

Rechargeable lithium battery with spinel-related MnO_2 II. Optimization of the LiMn_2O_4 synthesis conditions

A. Momchilov, V. Manev and A. Nassalevska

Central Laboratory of Electrochemical Power Sources, Bulgarian Academy of Sciences,
Sofia 1113 (Bulgaria)

A. Kozawa

Chubu University, Kasugai, Aichi 487 (Japan)

(Received July 24, 1992; in revised form October 19, 1992)

Abstract

The effect of the starting products and the synthesis temperature on electrochemical parameters of $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$ ($0 < x < 1$) are studied. Synthesis of LiMn_2O_4 spinel for lithium cells operating at low and medium discharge rates is not essentially affected by the nature of the starting products. Use of chemically-obtained manganese dioxide, instead of electrochemically obtained one, or LiNO_3 and LiOH , instead of Li_2CO_3 , displays significant advantages at high discharge rates. Thermal pretreatment of the reaction mixture in the temperature range of 350 to 550 °C improves the electrochemical behavior of the samples. Optimum results were obtained by a following reaction time of the main synthesis from 75 to 200 h at temperatures in the 650–750 °C range.

Introduction

The structural and electrochemical properties of spinel-related MnO_2 , usually described by $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$ ($0 < x < 1$) have been investigated previously [1–9]. In a series of papers using the synthesis suggested by Hunter [1], Thackeray *et al.* [3–5] and Ohzuku *et al.* [6, 7] demonstrated that $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$ of composition ($0.27 < x < 1$) can be cycled at about 4 V versus Li reference electrode. Recently, data for a very high-specific capacity and good reversibility of $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$ ($0 < x < 1$) at high discharge rates were presented [10]. This study showed that if chemical manganese dioxide (CMD) and LiNO_3 are used as starting compounds for $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$ synthesis at 750 °C, products with significant higher performance are obtained than by employing the classical method proposed by Hunter [1]. The remarkable increase in specific capacity was explained by the higher specific surface area and better stoichiometry of the samples. These results give rise to the following questions:

(i) How does the nature of the Li salt affect the electrochemical parameters of the product obtained?

(ii) What is the effect of the nature of the starting MnO_2 and are there any significant advantages in the use of CMD instead of electrochemically obtained manganese dioxides (EMD)?

(iii) Is the synthesis temperature of 750 °C optimum only for the fixed time of 48 h, or can we find a more suitable combination of synthesis duration and temperature for a better electrochemical performance of the samples?

The present work aims at finding out answers to these questions.

Experimental

Samples studied were produced by heating a stoichiometric mixture of MnO_2 and Li salt in a platinum crucible for 12 to 200 h in the temperature range of 450–850 °C. The Li salts used were Li_2CO_3 , LiNO_3 and LiOH , commercial products of Fluka, the manganese dioxides were EMD Knapsack manufactured by A. G. Hoechst, and CMD Faradizer M supplied by Sedema.

Electrochemical measurements were performed on test electrodes in a three-electrode cell containing 1 M LiAsF_6 in propylene carbonate:ethylene carbonate = 1:1 as electrolyte. The active mass of the test electrodes was a mixture of the compounds studied and teflonized acetylene black at 1:1 ratio by weight, homogenized by continuous stirring in ethers. After drying, test electrodes were formed by pressing 25 mg cm^{-2} of the active mass onto an expanded nickel grid at 5 t cm^{-2} . Thus the investigated compounds remained uniformly distributed in a highly porous (about 60%) electrically-conductive matrix. Under these conditions the samples were tested at high discharge rates without being affected by the contact resistance between electrode particles, or by the transport hindrance in the electrolyte which can be crucial in real electrodes. The huge amount of electroconductive binder and the high porosity exclude any macrostructural changes in the electrodes, due to continuous pulsation of the crystal lattice parameters of the intercalation compounds during cycling. These changes are typical of practical electrodes and commonly a source of incorrect conclusions regarding the reversibility of the materials studied.

