

# Rechargeable lithium battery with spinel-related $\lambda$ - $\text{MnO}_2$

## I. Synthesis of $\lambda$ - $\text{MnO}_2$ for battery applications

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### Abstract

The electrochemical properties of the lithium spinel  $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$  ( $0 < x < 1$ ) synthesized by three different methods are discussed. The synthesis of spinel  $\text{LiMn}_2\text{O}_4$  for secondary lithium cells should be performed at temperatures lower than  $750^\circ\text{C}$ , since a thermal treatment above this limit can cause a significant chemical reduction and thus decrease its specific capacity. Moreover, the increase of the synthesis temperature above  $750^\circ\text{C}$  leads to a considerable reduction of the specific surface area of the samples and correspondingly to deterioration of their utilization at high discharge rates. The use of  $\lambda$ - $\text{MnO}_2$  produced by chemical oxidation of  $\text{LiMn}_2\text{O}_4$  cannot be justified in real systems, since, despite the higher specific surface area of the chemically oxidized samples, they display lower mean discharge voltage and reversibility.

### Introduction

The structural relationships between the lithium spinel  $\text{LiMn}_2\text{O}_4$  [1] and  $\lambda$ - $\text{MnO}_2$  obtained by extraction of Li 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 using Hunter's method of synthesis, Thackeray *et al.* [4-6] demonstrated that  $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$  ( $0 < x < 1$ ) can be cycled at about 4 V versus Li reference electrode. Their studies have shown that the electrochemical extraction of Li from  $\text{LiMn}_2\text{O}_4$  at low current density proceeds only to a composition of  $\text{Li}_{0.4}\text{Mn}_2\text{O}_4$  corresponding to a specific capacity of about  $90 \text{ mA h g}^{-1}$ . Recently, data for very good reversibility of  $\lambda$ - $\text{MnO}_2$  have been presented, but a specific capacity lower than  $115 \text{ mA h g}^{-1}$  was obtained [7-10].

The processes of Li ion insertion in the  $\text{LiMn}_2\text{O}_4$  spinel have been studied in much greater detail [5-14]. By optimizing the  $\text{LiMn}_2\text{O}_4$  synthesis for Li intercalation in  $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$   $140$ - $170 \text{ mA h g}^{-1}$  have been achieved [13-14].

The present study aims to elucidate the reasons for the low electrochemical activity of the  $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$  ( $0 < x < 1$ ) produced by the classical methods and to establish conditions for the synthesis of  $\lambda$ - $\text{MnO}_2$  with high specific capacity and reversibility with respect to lithium ion intercalation.

## Experimental

Three different approaches to  $\text{LiMn}_2\text{O}_4$  synthesis were applied:

(i) the method first suggested by Hunter [2] and later used without significant alteration by numerous authors [4-8];

(ii) reproduction of the synthesis conditions under which optimum capacity and reversibility was obtained for the system  $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$  [13, 14], and

(iii) heating of a mixture of  $\text{MnO}_2$  (chemical manganese dioxide (CMD)) and  $\text{LiNO}_3$  for 48 h in the temperature range 450-900 °C.

The  $\text{LiMn}_2\text{O}_4$  synthesized by each of the above methods was oxidized electrochemically on the electrodes studied, or chemically in excess of strong inorganic acid ( $\text{H}_2\text{SO}_4$ ,  $\text{NH}_4\text{NO}_3$ ) at  $\text{pH}=1$  [2, 3, 14]. The electrochemical measurements were performed on test electrodes in a three-electrode cell with  $\text{LiAsF}_6/\text{PC-EC}$  electrolyte.

## Results and discussion

The discharge characteristics of a test electrode of  $\lambda\text{-MnO}_2$  obtained by electrochemical extraction of Li ions from  $\text{LiMn}_2\text{O}_4$  synthesized by Hunter's method [2], are shown in Fig. 1. A significant increase of the electrode polarization and a reduction of its capacity with the rise of the discharge current is observed, probably due to diffusion hindrances of  $\text{Li}^+$  in the  $\text{LiMn}_2\text{O}_4$  structure [4]. The  $\text{LiMn}_2\text{O}_4$  obtained by Hunter's method, with an initial specific surface area less than  $0.1 \text{ m}^2 \text{ g}^{-1}$ , was additionally subjected to continuous grinding. Following 12 h grinding the specific surface area increased to  $0.4 \text{ m}^2 \text{ g}^{-1}$ , and after 24 h treatment it reached  $1.3 \text{ m}^2 \text{ g}^{-1}$ .

