Chemical lithium extraction from manganese oxides for lithium rechargeable batteries*

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Abstract

Chemical lithium extraction has been carried out on the following manganese oxides: the spinel-type compounds $LiMn_2O_4$ and $Li_{4/3}Mn_{5/3}O_4$, and the rocksalt-related compound Li_2MnO_3. Lithium can be partially removed chemically from these compounds without destroying the host framework. Some compounds obtained by this method have been tested as cathodic materials in rechargeable lithium cells. Electrochemical results and X-ray diffraction patterns of cycled cathodes are presented. Electrochemical insertion/extraction of Li^+ ions occurs with tetragonal/cubic distortion in the spinel framework, whereas Li^+ ions can move in compounds having the rocksalt structure, without significant modification of the X-ray patterns.

Introduction

In our investigations to synthesize cathodic materials for lithium rechargeable batteries, we have studied [1] chemical lithium extraction from different manganese oxides using soft chemistry processes. Starting materials are synthesized by solid-state reaction in the ternary system Li–Mn–O. Some of these compounds, with the formula M_3O_4, assume the spinel structure without distortion of the cubic cell: $LiMn_2O_4$ [2] and $Li_{4/3}Mn_{5/3}O_4$ [3]. Some, with the formula MO, e.g., $LiMnO_2$ [4] and Li_2MnO_3 [5, 6], adopt the distorted rocksalt structure. A cationic order Li/Mn on the octahedral sites induces a lowering of the symmetry from cubic to orthorhombic for $LiMnO_2$ and to monoclinic for Li_2MnO_3.

In these compounds the anions form a cubic close packing. With regard to the spinel framework AB_2O_4 with the cubic symmetry $Fd3m$, the A cations occupy one-eighth of the tetrahedral sites (8a) of the oxygen network and the B cations one-half of the octahedral sites (16d). The remaining octahedral

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sites (16c) are therefore vacant. In the rocksalt structure, with the formula MO, all the octahedral sites of the oxygen network are filled by cations.

Experimental

Electrochemical tests were carried out at room temperature in button cells with a current density of 0.5 mA cm^{-2} (both charge and discharge). The end of discharge voltage was 2 V.

The cathode was prepared from a mixture of active material (80 wt.%), graphite (7.5 wt.%), acetylene black (7.5 wt.%), and Teflon binder (5 wt.%), pressed on a stainless steel grid. The anode was a lithium disc (thickness 0.6 mm). The electrolyte was a mixture of propylene carbonate, ethylene carbonate, and dimethoxyethane in the proportion 1:1:2, with LiAsF$_6$ as the lithium salt. Button cells were assembled in a dry room.

After cycling, the cells were opened and the cathodes rinsed with DME and dried under vacuum at 100 °C, before X-ray analysis. The X-ray diffraction patterns were obtained using Mo Kα radiation.

Results obtained with LiMn$_2$O$_4$

The insertion/extraction reaction of Li$^+$ ions in the spinel LiMn$_2$O$_4$ has been studied, both chemically and electrochemically, by many authors [7–14]. For the composition Li$_{1-x}$Mn$_2$O$_4$ ($0 \leqslant x \leqslant 1$) the symmetry is cubic, whereas, for the composition Li$_{1+x}$Mn$_2$O$_4$ ($1 \leqslant x \leqslant 2$) lithium insertion induces a Jahn–Teller distortion. This distortion is due to the increase in Mn^{3+} ions, reducing the symmetry from cubic to tetragonal.
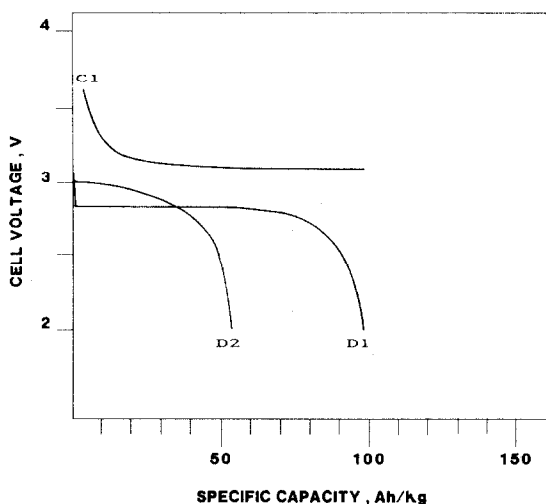

Fig. 1. Charge and discharge curves of LiMn$_2$O$_4$ (0.5 mA cm^{-2}).