X-ray analysis was carried out on a Philips APD 15 diffractometer with Cu K α radiation. The specific surface area was evaluated by the BET method using a Strohlein & Co. AREA-meter. Electron micrography was performed by JEOL-Superprobe 733.

Results and discussion

The temperature dependence of the specific surface area for samples synthesized for 48 h from different combinations of Li salts and manganese dioxides is demonstrated in Fig. 1. As shown in Fig. 1, Li_2CO_3 , LiNO_3 and LiOH were used in stoichiometric mixtures with CMD or EMD. It can be seen that higher specific surface area products are obtained from LiNO_3 and LiOH than by synthesis from Li_2CO_3 . The same effect is observed for use of CMD instead of EMD.

The effect of synthesis duration on the specific surface area of LiMn_2O_4 produced from Li_2CO_3 or LiNO_3 in combination with CMD or EMD at 750 °C is presented in Fig. 2. The results demonstrate that when using either LiNO_3 instead of Li_2CO_3 , or CMD instead of EMD, the time for reaching nearly constant specific surface values is remarkably shorter.

To elucidate this effect, a comparison was made of the change of specific surface area with time during heating of pure Mn_2O_3 and of LiMn_2O_4 (produced from LiNO_3 and CMD) at 750 °C (Fig. 3). To be more precise, both materials were continuously ground in a ball mill until an approximately equal starting specific surface area of about 5 m² g⁻¹ had been obtained. Results of this comparison at 650 and 750 °C indicate that in this temperature range, Mn_2O_3 has a considerably greater tendency of crystal growth by solid-state reaction than does LiMn_2O_4 . Considering also that above 550 °C EMD and CMD decompose to Mn_2O_3 , the results in Fig. 2 can be explained by the slowdown of reaction between Mn_2O_3 and Li salt when employing EMD instead of CMD, or Li_2CO_3 instead of LiNO_3 . This conclusion is supported by

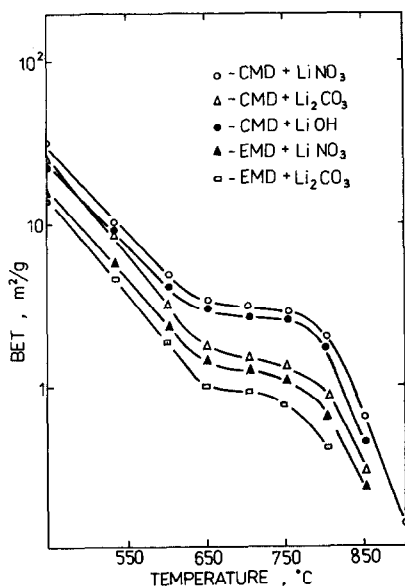


Fig. 1. Temperature dependences of the specific surface area of LiMn_2O_4 obtained from different combinations of lithium salts and manganese dioxides.

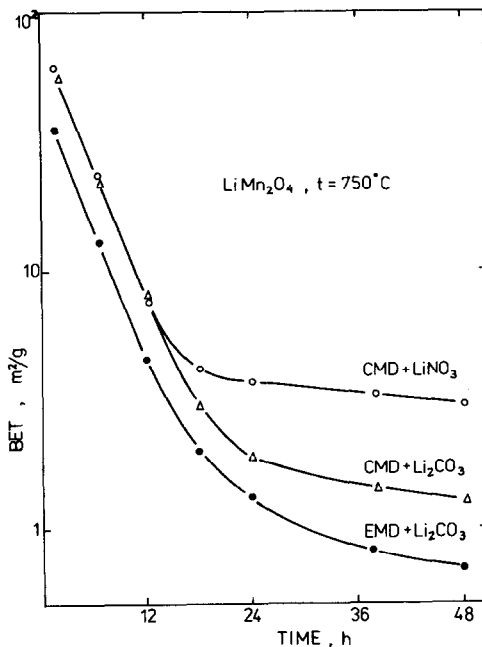


Fig. 2. The effect of the synthesis duration on the specific surface area of LiMn_2O_4 produced from Li_2CO_3 or LiNO_3 in combination with CMD or EMD at 750°C .