Figure 2 compares the dependence of the specific capacity of the ground samples on the discharge current with an untreated sample. In accordance with Atlung's model [15], the increase of the specific surface area of  $\text{LiMn}_2\text{O}_4$  leads to a remarkable

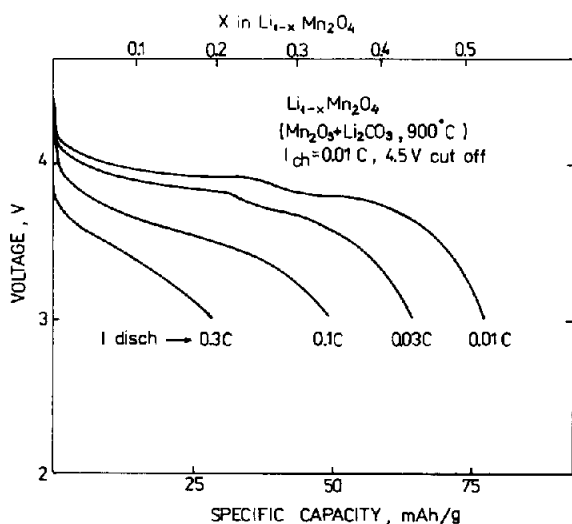


Fig. 1. Discharge curves at different currents for  $\text{LiMn}_2\text{O}_4$  obtained from  $\text{Mn}_2\text{O}_3$  and  $\text{Li}_2\text{CO}_3$  at 900 °C.

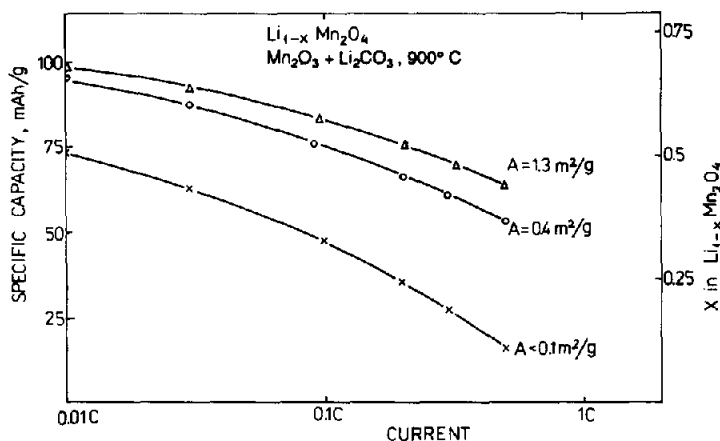


Fig. 2. Influence of the specific surface area on utilization-discharge rate relationship.

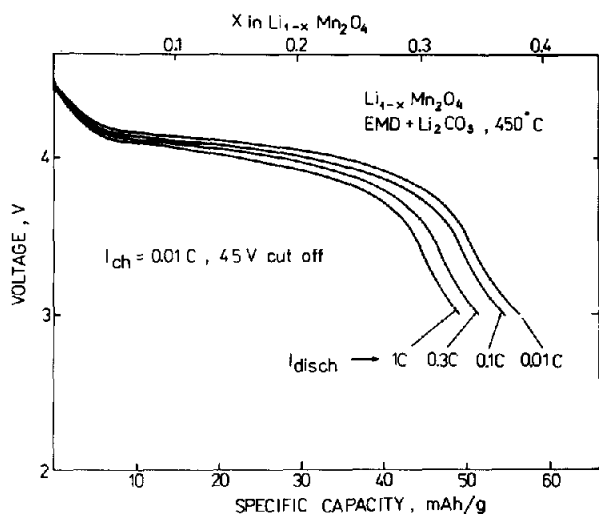


Fig. 3. Discharge curves at different currents for  $\text{LiMn}_2\text{O}_4$  obtained from EMD and  $\text{Li}_2\text{CO}_3$  at  $450^\circ\text{C}$ .

increase of its specific capacity but at 3 h discharge rate it is still equal to half of its theoretical value.