Mosbah *et al.* [8] placed Li^+ on the octahedral sites for the chemically reduced form, λ-$LiMnO_2$. This compound therefore has the ordered rocksalt structure. On the other hand, Thackeray *et al.* [9] concluded that Li^+ occupied both tetrahedral and octahedral sites in the chemically-reduced compound $Li_2Mn_2O_4$.

$LiMn_2O_4$, and λ-$Li_{0.5}Mn_2O_4$, which is prepared by oxidizing $LiMn_2O_4$ with $KMnO_4$ solution at pH = 4, have been tested as cathodic materials.

The results obtained for $LiMn_2O_4$ (Fig. 1) indicate an important loss of capacity at the second discharge, although lithium inserted in the first discharge is completely recovered. These results were confirmed by cyclic voltammetry.
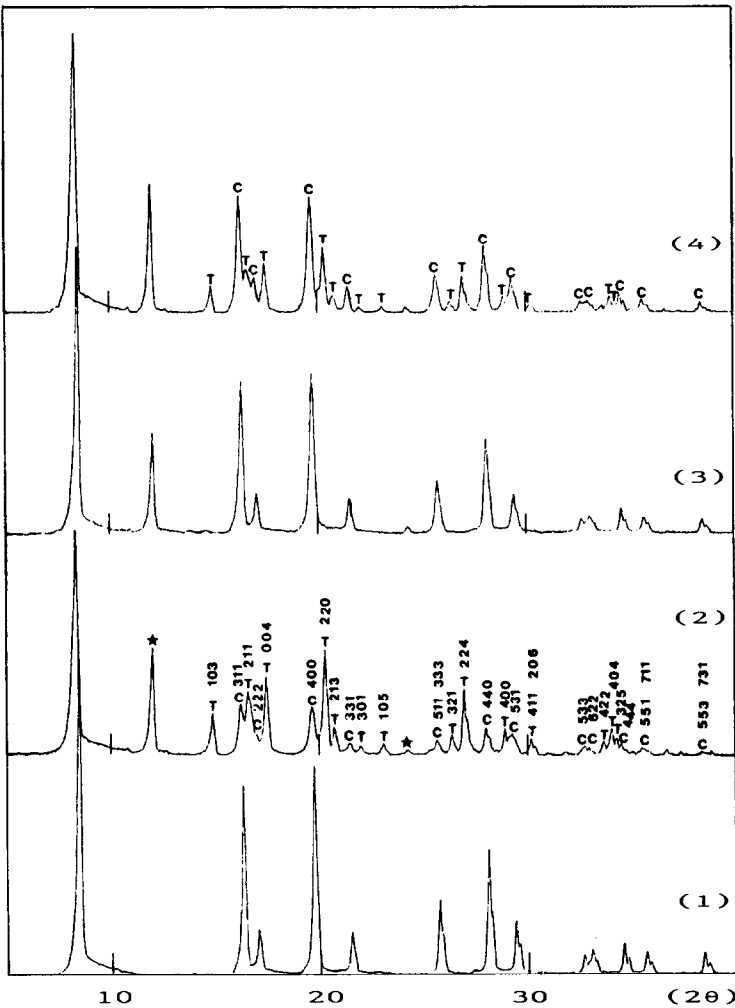

Fig. 2. X-ray diffraction patterns of $LiMn_2O_4$ cathodes (*, graphite). (1) $LiMn_2O_4$; (2) $Li_{1.64}Mn_2O_4$ (1st discharge); (3) $Li_{1.02}Mn_2O_4$ (1st charge); (4) $Li_{1.37}Mn_2O_4$ (2nd discharge).