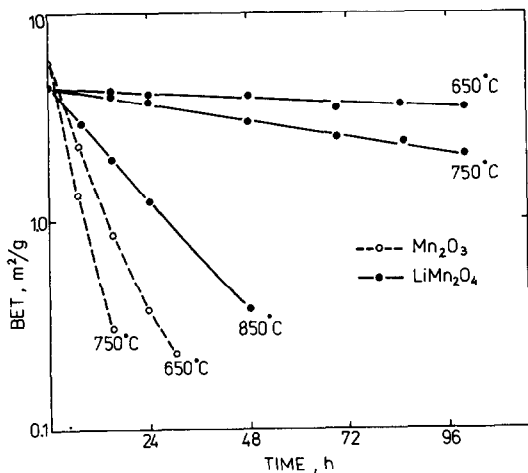


Fig. 3. Dependences of the specific surface area of pure Mn_2O_3 and LiMn_2O_4 on the heating time at 650 , 750 and 850°C .

the fact that LiNO_3 melts at a significantly lower temperature than Li_2CO_3 , and CMD has a higher porosity and a greater mean pore radius than EMD.

Scanning electron microscopy (SEM) pictures of the samples confirm this supposition. Figure 4 compares SEM pictures of starting CMD (Fig. 4(a) and (b)), with the ones of LiMn_2O_4 obtained from CMD and Li_2CO_3 at 650 °C (Fig. 4(c) and (d)) and 850 °C (Fig. 4(e) and (f)). It can be seen that the typical morphology of CMD particles is considerably preserved. This is possible only if the Li salt had penetrated into CMD particles during the synthesis.

The mean radius, r , of the LiMn_2O_4 crystals determined by the SEM pictures (Fig. 4(d) and (f)) coincide very well with that calculated by the specific surface area, A , using the formula:

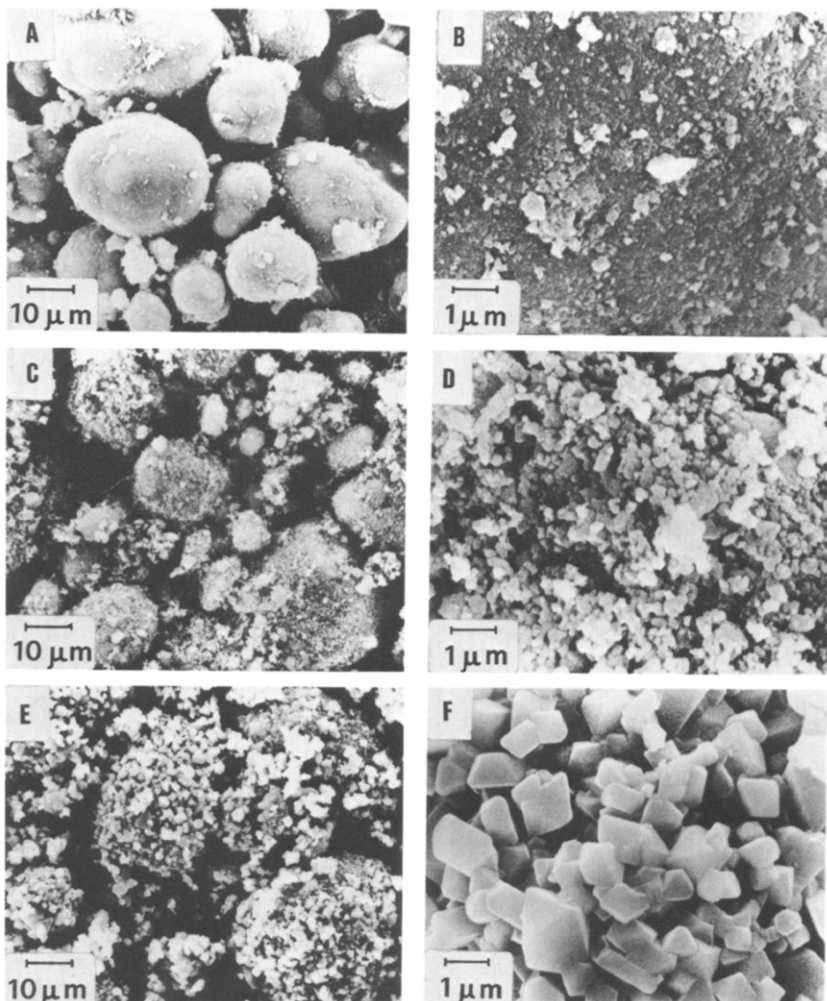


Fig. 4. SEM pictures of (a, b) the starting CMD, and (c, d) LiMn_2O_4 obtained from CMD and Li_2CO_3 at 650 °C and (e, f) at 850 °C.

$$r = \frac{3}{\rho A} \quad (1)$$

where ρ is the spinel specific density. This is a clear indication of micropores leaking into the LiMn_2O_4 crystals. For all combinations represented in Fig. 1, the LiMn_2O_4 obtained at synthesis duration from 24 to 200 h at temperatures in the range of 650–750 °C, the mean particle radius varies from 0.1 to 1.0 μm .

X-ray diffraction patterns unambiguously show that identical phase composition can be obtained if the lower synthesis temperatures are compensated by a longer synthesis duration. Table 1 presents diffraction patterns of samples produced by the combination of CMD with LiNO_3 , LiOH and Li_2CO_3 , synthesized at 650 °C for 200 h, compared with standard samples obtained by other authors [1–3] at considerably higher temperatures. As can be seen, the data reported in the present study are in better agreement with standard pattern (ASTM 18-736) than with the samples synthesized for 24 h at 900 °C [3].

Effects of synthesis duration on electrochemical utilization of samples synthesized at various temperatures is presented in Fig. 5. A well-defined maximum at 850 °C and an extremely flat one at 750 °C are observed, while the specific capacity of samples synthesized at 650 °C continuously increases within 120 h. From this behavior, one can conclude that by a proper choice of reacting time in the temperature range 650–750 °C, compounds with equal specific capacity can be produced.

The dependence of specific capacity of test electrodes on synthesis duration of LiMn_2O_4 at 700 °C for various combinations of starting products is displayed in Fig. 6. It is evident that, while for short synthesis times, use of CMD instead of EMD and of LiNO_3 instead of Li_2CO_3 has remarkable advantages, after longer reacting times the specific capacity reaches a nearly equal value. However, as shown in Fig. 6, this is valid only at low and medium discharge rates ($I=0.2$ C is applied). At high discharge rates, probably owing to the considerable difference in the specific surface area of the samples (Fig. 2), the advantage of employing CMD and LiNO_3 or LiOH instead of EMD and Li_2CO_3 is significant. This fact is illustrated in Fig. 7, where

