



ELSEVIER

Journal of Power Sources 54 (1995) 323–328

JOURNAL OF  
POWER  
SOURCES

## Rechargeable lithium battery with spinel-related $\lambda$ - $\text{MnO}_2$ III. Scaling-up problems associated with $\text{LiMn}_2\text{O}_4$ synthesis

V. Manev<sup>a</sup>, A. Momchilov<sup>a</sup>, A. Nassalevska<sup>a</sup>, Atsushi Sato<sup>b</sup><sup>a</sup> Central Laboratory of Electrochemical Power Sources, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria<sup>b</sup> Chubu University, Department of Industrial Chemistry, Kasugai, Aichi-ken 487, Japan

### Abstract

The scaling-up problems connected with the  $\text{LiMn}_2\text{O}_4$  synthesis were studied. A strong effect of the mass of the starting materials and of the air flow rate through the furnace during the synthesis on the specific capacity was observed. The increase of the batch amount brings about a reduction in the specific surface area of the product, which cannot be compensated by grinding because it leads to considerable reduction of its electrochemical utilization. The very fast or slow cooling of the synthesized material have a negative effect on the specific capacity. The process of preparation of  $\text{LiMn}_2\text{O}_4$  spinel with high electrochemical performance is a rather complex procedure, but it is possible to obtain a product, which is capable to exchange reversibly up to 0.9 equiv. Li per mole.

**Keywords:** Rechargeable lithium batteries; Manganese oxide

### 1. Introduction

From the more than 200 materials for positive electrodes intensively investigated during the last two decades the manganese oxides are the most promising from the point of view of specific energy, toxicity and costs. Several manganese oxides with different structures and stoichiometry were investigated as materials for secondary lithium batteries. However, the only candidate for the recently proposed innovative lithium-ion (rocking-chair) battery, where the lithium metal anode is replaced by carbon, is the lithium spinel  $\text{LiMn}_2\text{O}_4$ .

The structural relationships between the lithium spinel  $\text{LiMn}_2\text{O}_4$  [1] and  $\lambda$ - $\text{MnO}_2$  obtained by extraction of lithium from the former compound and usually denoted by the formula  $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$  ( $0 < x < 1$ ) were first described by Hunter [2] and confirmed by Mosbah et al. [3]. In a series of papers, Thackeray et al. [4,5] for the first time demonstrated that  $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$  ( $0 < x < 1$ ) can be cycled at about 4 V versus a Li reference electrode. Later, a good reversibility of  $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$  ( $0 < x < 1$ ) has been reported by Ohzuku et al. [6,7] and data that the electrochemical oxidation of  $\text{LiMn}_2\text{O}_4$  proceeds topotactically in two steps have been presented.

Recently in a series of papers and patents Tarascon and co-workers [8–17] reported in detail the electrochemical behavior of  $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$  ( $0 < x < 1$ ) as a func-

tion of the preparation method, charge cutoff voltage, current rate and operating temperature. By introducing new methods for  $\text{LiMn}_2\text{O}_4$  preparation and a new electrolyte compatible with the  $\text{LiMn}_2\text{O}_4$  positive electrode up to 5 V versus Li electrodes, they have made a decisive step towards commercialization of the lithium-ion  $\text{LiMn}_2\text{O}_4$ /carbon battery. However, in spite of the fact that the theoretical specific capacity of  $\text{LiMn}_2\text{O}_4$  is  $148 \text{ mAh g}^{-1}$ , the reversible part of the capacity obtained by these authors is lower than  $115 \text{ mAh g}^{-1}$ .

Several attempts have been made to improve this achievement by partial substitution of manganese in  $\text{LiMn}_2\text{O}_4$  with other transition metals. Nickel [8,18], cobalt [19] and chromium [20] have been tested but the reported results were lower than the ones obtained by Tarascon and co-workers [8–17] for pure  $\text{LiMn}_2\text{O}_4$ . No progress from this point of view has been made by the use of a new sol-gel synthesis of the  $\text{LiMn}_2\text{O}_4$  [21].