The discharge characteristics of  $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$  ( $0 < x < 1$ ) synthesized under conditions for optimum  $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$  ( $0 < x < 1$ ) behavior [13, 14] are given in Fig. 3. It can be seen that with the change of the discharge current with two orders of magnitude from  $I = 0.01\text{ C}$  to  $I = 1\text{ C}$ , the specific capacity slightly decreases. Unfortunately, the obvious advantage of this material at high discharge rates, presumably due to its high specific area of  $16\text{ m}^2\text{ g}^{-1}$ , is combined with relatively low specific capacity which at  $I = 0.3\text{ C}$  is one third of the theoretical one.

The long-term cycling tests at the 3 h rate of 24 h ground  $\text{LiMn}_2\text{O}_4$  produced by Hunter's method and of  $\text{LiMn}_2\text{O}_4$  synthesized under the optimum conditions for

the  $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$  system [13, 14], are illustrated in Fig. 4. It can be seen that  $\text{LiMn}_2\text{O}_4$  synthesized by Hunter's method has excellent reversibility. The samples synthesized under conditions, where according to Nagaura *et al.* [14],  $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$  shows splendid reversibility [13, 14], exhibit surprising instability in the  $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$  system (Fig. 4). A plausible explanation of this fact is that the increase of the  $\text{LiMn}_2\text{O}_4$  distortions [13, 14] favors the reversibility of the Li ion intercalation connected with the phase transition [8, 11] and affects negatively the reversibility during Li ion extraction where the cubic crystal structure remains unchanged [2–8]. These results directed our investigations towards an optimum compromise between the well-ordered spinel structure and high specific surface area of the samples. Following a series of preliminary experiments which showed that the specific surface area of the synthesized product essentially depends on that of the starting manganese oxide, CMD Faradiser M, provided by Sedema, was chosen because of its higher specific surface area.

The diffraction patterns of  $\text{LiMn}_2\text{O}_4$  obtained from CMD and  $\text{LiNO}_3$  heated for 48 h at 450, 550, 650, 750 and 850 °C, presented in Fig. 5, are in accordance with those reported by other authors using electrochemical manganese oxide (EMD) and  $\text{Li}_2\text{CO}_3$  as starting products [8, 13, 14].

The dependence of the specific surface area of the samples (CMD and  $\text{LiNO}_3$ ) on the synthesis temperature is shown in Fig. 6. Figure 6 gives the change of the stoichiometric coefficient  $y$  in  $\text{LiMn}_2\text{O}_{4-y}$  with the increase of the synthesis temperature. It can be seen that up to 650 °C the specific surface area regularly decreases, while between 650 and 750 °C a well-defined plateau appears, and above 750 °C the specific surface area is reduced again. Between 600 and 800 °C the stoichiometric product ( $y=0$ ) is synthesized, and subsequently in the range 800 to 900 °C a considerable decrease of the stoichiometric coefficient  $y$  is observed reflecting the partial chemical reduction of the  $\text{LiMn}_2\text{O}_4$  spinel.

The thermogravimetric studies of samples synthesized at 650 °C (Fig. 7) confirm the results of the chemical analysis (Fig. 6). The weight losses of the dry samples