TABLE 1

Power X-ray diffraction data for LiMn_2O_4

ASTM 18-736			Ref. 3 24 h, 900 °C			CMD + LiNO_3 200 h, 650 °C			CMD + LiOH 200 h, 650 °C			CMD + Li_2O_3 200 h, 650 °C		
<i>h k l</i>	<i>d</i>	<i>I/I₀</i>	<i>d</i>	<i>d</i>	<i>I/I₀</i>	<i>d</i>	<i>I/I₀</i>	<i>d</i>	<i>I/I₀</i>	<i>d</i>	<i>I/I₀</i>			
1 1 1	4.72	100	4.749	4.720	100	4.705	100	4.720	100	4.720	100			
3 1 1	2.47	90	2.483	2.468	94	2.468	95	2.468	96	2.468	96			
2 2 2	2.37	5	2.379	2.368	20	2.362	20	2.367	10	2.367	10			
4 0 0	2.05	100	2.060	2.049	100	2.049	95	2.049	100	2.049	100			
3 3 1	1.88	10	1.89	1.881	15	1.881	18	1.884	15	1.884	15			
3 3 3	1.58	50	1.586	1.580	50	1.577	60	1.580	50	1.580	50			
4 4 0	1.45	90	1.457	1.451	90	1.451	90	1.453	95	1.453	95			
5 3 1	1.39	30	1.393	1.389	35	1.388	40	1.389	40	1.389	40			
5 3 3	1.25	10	1.257	1.252	10	1.252	10	1.253	10	1.253	10			
6 2 2	1.24	5	1.243	1.238	10	1.238	10	1.253	10	1.253	10			

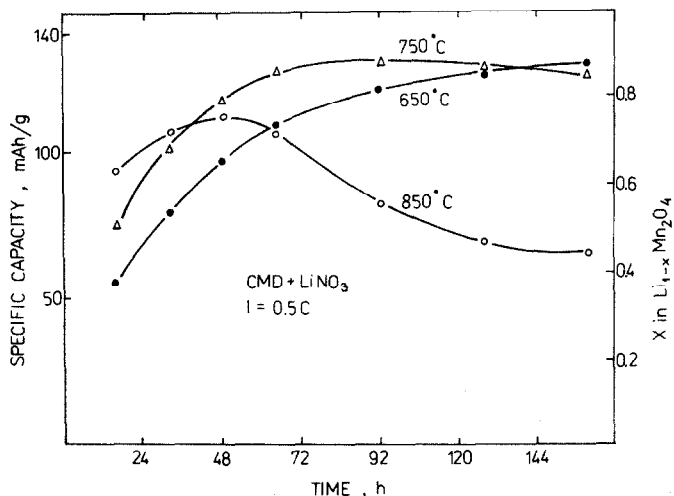


Fig. 5. Effect of the synthesis duration on the specific capacity of samples synthesized at 650, 750 and 850 °C.

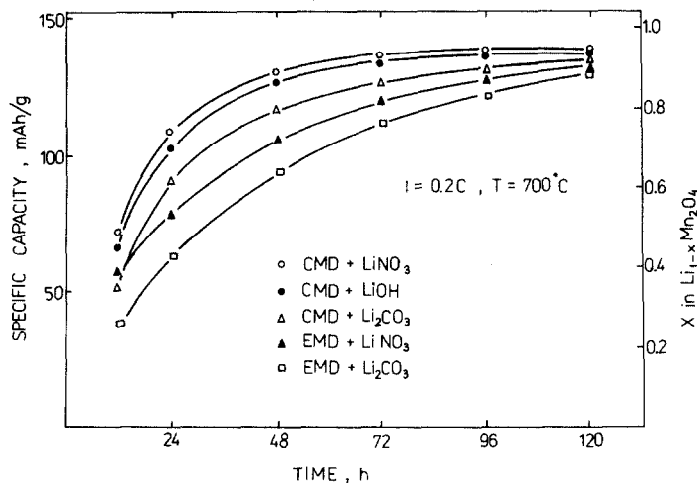


Fig. 6. Dependences of the specific capacity on the duration of the LiMn_2O_4 synthesis at 700 °C for various combinations of starting products.

discharge curves of test electrodes obtained from CMD with LiNO_3 and from EMD with Li_2CO_3 at $I=2\text{ C}$ are presented. At high discharge rates electrodes made from CMD and LiNO_3 display a substantially higher utilization and mean discharge voltage in comparison with EMD and Li_2CO_3 .