Using a standard muffle furnace with about 3 l air space and a batch of 10 g of the starting components we have demonstrated that the electrochemical properties of lithium spinel  $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$  ( $0 < x < 1$ ) are affected by the nature of the starting products, the temperature and the duration of the synthesis [22,23]. By optimization of the  $\text{LiMn}_2\text{O}_4$  synthesis conditions using the same batch amount we have succeeded to obtain a specific capacity of the system  $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$

( $0 < x < 1$ ) very near to its theoretical limits [23]. Later, during our attempt to scale up the batch amount we have met unexpected phenomena which have hindered our efforts to reproduce our results with small amounts of the starting materials.

The present paper aims to elucidate and to overcome some of the problems connected with the scaling-up of the  $\text{LiMn}_2\text{O}_4$  synthesis.

## 2. Experimental

The  $\text{LiMn}_2\text{O}_4$  samples were produced by heating a mixture of  $\text{MnO}_2$  and a lithium salt in a platinum or nickel crucible for 12 to 200 h in the temperature range from 450 to 850 °C. The lithium salts  $\text{Li}_2\text{CO}_3$  and  $\text{LiNO}_3$  used were produced by Fluka and, the manganese dioxide were CMD Faradizer M supplied by Sedema. The syntheses are performed in a standard muffle furnace with about 3 l air space, with or without additional air flow, using up to 250 g batches.

The electrochemical measurements were performed in two-electrode laboratory button cells with 1 M  $\text{LiPF}_6$  in ethylene carbonate–dimethylcarbonate (1:1) as the electrolyte. The active mass of the electrodes used in the button cells was a mixture of  $\text{LiMn}_2\text{O}_4$  and teflonized acetylene black at a 4:1 ratio by weight, homogenized by continuous stirring in alcohol. After drying, the electrodes were formed by pressing  $15 \text{ mg cm}^{-2}$  of the active mass on an aluminum foil at  $5 \text{ t cm}^{-2}$  and then sintered at 340 °C for 10 min.

The X-ray diffraction (XRD) analysis was carried out on a Philips APD 15 diffractometer with Cu K $\alpha$  radiation. The specific surface area was evaluated using a Strohlein and Co. AREA meter.

## 3. Results and discussion

### 3.1. Effect of air convection

The attempt to increase the amount of the batch under the optimum synthesis conditions determined in the small amounts of the  $\text{LiMn}_2\text{O}_4$  synthesis discussed previously [22,23] met unexpected complications.

The effect of the mass of the starting materials on the specific capacity of the product is illustrated in Fig. 1. The data refer to the synthesis from chemical manganese dioxide (CMD) with  $\text{Li}_2\text{CO}_3$  or  $\text{LiNO}_3$  as a lithium source in a standard muffle furnace at 750 °C for 48 h. The considerable reduction of the specific capacity with the increase of the mass of the synthesis batch can be explained with the influence of the nitrogen oxides or carbon dioxide emitted during the synthesis. The latter produces an inert atmosphere around the reaction mixture leading to a partial reduction of the

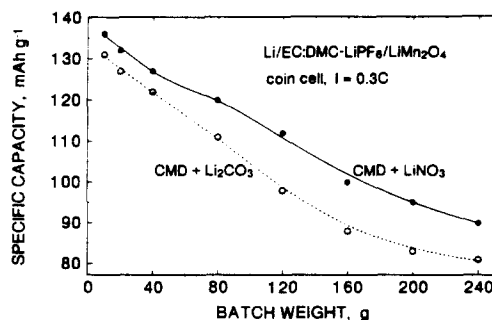


Fig. 1. Amounts of the starting materials vs. specific capacity of the product in a standard muffle furnace without air convection.