In agreement with electrochemical results, cubic symmetry of $LiMn_2O_4$ was observed in the charged state, whereas the diffraction peaks of the tetragonal phase were stronger for the first discharge than for the second (Fig. 2). Refined unit cell parameters and formulae deduced from electrochemical results are given in Table 1.

By contrast with $LiMn_2O_4$, inserted lithium was only partially recovered from charged λ-$Li_{0.50}Mn_2O_4$ (Fig. 3). Previous chemical extraction of Li^+

TABLE 1

Cell parameters for $LiMn_2O_4$

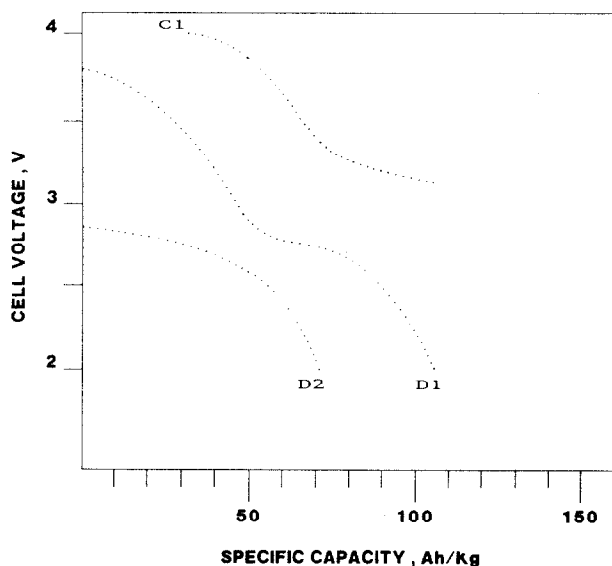|	Formula	Cell parameters (Å)		Tetragonal distortion
	$LiMn_2O_4$	$a_c = 8.269(3)$		
1st discharge	$Li_{1.64}Mn_2O_4$	$a_c = 8.296(4)$	$a_t = 5.686(4)$ $c_t = 9.331(7)$	1.160
1st charge	$Li_{1.02}Mn_2O_4$	$a_c = 8.272(3)$		
2nd discharge	$Li_{1.37}Mn_2O_4$	$a_c = 8.289(5)$	$a_t = 5.685(3)$ $c_t = 9.328(5)$	1.160

a_c, cubic unit cell.
a_t, c_t, tetragonal unit cell.

Fig. 3. Charge and discharge curves of λ-$Li_{0.50}Mn_2O_4$ (0.5 mA cm^{-2}).