The obvious advantages of samples having larger specific surface area at high discharge rates provoked a search for those conditions which provide higher specific surfaces of the final product. One such possibility arises from results shown in Fig. 3 and from the fact that the most suitable synthesis temperature lies in the 600–800 °C range. Above 550 °C, MnO_2 decomposes spontaneously to Mn_2O_3 , and thus

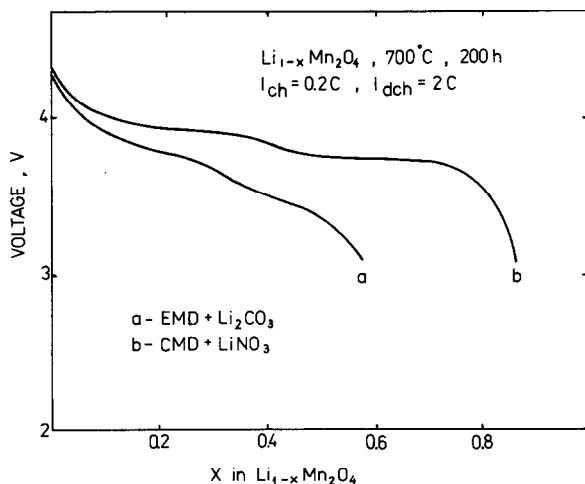
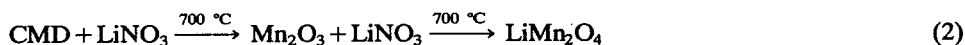


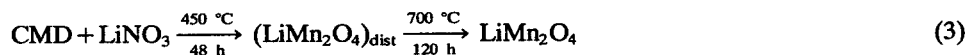
Fig. 7. Discharge curves of test electrodes with LiMn_2O_4 produced from CMD with LiNO_3 and from EMD with Li_2CO_3 at $I=2\text{ C}$.

LiMn_2O_4 synthesis is accomplished by reaction of Mn_2O_3 with the respective Li salt, instead of MnO_2 and the Li salt. For LiMn_2O_4 produced from CMD and LiNO_3 at $700\text{ }^\circ\text{C}$ the reaction proceeds as follows:



During synthesis, two competitive processes take place. On one hand, the Mn_2O_3 crystals grow by a solid-state reaction, which leads to a decrease of surface area (Fig. 3). On the other hand, LiMn_2O_4 is produced via the reaction of Mn_2O_3 with the Li salt. The remarkably higher rate of the former reaction (Fig. 3) is the most plausible reason for the substantial decrease of specific surface area in the synthesized product.

As shown earlier [10–12], LiMn_2O_4 with distorted spinel structure is produced at temperatures below $550\text{ }^\circ\text{C}$, which allows the synthesis to be performed following a reaction model different from eqn. (2). Initially, at a temperature below $550\text{ }^\circ\text{C}$ a spinel with distorted structure, $(\text{LiMn}_2\text{O}_4)_{\text{dist}}$, can be synthesized and then, after longer heating in the range $600\text{--}800\text{ }^\circ\text{C}$, stoichiometric LiMn_2O_4 with ordered structure would be produced. Thus, using the model



a stoichiometric LiMn_2O_4 spinel with a well-ordered crystal structure can be synthesized without passing through the Mn_2O_3 phase as intermediate product.

As can be seen from Fig. 8, the intermediate $(\text{LiMn}_2\text{O}_4)_{\text{dist}}$ obtained by heating of the reaction mixture for 48 h at $450\text{ }^\circ\text{C}$ ensures a considerably higher specific surface area of the final product. It has been experimentally established that this effect is much stronger if thermal pretreatment is performed by continuous temperature sweep of 2 to $10\text{ }^\circ\text{C/h}$ within $350\text{--}550\text{ }^\circ\text{C}$. The dependence of specific surface area on the duration of synthesis for a thermally-pretreated sample by a temperature sweep of $5\text{ }^\circ\text{C/h}$ in the range $350\text{--}550\text{ }^\circ\text{C}$ is also illustrated in Fig. 8.