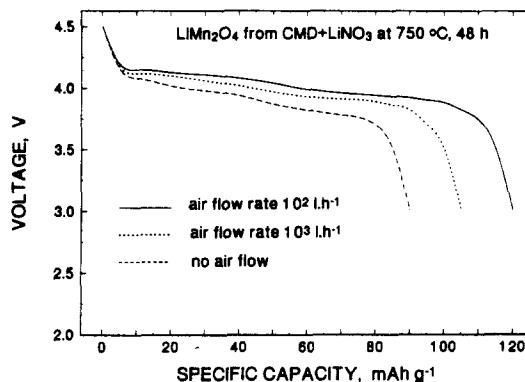


Fig. 2. Effect of air flow rate through the furnace with a 250 g batch on the discharge curves of  $\text{LiMn}_2\text{O}_4$  synthesized at 750 °C for 48 h.

product. The same effect is probably also realized by the considerable amounts of water, present in CMD as capillary and structurally bound water, part of which is evolved at rather high temperatures [24]. The decrease of the specific capacity as a result of the chemical reduction of  $\text{LiMn}_2\text{O}_4$  was explained in detail in Ref. [22]. The same gases are evolved also in the small batch synthesis, but in this case the higher ratio between the furnace space and the volume of the gases evolved considerably eliminates their disturbing effect. Another positive factor in the synthesis of a small amount of  $\text{LiMn}_2\text{O}_4$  is the slight but always existing convection between the standard muffle furnace and the ambient atmosphere, which at sufficiently small batches can become comparable with the flow rate of the evolved gases from the reaction mixture.

It is to be expected that the introduction of an air flow in the furnace will reduce the negative effect of the evolved gases. As shown in Fig. 2 such an effect is observed at a constant slow air flow rate. The increase in the air flow rate, however, brings about a considerable reduction in the specific capacity in comparison with the slow air flow rate. The most probable explanation of this effect is that at the optimum synthesis temperatures which are between 700 and 800 °C, the partial pressure of  $\text{Li}_2\text{O}$  although very low is not zero. Hence, at high air flow rates significant amounts of  $\text{Li}_2\text{O}$  can

be removed. As a result, the stoichiometry of the product will be disturbed, which cannot be detected by XRD analysis. As shown by Rossouw et al. [25] even for products with a high deficiency of lithium as, e.g.,  $\text{Li}_{0.86}\text{Mn}_2\text{O}_4$ , obtained at 800 °C for 24 h with Mn:Li = 7:3, the XRD pattern is the same as that of the stoichiometric spinel  $\text{LiMn}_2\text{O}_4$ . At the same time, the clearly expressed traces of  $\text{Mn}_2\text{O}_3$  obtained in the synthesis at 700 °C and  $\text{Mn}_3\text{O}_4$  in the synthesis at 900 °C for the same composition  $\text{Li}_{0.86}\text{Mn}_2\text{O}_4$  [25] indicate, that most probably at a synthesis temperature of 800 °C (24 h) both phases are present but, due to phase transition from  $\text{Mn}_2\text{O}_3$  to  $\text{Mn}_3\text{O}_4$ , they behave as amorphous compounds with respect to the XRD. The same argument can be applied in the temperature range from 700 to 800 °C for a longer synthesis time. It follows that, when a larger air flows rate is used in this temperature range, products with a considerable deficiency of lithium can be obtained which cannot be detected by the usual XRD analyses. It is obvious that the lithium deficiency in the compound  $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$  can be due to the presence of electrochemically inactive phases such as  $\text{Mn}_2\text{O}_3$  and  $\text{Mn}_3\text{O}_4$ , whereby the specific capacity of the product will be substantially reduced.