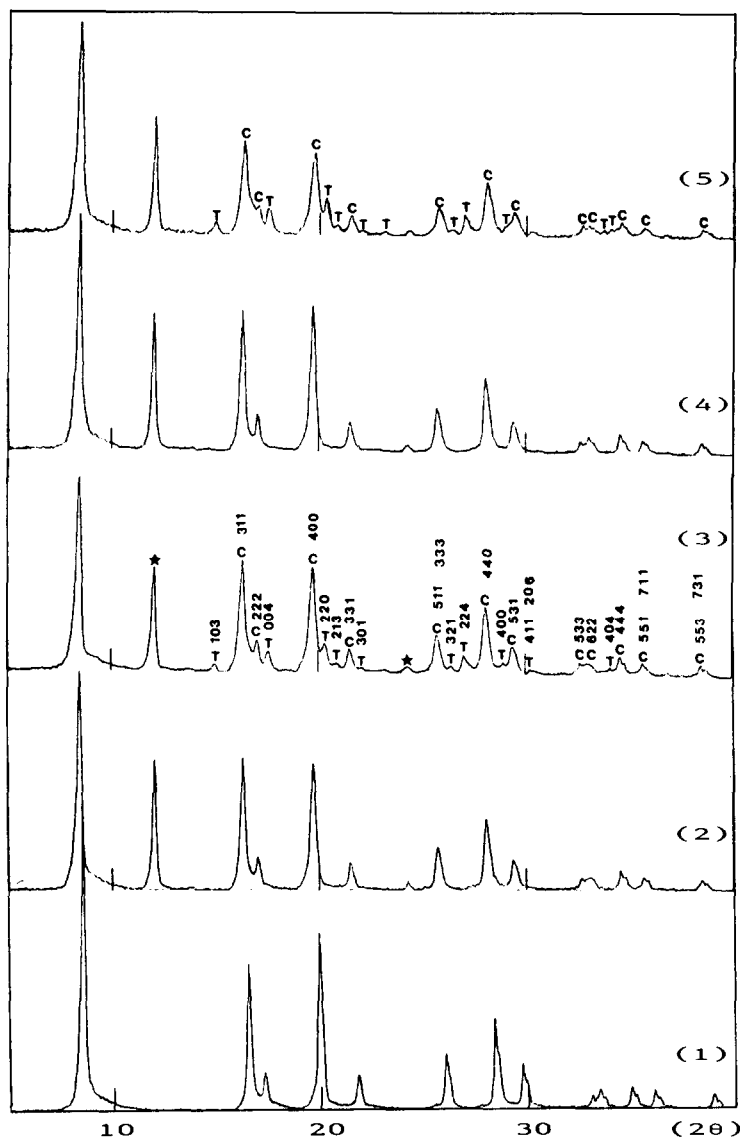Fig. 4. X-ray diffraction patterns of λ-$Li_{0.50}Mn_2O_4$ cathodes (*, graphite). (1) λ-$Li_{0.50}Mn_2O_4$; (2) $Li_{0.80}Mn_2O_4$ (1st half-discharge $\rightarrow$ 2.8 V); (3) $Li_{1.20}Mn_2O_4$ (1st discharge); (4) $Li_{0.75}Mn_2O_4$ (1st charge); (5) $Li_{1.17}Mn_2O_4$ (2nd discharge).

ions does not significantly increase the capacity. The x value in $Li_{1+x}Mn_2O_4$ — obtained for the first discharge — is lower for $Li_{0.50}Mn_2O_4$ than for $LiMn_2O_4$ (giving $Li_{1.20}Mn_2O_4$ and $Li_{1.64}Mn_2O_4$, respectively).

The X-ray diffraction patterns of cycled cathodes are presented in Fig. 4, and unit cell parameters obtained for the different compositions are given in Table 2.

TABLE 2

Cell parameters for λ-$Li_{0.5}Mn_2O_4$

	Formula	Cell parameters (Å)		Tetragonal distortion
	$Li_{0.50}Mn_2O_4$	$a_c = 8.173(3)$		
1st discharge	$Li_{1.20}Mn_2O_4$	$a_c = 8.275(4)$	$a_t = 5.679(3)$ $c_t = 9.285(6)$	1.156
1st charge	$Li_{0.75}Mn_2O_4$	$a_c = 8.275(3)$		
2nd discharge	$Li_{1.17}Mn_2O_4$	$a_c = 8.269(3)$	$a_t = 5.671(4)$ $c_t = 9.294(8)$	1.159