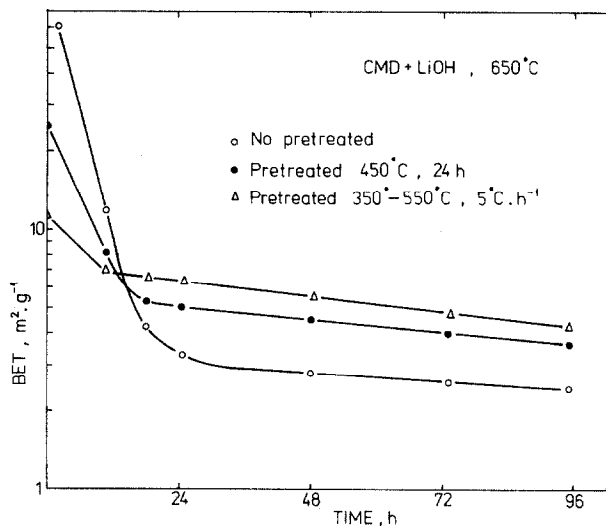


Fig. 8. Dependences of the specific surface area on the synthesis duration for a sample thermally pretreated at 450 °C for 24 h and by temperature sweep of 5 °C/h in the range 350–550 °C.

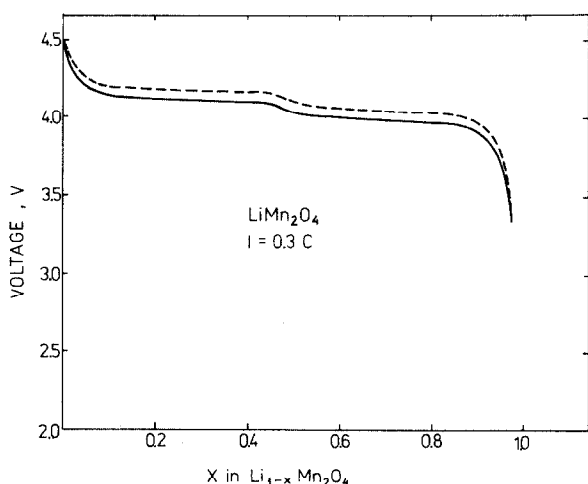


Fig. 9. Charge/discharge curves at 3 h rate of LiMn_2O_4 produced from a mixture of CMD and LiNO_3 , preheated by temperature sweep of 5 °C/h in the range 350–550 °C and then synthesized at 700 °C for 120 h.

Figure 9 presents charge/discharge curves at 3 h rate of a LiMn_2O_4 test electrode obtained from a mixture of CMD and LiNO_3 , preliminary heated at 350–550 °C at 5 °C/h and subsequently synthesized for 120 h at 700 °C. Despite the relatively high rate of the electrochemical process, the charge and discharge curves are identical, differing by less than 100 mV.

The surprisingly low electrode polarization, obtained under conditions specified in Fig. 9, is confirmed also by their discharge curves recorded from $I_{\text{dch}} = 0.2$ C to

$I_{\text{dch}} = 5 \text{ C}$, shown in Fig. 10. All discharge curves presented in Fig. 10 were taken after charge at $I_{\text{ch}} = 0.2 \text{ C}$. It can be seen that even at extremely high discharge rates corresponding to $I_{\text{dch}} = 5 \text{ C}$ the electrode preserves over 50% of its theoretical capacity.

Thermal pretreatment at lower temperatures, in combination with following synthesis at $650\text{--}750 \text{ }^\circ\text{C}$, leads to an improvement of electrode reversibility. Long-term cycling tests of electrodes optimized in this way are demonstrated in Fig. 11. It is evident that, together with very high specific energy, these samples exhibit good reversibility, properties that establish them as very promising materials for positive electrodes in secondary Li batteries.