### 3.2. Effect of the starting materials ratio

Fig. 3 shows the dependence of the specific capacity at 3 h discharge rate ( $I=0.3C$ ) on the ratio Li/Mn<sub>2</sub> in the starting materials expressed in percents. It is seen that the excess of the lithium salt up to 2.5% has a positive effect on the specific capacity of the product. Above this ratio the electrode efficiency decays monotonously. In contrast with that, the decrease of the Li/Mn<sub>2</sub> ratio under the stoichiometric value leads drastically to a decrease in the product specific capacity. The Li/Mn<sub>2</sub> ratio has also an influence on the reversibility of the  $\text{LiMn}_2\text{O}_4$  cathodes. As seen in Fig. 4 the increase in lithium excess up to 5% over the stoichiometric one in the reaction mixture improves the reversibility of

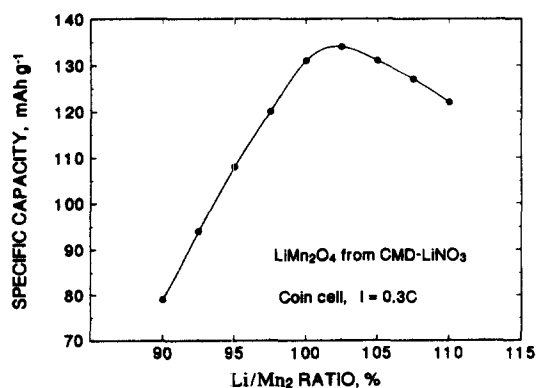


Fig. 3. Specific capacity of the product vs. ratio Li/Mn<sub>2</sub> in the starting batch in %.

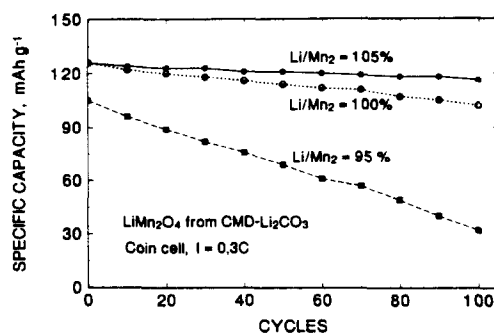


Fig. 4. Long-term cycling test of the  $\text{LiMn}_2\text{O}_4$  electrodes obtained with different starting Li/Mn<sub>2</sub> ratios.

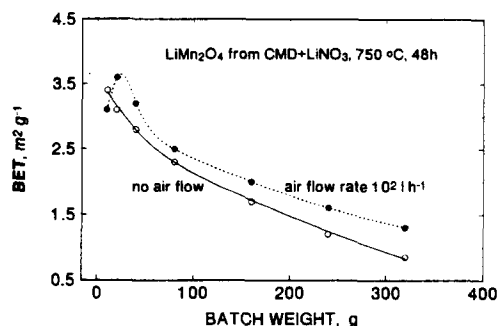


Fig. 5. Specific surface area of the synthesized  $\text{LiMn}_2\text{O}_4$  vs. amount of the reaction mixture.

the  $\text{LiMn}_2\text{O}_4$ , while 5% lithium deficiency leads to dramatic reduction in its reversibility. It is interesting to note that even a 10% excess of lithium has no effect on the XRD diagram. It is most probable that this is associated with the fact that under these conditions the lithium-rich spinel  $\text{Li}_4\text{Mn}_5\text{O}_{12}$  [25–27] is obtained together with the  $\text{LiMn}_2\text{O}_4$ . As shown by Thackeray and co-workers [25,27] the XRD diagram of  $\text{Li}_4\text{Mn}_5\text{O}_{12}$  can hardly be distinguished from that of  $\text{LiMn}_2\text{O}_4$ , so that its detection, when it is as an impurity in the stoichiometric spinel  $\text{LiMn}_2\text{O}_4$ , is practically impossible. The results demonstrated in Figs. 3 and 4 emphasize the importance of the good homogenization of the starting mixture the possibility for which decrease as the batch amount is scaled up.