a_c, cubic unit cell.
a_t, c_t, tetragonal unit cell.
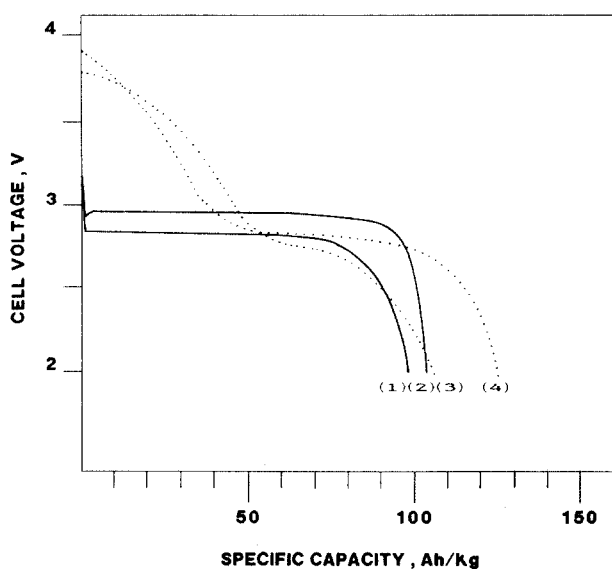
Fig. 5. First discharge of $LiMn_2O_4$ and λ-$Li_{0.50}Mn_2O_4$. (1) $LiMn_2O_4$ (0.5 mA cm^{-2}); (2) $LiMn_2O_4$ (0.05 mA cm^{-2}); (3) $Li_{0.50}Mn_2O_4$ (0.5 mA cm^{-2}); (4) $Li_{0.50}Mn_2O_4$ (0.05 mA cm^{-2}).

Lithium electrochemical insertion has also been studied using a lower current density (0.05 mA cm^{-2} instead of 0.5 mA cm^{-2} in practical cells). The operating voltage is higher, but the amount of inserted lithium is not significantly greater (Fig. 5). From these results, it appears that the electrochemical insertion of Li$^+$ ions in the spinel framework is not limited by the rate of discharge.
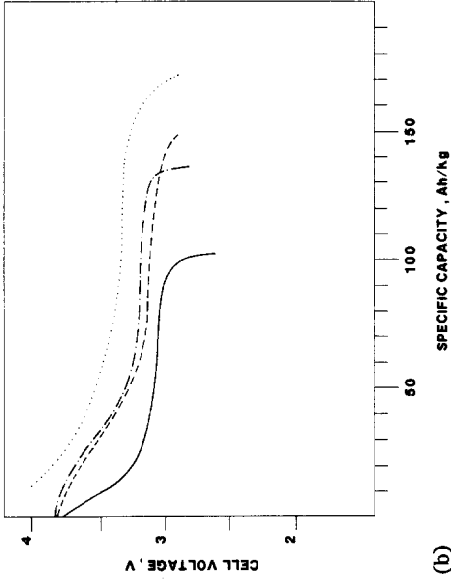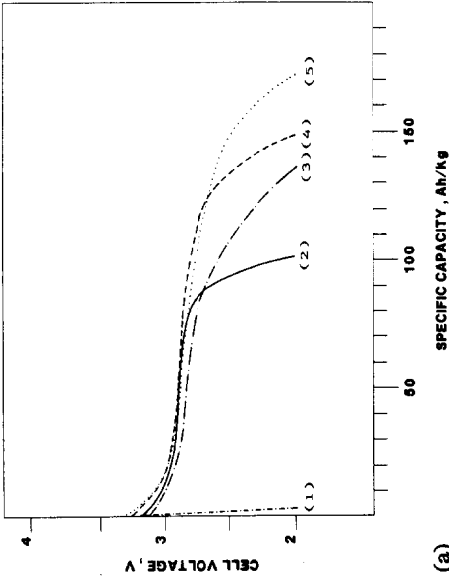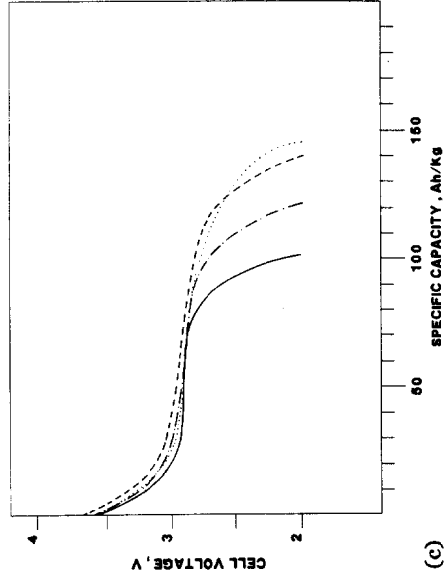
Fig. 6. Charge and discharge curves of compounds obtained by chemical lithium extraction from Li_2MnO_3. (a) 1st discharge; (b) 1st charge; (c) 2nd discharge. (1) Li_2MnO_3; (2) $Li_{1.34}Mn_{1.16}O_3$; (3) $LiMn_{1.25}O_3$; (4) '$Li_{0.78}Mn_{1.30}O_3$'; (5) '$Li_{0.57}Mn_{1.38}O_3$'.
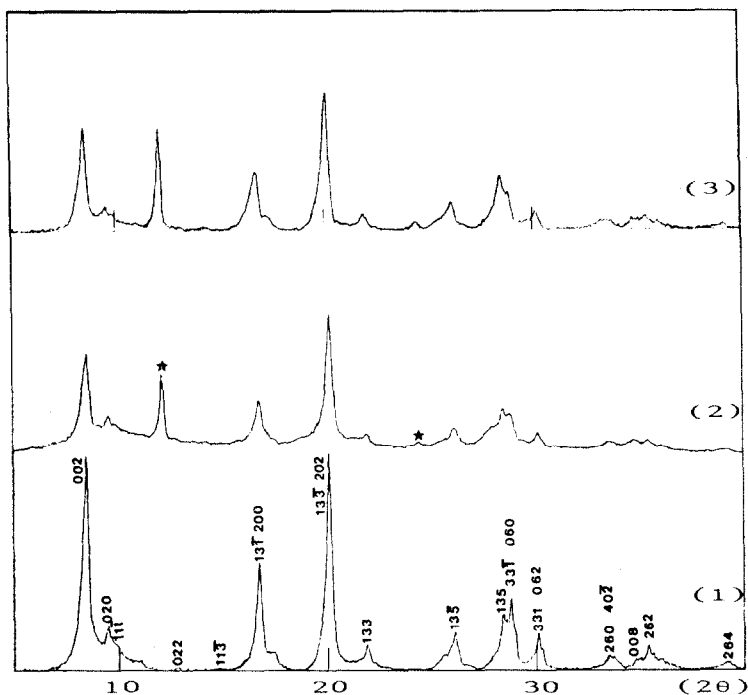
Fig. 7. X-ray diffraction patterns of $Li_{1.34}Mn_{1.16}O_3$ cathodes (*, graphite). (1) $Li_{1.34}Mn_{1.16}O_3$; (2) 1st discharge; (3) 10th charge.