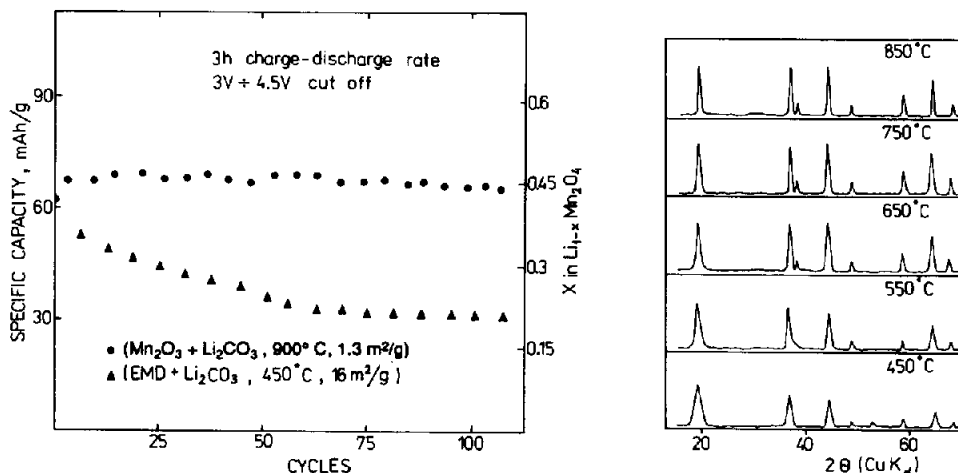


Fig. 4. Specific capacity vs. cycle number for  $\text{LiMn}_2\text{O}_4$  obtained from EMD and  $\text{Li}_2\text{CO}_3$  at 450 °C and from  $\text{Mn}_2\text{O}_3$  and  $\text{Li}_2\text{CO}_3$  at 900 °C.

Fig. 5. Powder X-ray diffraction patterns of the reaction products of CMD and  $\text{LiNO}_3$  heated for 48 h at different temperatures.

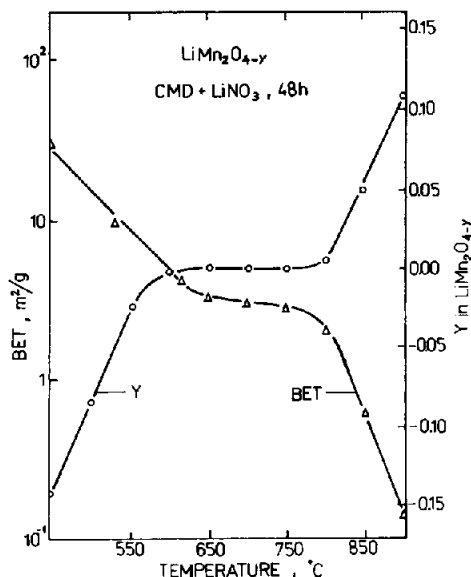


Fig. 6. Temperature vs. specific surface area and stoichiometry of the reaction products obtained from CMD and  $\text{LiNO}_3$ .

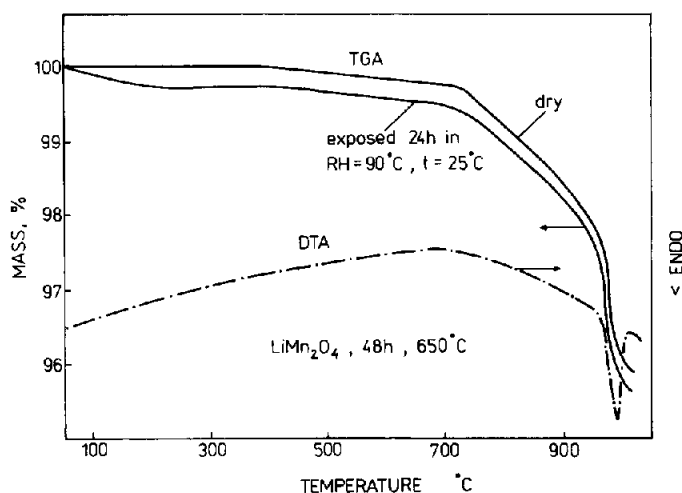
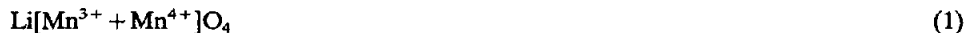


Fig. 7. Thermogravimetric (TGA) and differential thermal (DTA) analysis of  $\text{LiMn}_2\text{O}_4$  synthesized from CMD and  $\text{LiNO}_3$  at  $650^\circ\text{C}$ .