### 3.3. Effect of the grinding procedure

Fig. 5 shows the change in the specific surface area of the synthesized  $\text{LiMn}_2\text{O}_4$  with the increase in the amount of the reaction mixture. The observed decrease in the specific surface area of the product with the increase of the batch amount is an unexpected finding, for which no satisfactory explanation can be offered for the present. It is possible that this effect is a result of the higher concentration of the evolved gases  $\text{NO}_2$ ,  $\text{CO}_2$  and  $\text{H}_2\text{O}$  in the reaction mixture, which could enhance the transition of  $\text{MnO}_2$  to  $\text{Mn}_2\text{O}_3$ , the negative effect being discussed earlier [22]. This effect, however, is not without consequences for the electrochemical behavior of the product, since the decrease in the specific surface area of  $\text{LiMn}_2\text{O}_4$  brings about a re-

duction of its reversibility as well as its power capability. The classic solution of this problem is grinding the product, but applying it we encountered an unexpected result – the grinding of  $\text{LiMn}_2\text{O}_4$  leads to a considerable reduction of its utilization.

Fig. 6 shows the effect of the grinding time of  $\text{LiMn}_2\text{O}_4$  in a laboratory ball mill on its specific surface area as well as on its specific capacity. It is clear that while the specific surface area grows with the time of grinding, the specific capacity considerably falls. This is in contrast with our 15-year long experience with intercalation compounds, which inevitably raised their specific capacity by increasing their surface area. A possible reason for this anomalous behavior is some structural changes in  $\text{LiMn}_2\text{O}_4$  due to its long time mechanical treatment. In fact the XRD diagram reveals (Fig. 7) that the (400) peak, determining the lattice parameter  $a$  of  $\text{LiMn}_2\text{O}_4$  shifts after grinding to higher angles showing some contraction of the crystal lattice. An explanation of this finding is that the electrochemically active  $\text{LiMn}_2\text{O}_4$  is a nonequilibrium system, which, when subjected to strong mechanical stress (as is during the milling process) tends to its equilibrium state.

### 3.4. Effect of the cooling rate

In contrast with the data of Tarascon et al. [8], according to which the electrochemical behavior of  $\text{LiMn}_2\text{O}_4$  is independent of the rate of cooling, we have

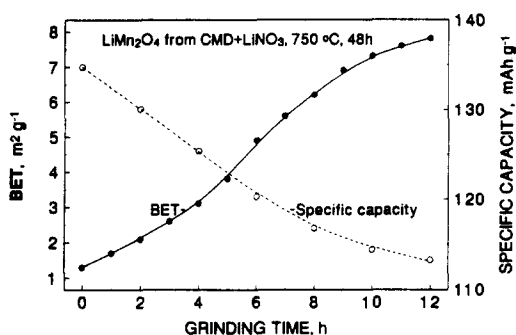


Fig. 6. Effect of the grinding time on the specific surface area and on the specific capacity of  $\text{LiMn}_2\text{O}_4$ .

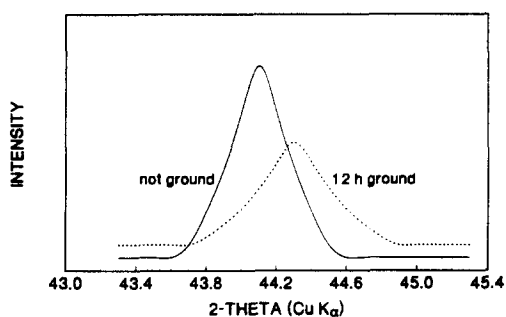


Fig. 7. Effect of the grinding procedure on the (400) peak determining the lattice parameter  $a$  of  $\text{LiMn}_2\text{O}_4$ .

found that such a dependence exists. As shown in Fig. 8 the very slow cooling and the quenching of the synthesized material lead to practically the same specific capacity which is in agreement with the results reported by Tarascon et al. [8]. The fast cooling, however, at a rate of several tens of degrees per minute has a considerable advantage over the two preceding cooling modes since it brings about a higher specific capacity. The lower capacity observed after quenching is probably due to the formation of the amorphous phase. Our own experimental data and these of the other authors [20,22] show that high performance characteristics can be obtained only by well-ordered crystal phases. The negative effect of the very slow cooling is related to the fact that in this case conditions are favorable to the formation of the oxygen-rich spinel  $\text{Li}_2\text{Mn}_4\text{O}_9$ . As demonstrated by Thackeray and co-workers [25–28] this spinel is obtained at a temperature around 400 °C and has a considerably lower electrochemical activity in the 4 V region with respect to lithium than that of  $\text{LiMn}_2\text{O}_4$  [25,28,29]. Probably, the slow cooling rate favors the process of  $\text{LiMn}_2\text{O}_4$  oxidation at about 400 °C by the reaction:



