are presented in Fig. 12. It can be seen that the capacity decreases as the heating time increases. This is due to a reduction in the surface area.

The results in Fig. 11 and Fig. 12 also show that the value of the a_0 parameter of those samples with large capacity lies in the range $8.23\text{--}8.24 \text{ \AA}$.

All the above results suggest that the optimum heating time for preparing a spinel with LiOH and CMD in N_2 is less than 48 h.

3.2.3. Electrochemical reversibility

The sample optimized in above way exhibits good reversibility. The charge/discharge profile of LiMn_2O_4 at different current densities is given in Fig. 13. It indicates that even at a higher current rate (i.e., one corresponding to 3C), the sample can deliver about 120 mAh/g . The electrochemical reversibility has also been characterized by cyclic voltammetric measurements. The experiment was carried out in a three-electrode system; Li was used as both a counter and a reference electrodes. The scan voltage was kept in the range

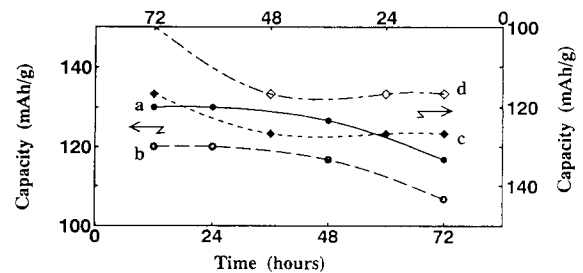


Fig. 12. Effect of heating time on first discharge capacity and rechargeability for compounds prepared from LiOH and CMD at 470°C for 12 h in air, and at 700°C for various times in N_2 . Samples heated only at 700°C in N_2 without preheating correspond to 12 h. (a) First and (b) 30th discharge for LiMn_2O_4 ; (c) first and (d) 30th discharge for $\text{Li}_{1.04}\text{Mn}_2\text{O}_4$.

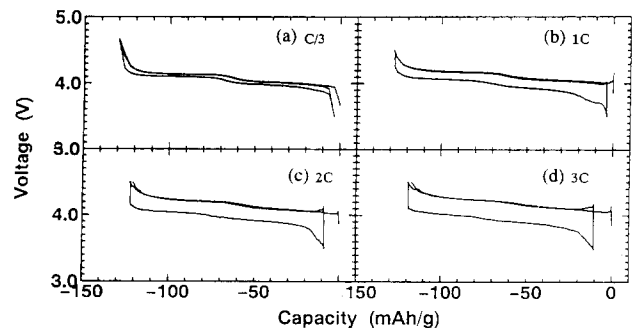


Fig. 13. Charge/discharge curves at different currents for LiMn_2O_4 obtained from LiOH on reaction with CMD in N_2 : (a) $C/3$ (1 mA); (b) 1C (3 mA); (c) 2C (6 mA), and (d) 3C (9 mA).

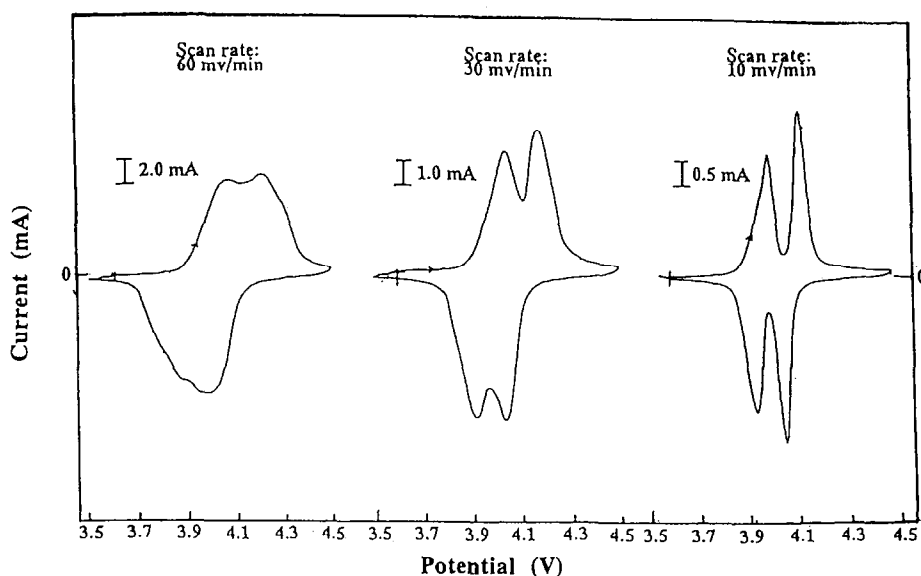


Fig. 14. Cyclic voltammograms for LiMn_2O_4 at different scan rates.