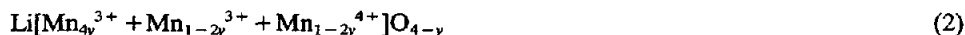
start at  $400^\circ\text{C}$ , and up to  $750^\circ\text{C}$  are about 0.2%, probably due to surface oxygen losses. In the temperature range  $750$  to  $900^\circ\text{C}$  about 1 to 1.2% weight decrease of the samples is observed, which corresponds to the stoichiometric deviations of the oxygen content determined by chemical analysis (Fig. 6). The differential thermal analysis (DTA) (Fig. 7) indicates that the significant losses of oxygen in this range are not accompanied by a phase transition, which is observed as high as  $980^\circ\text{C}$ .

The discharge curves at the 3 h charge/discharge rate of test electrodes consisting of samples synthesized for 48 h from  $\text{LiNO}_3$  and CMD ( $I_{\text{ch}} = I_{\text{dch}} = 0.3 \text{ C}$ ) at different temperatures, are given in Fig. 8. Obviously with the temperature rise the specific capacity increases, reaching at  $750^\circ\text{C}$  a maximum value equal to 0.92 of the theoretical one, and after that, decreases again. Considering the results presented in Fig. 6 the lower specific capacity of the product synthesized at  $850^\circ\text{C}$  may be attributed either to the reduced specific surface area or to the disturbed stoichiometry.

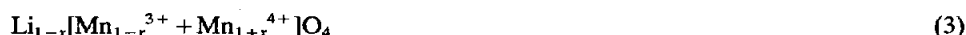
The effect of the disturbed stoichiometry can be explained by the fact that, while in the stoichiometric spinel half of the manganese is of 3+ valency and the other half is of 4+ valency [4, 11]:



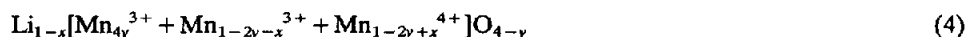
in the partially-reduced spinel, the reduction most probably leads to a decrease of the 4+ manganese on account of the increase of the 3+ one. Considering that oxygen is of 2- valency, it follows that the change in the reduced spinel  $\text{LiMn}_2\text{O}_{4-y}$  can be presented analogously to eqn. (1):



where  $\text{Mn}_{4y}^{3+}$  is the amount of 3+ manganese on account of the oxygen vacancies, which cannot be transformed to 4+ during the extraction of Li ions. Furthermore, using Thackeray's expression of the intercalation process [11] for the stoichiometric spinel:



for the partially-reduced spinel we obtain:



The latter expression can be defined only at  $0 < x < 1 - 2y$ . Taking into account the condition  $x < 1 - 2y$ , one can easily estimate that at  $y = 0.1$ , observed at a synthesis

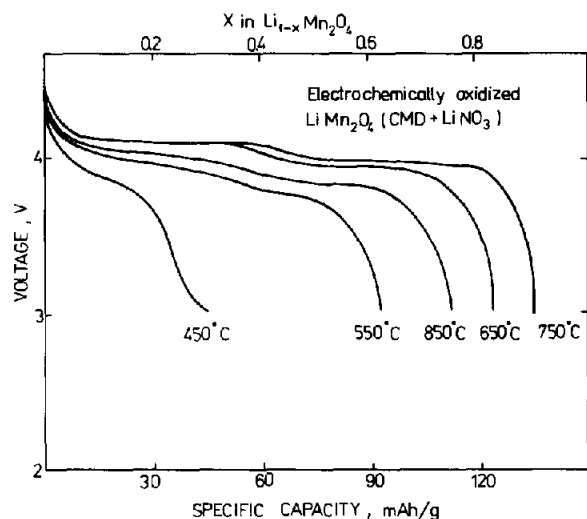


Fig. 8. Discharge curves at 2 h rate of  $\text{LiMn}_2\text{O}_4$  produced from CMD and  $\text{LiNO}_3$  at different temperatures.

temperature of 900 °C, the theoretical specific capacity is reduced from 154 to 123 mA h g<sup>-1</sup>. This can explain the reduction of the specific capacity with the rise of the temperature above 800 °C, observed in Fig. 8, as well as the results obtained by other authors [3, 8].