This assumption is corroborated by the finding that if the  $\text{LiMn}_2\text{O}_4$  spinel, synthesized in the temperature range from 700 to 800 °C, is subjected to an additional thermal treatment at about 400 °C for 24 h it loses at least 20% of its initial capacity. From the data published by Thackeray and co-workers [25] it follows that in this case also the XRD analysis cannot distinguish the presence of the  $\text{Li}_2\text{Mn}_4\text{O}_9$  in  $\text{LiMn}_2\text{O}_4$  on account of their similar XRD patterns.

### 3.5. Behavior of optimized $\text{LiMn}_2\text{O}_4$ spinel in $\text{Li}/\text{LiMn}_2\text{O}_4$ coin cells

The above exposition makes it clear that the synthesis of  $\text{LiMn}_2\text{O}_4$  with a high specific capacity and reversibility is a very complex process, since it is always possible to create conditions for the production of compounds, poorer or richer in lithium and oxygen, which possess

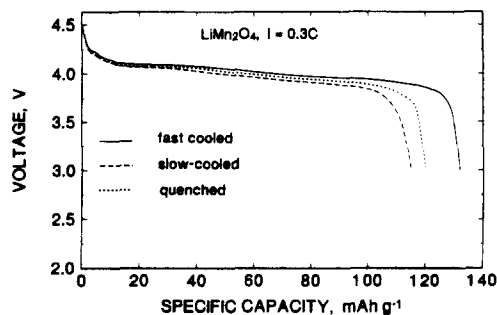


Fig. 8. Discharge curves of the  $\text{LiMn}_2\text{O}_4$  obtained using different cooling rates of the synthesized material.

a lower electrochemical activity. Moreover, it often happens that part of the product is with a deficiency in lithium or oxygen, while another part has an excess of them. A typical example is a product, synthesized under a slow air flow rate, which is then slowly cooled. In this case, conditions exist in the core of the batch for the formation of oxygen-poor phase  $\text{LiMn}_2\text{O}_{4-y}$ , while during the slow cooling the oxygen-rich phase  $\text{Li}_2\text{Mn}_4\text{O}_9$  will be obtained at the surface of the same batch. Unfortunately, neither the chemical nor the XRD analysis can distinguish these products from the normal stoichiometric spinel  $\text{LiMn}_2\text{O}_4$ . It is reasonable to conclude that the insufficient preliminary homogenization of the starting materials can result in products containing the lithium-rich spinel  $\text{Li}_4\text{Mn}_5\text{O}_{12}$  as well as lithium-poor phases, in spite of the fact that the overall ratio  $\text{Li}/\text{Mn}_2$  corresponds to the stoichiometric one. In this case the identification of these impurities will also be a serious problem.

By selection of the starting materials, the synthesis temperature and the preliminary thermal treatment [22,23], as well as by the optimization of the mode of homogenization, the condition for a forced air convection, the ratio of the starting materials and the cooling rate we succeeded to synthesize a batch of 250 g  $\text{LiMn}_2\text{O}_4$ , whose electrochemical behavior is demonstrated in the Figs. 9 and 10.