3.5–4.5 V (versus Li). Typical cyclic voltammograms are given in Fig. 14. Two pairs of clearly separated redox peaks (located at 4.00, 3.94 V; 4.12, 4.05 V) were observed at a scan rate of 10 mV/min. These relate to the reversible two-step process for Li-ion de-intercalation and intercalation in LiMn_2O_4 . The results described here agree well with those reported previously [18]. The measured parameter of the ratio of peak currents i_{pa}/i_{pc} , and the separation of peak potentials, $E_{pa}-E_{pc}$, for the first pair of peaks, are nearly 1 and 60 mV at low scan speed. This characterizes the signature of a reversible reaction. The results demonstrate that Li ions are intercalated and de-intercalated reversibly in this compound. There is also support for the fact that the electrode exhibits good rechargeability. Moreover, the peak current i_p increases linearly with $\nu^{1/2}$. The relationship between these two parameters can be described simply by Eq. (4):

$$i_p(\text{mA}) = (2.69 \times 10^8) n^{3/2} A \Delta C^* D^{1/2} \nu^{1/2} = 263 \times \nu^{1/2} \quad (4)$$

It is assumed that the intercalation reaction is controlled by the solid-state diffusion of Li ions. The electrode consists of

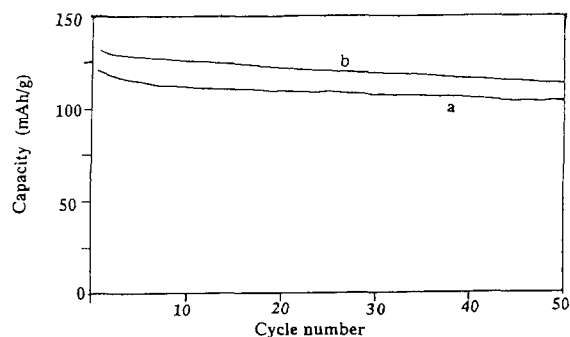


Fig. 15. Capacity vs. cycle number for Li/ LiMn_2O_4 cell at current density of 0.4 mA/cm^2 ($C/3$): (a) LiMn_2O_4 obtained from LiNO_3 and EMD, and (b) LiMn_2O_4 prepared from LiOH and CMD.

a mound of spherical active particles that is contact with the electrolyte solution. The chemical diffusion coefficient of Li can be evaluated from a knowledge of the total electrode surface area (A) and the Li-ion concentration (C^*) [19,20]. The value of A and C^* used here is calculated from the density (1.7 g/cm^3) and the average particle size ($40 \mu\text{m}$) of LiMn_2O_4 . The calculated value of the coefficient is about $4.89 \times 10^{-9} \text{ cm}^2/\text{s}$. It should be noted that this value is less accurate than the approximation in the above formulation, but the value agrees with that investigated by potentiostatic intermittent titration technique methods in Ref. [5].

3.3. Rechargeability test of resulting compounds

The rechargeability test was performed on compounds that were synthesized according to the above optimum conditions in CR2032 button cells. Sample (a) was prepared by LiNO_3 reaction with EMD at 260°C for 12 h in air and 650°C for 24 h in N_2 . Sample (b) was obtained from LiOH and CMD at 470°C for 12 h in air and 700°C for 24 h in N_2 . Both samples yield large capacity and good rechargeability at a current rate of $C/3$ between a cycled voltage of 4.5 and 3.5 V, as illustrated in Fig. 15. A slightly higher capacity was obtained for sample (b), which may be attributed to the fact the sample (b) has a larger surface area than sample (a).

4. Conclusions

Significant progress has been made in the synthesis of promising spinel structure material as a cathode for 'lithium-ion' batteries by a melt-impregnation method. For optimum synthesis, the preparation of spinel $\text{Li}_x\text{Mn}_2\text{O}_4$ from LiNO_3 and EMD, or LiOH and CMD should be performed in an N_2 atmosphere at a temperature lower than 750°C and for a time of less than 48 h.

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