Proposing the above explanation we do not assume that the partial reduction of the samples synthesized at high temperatures leads to a new phase nucleation, since neither the X-ray patterns nor the DTA justify this suggestion. Certainly the formation of a new phase, amorphous with respect to the X-ray diffraction, may be also considered.

Figure 9 presents the distribution of the differential capacity as a function of the potential of samples of electrochemically oxidized LiMn<sub>2</sub>O<sub>4</sub> obtained by slow (0.02 mV s<sup>-1</sup>) cyclic voltammetry. It should be emphasized that the two peaks display considerable symmetry and slightly higher potentials in comparison with the data published earlier [8], which may be explained with the higher oxidation state of the samples studied.

The preparation of samples of Li<sub>1-x</sub>Mn<sub>2</sub>O<sub>4</sub> (0 < x < 1) can be accomplished either by electrochemical extraction of Li<sup>+</sup> from LiMn<sub>2</sub>O<sub>4</sub> spinel or by Li<sup>+</sup> insertion into λ-MnO<sub>2</sub> obtained by chemical oxidation of the same spinel [1, 2]. Our experimental results show that the specific surface area of chemically-oxidized λ-MnO<sub>2</sub> increases nearly three times as compared with that of the starting spinel LiMn<sub>2</sub>O<sub>4</sub>. After oxidation with H<sub>2</sub>SO<sub>4</sub> the specific surface area increased from 3.45 to 9.6 m<sup>2</sup> g<sup>-1</sup>, and after treatment with HNO<sub>3</sub> to 10.3 m<sup>2</sup> g<sup>-1</sup>. Nevertheless, as can be seen from Fig. 10, the specific capacity of these compounds practically does not differ, and only a slight change in the mean discharge voltage is observed.

The results of the long-term cycling of test electrodes of LiMn<sub>2</sub>O<sub>4</sub> synthesized from LiNO<sub>3</sub> and CMD at different temperatures are shown in Fig. 11. It can be

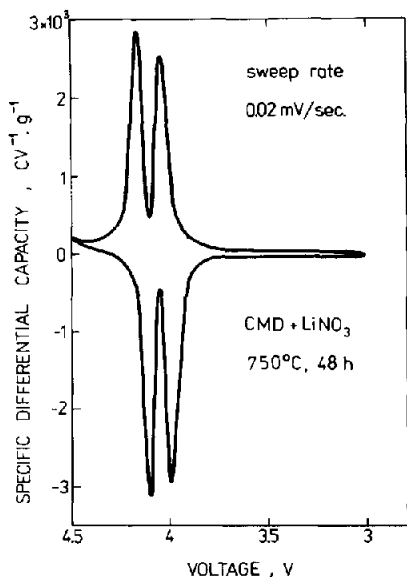


Fig. 9. Differential capacity/potential dependence of LiMn<sub>2</sub>O<sub>4</sub> synthesized from CMD and LiNO<sub>3</sub> at 750 °C.

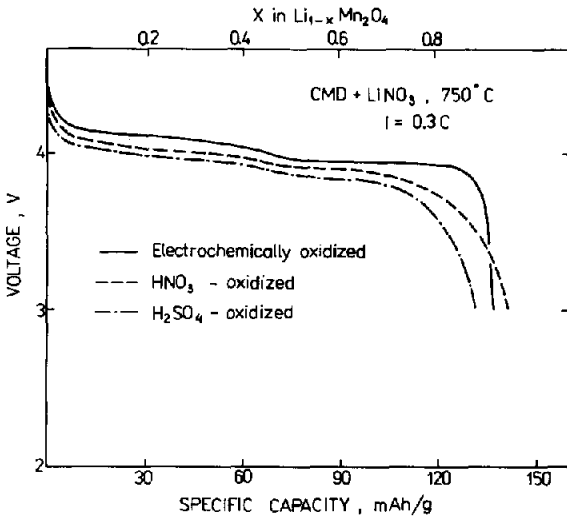


Fig. 10. Discharge curves of chemically- and electrochemically-oxidized  $\text{LiMn}_2\text{O}_4$  synthesized from CMD and  $\text{LiNO}_3$  at 750 °C.