Fig. 9 presents the first charge/discharge curves of a  $\text{Li}/\text{LiMn}_2\text{O}_4$  coin cell with an electrolyte 1 M  $\text{LiPF}_6$  in EC–DMC (1:1), at a 3 h rate ( $I_c = I_d = 0.3$  C), with a  $\text{LiMn}_2\text{O}_4$ -positive electrode, prepared from a 250 g batch. Despite the relatively high rates of charge and discharge, the specific capacity of the first charge corresponding to  $144 \text{ mAh g}^{-1}$  is close to the theoretical one,  $148 \text{ mAh g}^{-1}$ , which reflects the almost complete extraction of lithium to a value equivalent to the compound  $\text{Li}_{0.93}\text{Mn}_2\text{O}_4$ . The same Figure shows that the initially reversible capacity is  $134 \text{ mAh g}^{-1}$ , which indicated that at this rate of the charge/discharge process, part of the lithium, amounting to  $\sim 10 \text{ mAh g}^{-1}$ , cannot be fully inserted back into the crystal lattice of

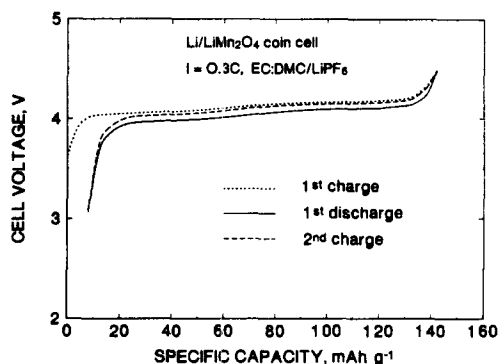


Fig. 9. First charge/discharge curves of  $\text{LiMn}_2\text{O}_4$  from a 250 g batch synthesized under optimal conditions.

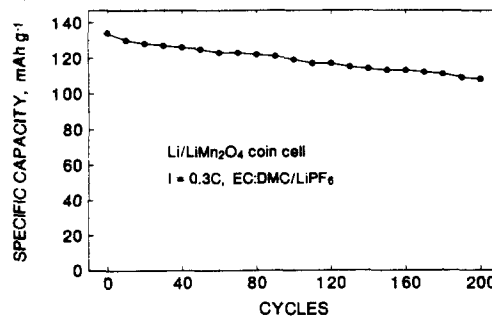


Fig. 10. Specific capacity vs. cycle number for optimized  $\text{LiMn}_2\text{O}_4$  from a 250 g batch.

the spinel so that, at the end of the first discharge, the compound  $\text{Li}_{0.93}\text{Mn}_2\text{O}_4$  is obtained. This result shows, that even in a practical cell, it is possible to cycle reversibly 0.9 M of lithium in the structure of the  $\text{LiMn}_2\text{O}_4$  spinel. As seen in Fig. 9, the charge and discharge curves are rather close, due to the low average polarization of the electrode during charge and discharge, which is in the order of 30 to 40 mV. One of the factors determining this low polarization is the use of the excellent electrolyte in this cell proposed by Tarascon and co-workers [15,17].

The behavior of the  $\text{LiMn}_2\text{O}_4$  electrode, subjected to long cycling test is illustrated in Fig. 10, where the specific capacity of the  $\text{LiMn}_2\text{O}_4$  in a  $\text{Li}/1 \text{ M LiPF}_6$  in an EC:DMC/ $\text{LiMn}_2\text{O}_4$  coin cell is plotted versus the number of cycles at 3 h charge/discharge rate. The  $\text{LiMn}_2\text{O}_4$  used in this cell is obtained by synthesis of a 250 g batch. It is seen that the average specific capacity in the first 100 cycles is about  $125 \text{ mAh g}^{-1}$ .

#### 4. Conclusions

The results demonstrated in Figs. 9 and 10, combined with the fact that from the point of view of the starting materials, price and toxicity, that  $\text{LiMn}_2\text{O}_4$  has a considerable advantage over  $\text{LiNiO}_2$  and  $\text{LiCoO}_2$ , and make  $\text{LiMn}_2\text{O}_4$  exceptionally prospective for lithium-ion batteries. The synthesis process of the  $\text{LiMn}_2\text{O}_4$  spinel with a high electrochemical performance depends on many parameters and the final product can be hardly characterized by any other methods except by electrochemical testing. This renders the synthesis a rather complex procedure and very hard to be reproduced. In spite of these obstacles it is possible to obtain a product, which is capable to exchange reversibly initially 0.9 equiv. of lithium at a 3 h rate and still to exchange more than 0.7 equiv. after 200 cycles.