Results obtained with Li_2MnO_3

Lithium cannot be extracted from Li_2MnO_3 by oxidation (chemical or electrochemical) because the oxidation state of manganese ions is $+4$. Extraction of lithium is carried out by an exchange reaction, $H^+ \rightarrow Li^+$, using 1 N HCl solution. Under these conditions up to half the lithium ions can be extracted without destroying the Li_2MnO_3 framework. The $+4$ oxidation state of the manganese ions is preserved after the reaction. When the amount of extracted lithium increases, two phases are obtained: a phase with an Li_2MnO_3-related structure and γ-MnO_2. Protons are eliminated from the structure by a further thermolysis at 300 °C. Synthesis of these compounds will be discussed in a further paper [15].

Compounds having the following formulae have been tested as cathodic materials: $Li_{1.34}Mn_{1.16}O_3$, $LiMn_{1.25}O_3$, '$Li_{0.78}Mn_{1.30}O_3$', and '$Li_{0.57}Mn_{1.36}O_3$'. The $Li_{1.34}Mn_{1.16}O_3$ and $LiMn_{1.25}O_3$ materials refer to a single phase with an Li_2MnO_3-related structure, whereas '$Li_{0.78}Mn_{1.30}O_3$' and '$Li_{0.57}Mn_{1.36}O_3$' are average compositions of biphasic systems (Li_2MnO_3-related structure and γ-MnO_2).