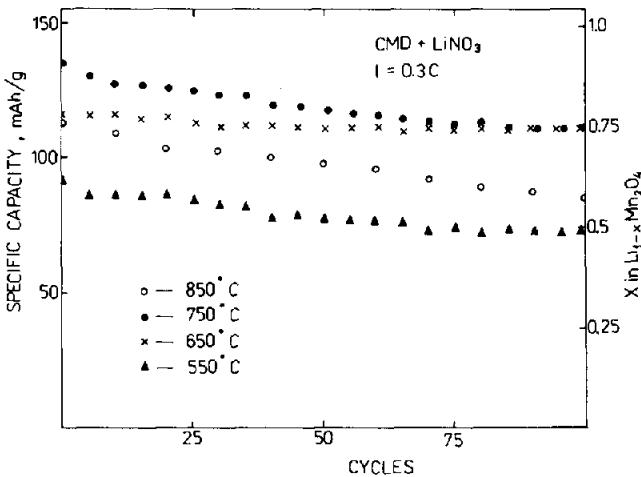


Fig. 11. Specific capacity vs. cycle number for  $\text{LiMn}_2\text{O}_4$  synthesized from CMD and  $\text{LiNO}_3$  at different temperatures.

concluded from this Fig. that the reversibility of the samples synthesized at 650 and 750 °C is very good.

The comparison between the cycleability of samples obtained by electrochemical oxidation of  $\text{LiMn}_2\text{O}_4$  and of  $\lambda\text{-MnO}_2$  produced by chemical oxidation of  $\text{LiMn}_2\text{O}_4$  with  $\text{H}_2\text{SO}_4$  or  $\text{HNO}_3$  is illustrated in Fig. 12. It follows from this Fig. that the slightly higher initial capacity obtained for the samples chemically oxidized with  $\text{HNO}_3$  (Fig. 10) is on account of their lower reversibility in comparison with the electrochemically oxidized ones.



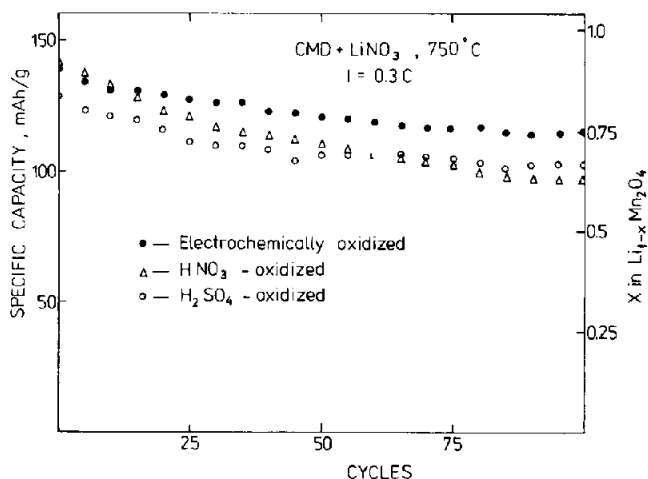


Fig. 12. Specific capacity vs. cycle number for chemically- and electrochemically-oxidized  $\text{LiMn}_2\text{O}_4$  synthesized from CMD and  $\text{LiNO}_3$  at  $750^\circ\text{C}$ .

## Conclusion

The synthesis of  $\text{LiMn}_2\text{O}_4$  spinel for 4 V secondary lithium cells should be performed at temperatures lower than  $750^\circ\text{C}$ , since a thermal treatment above this limit can cause a substantial chemical reduction reflecting in a decrease of its specific capacity. Simultaneously, the increase of the synthesis temperature above  $750^\circ\text{C}$  leads to a considerable reduction of the specific surface area of the samples and correspondingly to a decrease of their utilization at high discharge rates. The use of  $\lambda\text{-MnO}_2$  produced by chemical oxidation of  $\text{LiMn}_2\text{O}_4$  has no advantages in comparison with the electrochemically-obtained one.

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