#### References

- [1] D. Wickham and W. Croft, *J. Phys. Chem. Solids*, 7 (1958) 351.
- [2] J. Hunter, *J. Solid State Chem.*, 39 (1981) 142.

- [3] A. Mosbah, A. Verbaere and M. Tournoux, *Mater. Res. Bull.*, 18 (1983) 1375.
- [4] M. Thackeray, P. Johnson, L. de Picciotto, P. Bruce and J. Goodenough, *Mater. Res. Bull.*, 19 (1984) 179.
- [5] M. Thackeray, L. de Picciotto, A. de Kock, P. Johnson, V. Nicholas and K. Adendorff, *J. Power Sources*, 21 (1987) 1.
- [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] J. Tarascon, E. Wang, F. Shokooki, W. McKinnon and S. Colson, *J. Electrochem. Soc.*, 138 (1991) 2859.
- [9] J. Tarascon and D. Guyomard, *J. Electrochem. Soc.*, 138 (1991) 2864.
- [10] F. Shokooki, J. Tarascon, B. Wilkens, D. Guyomard and C. Chang, *J. Electrochem. Soc.*, 139 (1992) 1845.
- [11] D. Guyomard and J. Tarascon, *J. Electrochem. Soc.*, 139 (1992) 937.
- [12] J. Tarascon, D. Guyomard, B. Wilkens, W. McKinnon and P. Barboux, *Solid State Ionics*, 57 (1992) 113.
- [13] P. Barboux, F. Shokooki and J. Tarascon, *US Patent No. 5 135 732* (1992).
- [14] P. Barboux, F. Shokooki and J. Tarascon, *US Patent No. 5 211 933* (1993).
- [15] D. Guyomard and J. Tarascon, *US Patent No. 5 192 629* (1993).
- [16] J. Tarascon and D. Guyomard, *Electrochim. Acta*, 38 (1993) 1221.
- [17] J.M. Tarascon, D. Guyomard and G. Baker, *J. Power Sources*, 43/44 (1993) 689.
- [18] E. Rossen, C. Jones and J. Dahn, *Solid State Ionics*, 57 (1992) 311.
- [19] R. Bittihn, R. Herr and D. Hoge, *J. Power Sources*, 43/44 (1993) 223.
- [20] G. Pistoia and G. Wang, *Solid State Ionics*, 66 (1993) 135.
- [21] S. Bach, J. Pereira-Ramos, N. Baffier and R. Messina, *Electrochim. Acta*, 37 (1992) 1301.
- [22] V. Manev, A. Momchilov, A. Nassalevska and A. Kozawa, *J. Power Sources*, 43/44 (1993) 551.
- [23] A. Momchilov, V. Manev, A. Nassalevska and A. Kozawa, *J. Power Sources*, 41 (1993) 305.
- [24] V. Manev, N. Ilchev and A. Nassalevska, *J. Power Sources*, 25 (1989) 167.
- [25] M. Rossouw, A. de Kock, L. de Picciotto, M. Thackeray, W. David and R. Ibberson, *Mater. Res. Bull.*, 25 (1990) 173.
- [26] M. Thackeray, A. de Kock, M. Rossouw and D. Liles, *178th Meet. The Electrochemical Society., Seattle, WA, USA, 14–19 Oct. 1990*, p. 326.
- [27] M. Thackeray, A. de Kock, M. Rossouw, D. Liles, R. Bittihn and D. Hoge, *J. Electrochem. Soc.*, 139 (1992) 363.
- [28] A. de Kock, M. Rossouw, L. de Picciotto, M. Thackeray, W. David and R. Ibberson, *Mater. Res. Bull.*, 25 (1990) 657.
- [29] M. Rossouw and M. Thackeray, *Mater. Res. Bull.*, 26 (1991) 463.