Electrochemical results are presented in Fig. 6(a)–(c).

The discharged capacity — the loss of capacity between the first and the second discharge — increases with the amount of extracted lithium. The electrochemical activity of $Li_{1.34}Mn_{1.16}O_3$ and $LiMn_{1.25}O_3$ contrasts with the
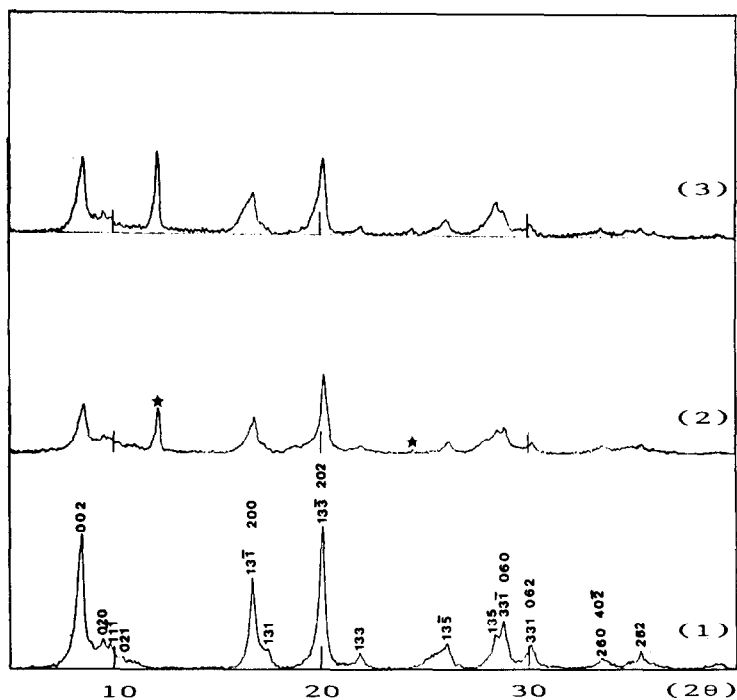
Fig. 8. X-ray diffraction patterns of $LiMn_{1.25}O_3$ cathodes (*, graphite). (1) $LiMn_{1.25}O_3$; (2) 1st discharge; (3) 20th charge.

complete inactivity of Li_2MnO_3. These compounds, which present a cationic deficiency, can be formulated as $M_{0.83}O$ and $M_{0.75}O$, compared with the formula MO of the stoichiometric oxide Li_2MnO_3. The X-ray patterns of charged and discharged cathodes (Figs. 7 and 8) do not show major modifications (despite the presence of Mn^{3+} ions in discharge). Lithium can therefore move in and out of the rocksalt structure without the appearance of other phases.

Results obtained with $Li_{4/3}Mn_{5/3}O_4$

The spinel $Li_{4/3}Mn_{5/3}O_4$ differs from $LiMn_2O_4$ because one part of the 16d octahedral sites (space group $Fd3m$) is occupied by Li^+ ions. In this compound lithium occupies both tetrahedral (8a) and octahedral (16d) sites. The manganese oxidation state is $+4$, and, as with Li_2MnO_3, lithium cannot be extracted from $Li_{4/3}Mn_{5/3}O_4$ by oxidation processing.