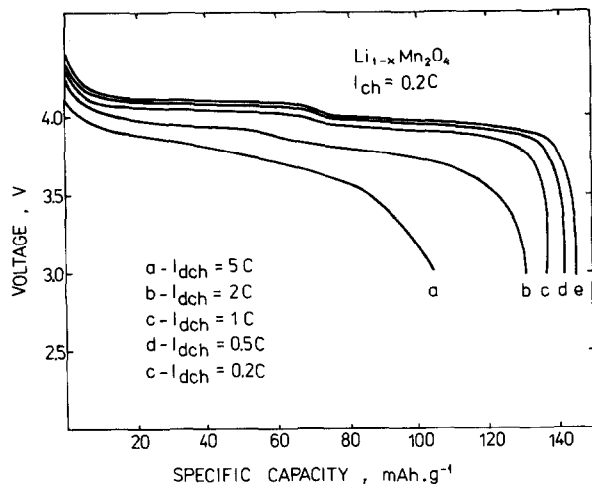


Fig. 10. Discharge curves at different currents for test electrodes with LiMn_2O_4 , produced from CMD and LiNO_3 at $700 \text{ }^\circ\text{C}$, after charge at $I_{\text{ch}} = 0.2 \text{ C}$.

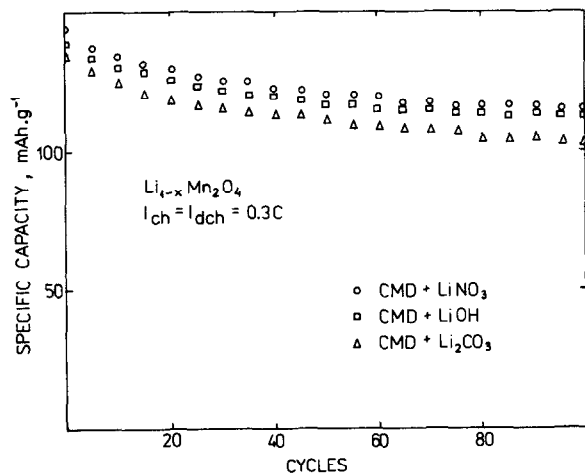


Fig. 11. Specific capacity vs. cycle number for test electrodes with LiMn_2O_4 , synthesized from CMD and LiNO_3 at $700 \text{ }^\circ\text{C}$ for 120 h.

References

- 1 J. Hunter, *J. Solid State Chem.*, 39 (1981) 142.
- 2 A. Mosbah, A. Verbaere and M. Tournoux, *Mater. Res. Bull.*, 18 (1983) 1375.
- 3 M. Thackeray, P. Johnson, L. de Picciotto, P. Bruce and J. Goodenough, *Mater. Res. Bull.*, 19 (1984) 179.
- 4 M. Thackeray, L. de Picciotto, A. de Kock, P. Johnson, V. Nicholas and K. Adendorff, *J. Power Sources*, 21 (1987) 1.
- 5 M. Thackeray, *Proc. Mater. Res. Soc. Symp.*, 135 (1989) 585.
- 6 T. Ohzuku, H. Fukuda and T. Hirai, *Chem. Express*, 2 (1987) 543.
- 7 T. Ohzuku, M. Kitagawa and T. Hirai, *J. Electrochem. Soc.*, 137 (1990) 769.
- 8 F. Lubin, A. Lecert, M. Broussely and J. Labat, *J. Power Sources*, 34 (1991) 161.
- 9 Yang Hanx, Li Shengxian and Wu Zhiyuan, *Ext. Abstr. 5th Int. Meet. on Lithium Batteries, Beijing, May 1990*, p. 287.
- 10 V. Manev, A. Momchilov, A. Nassalevska and A. Kozawa, *J. Power Sources*, in press.
- 11 W. Macklin, R. Neat and R. Powell, *J. Power Sources*, 34 (1991) 39.
- 12 T. Nagaura, M. Yokokawa and T. Hashimoto, *Br. Patent No. 2 196 785* (1988).