Lithium extraction is carried out using HCl solution. Under these conditions lithium is extracted without modification of the manganese oxidation state. Three compounds prepared by this method have been tested electrochemically.
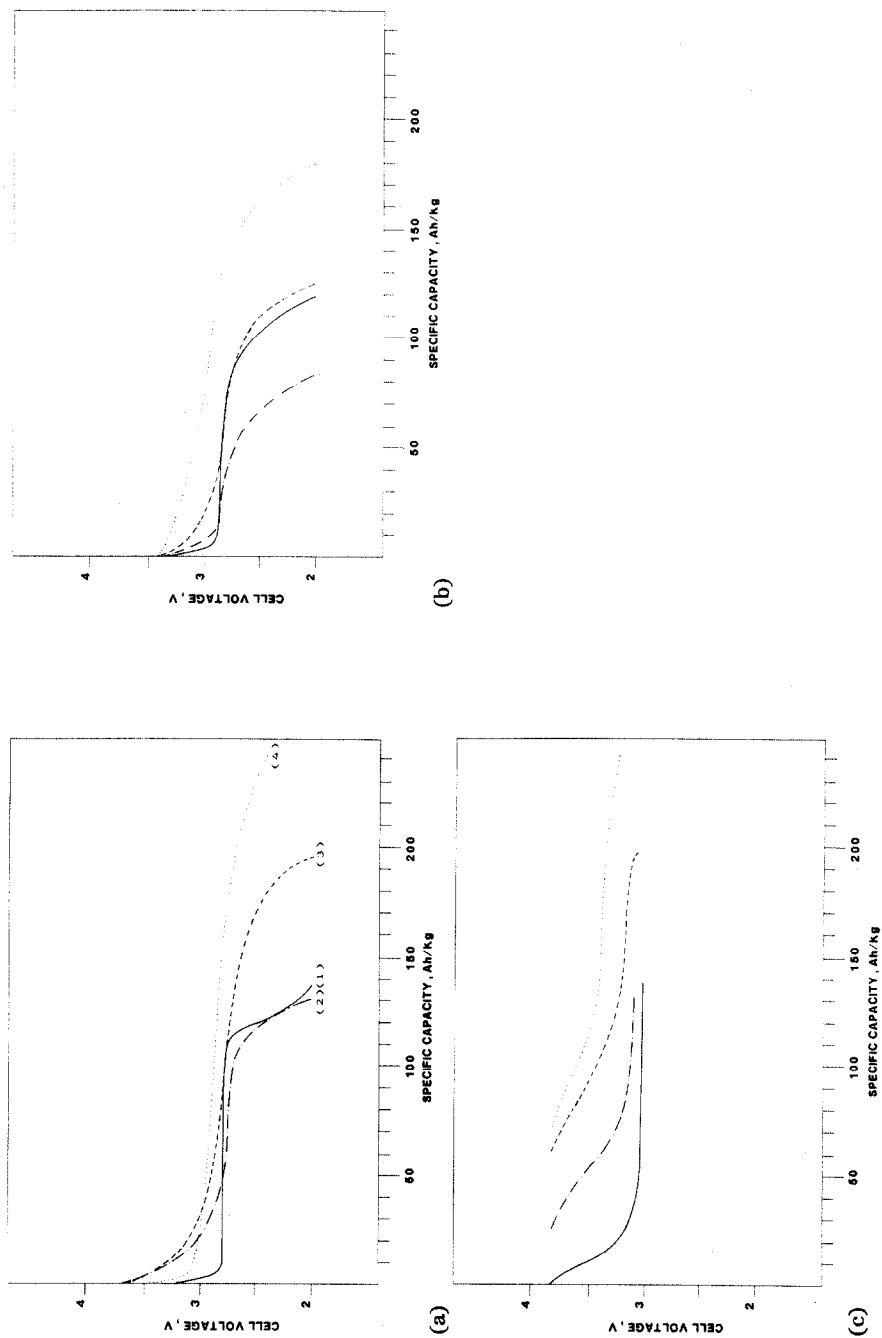
Fig. 9. Charge and discharge curves of compounds obtained by chemical lithium extraction from $Li_{4/3}Mn_{5/3}O_4$. (a) 1st discharge; (b) 1st charge; (c) 2nd discharge. (1) $Li_{4/3}Mn_{5/3}O_4$; (2) $Li/Mn = 0.40$; (3) $Li/Mn = 0.03$; (4) $Li/Mn = 0.00$ (γ-MnO_2).
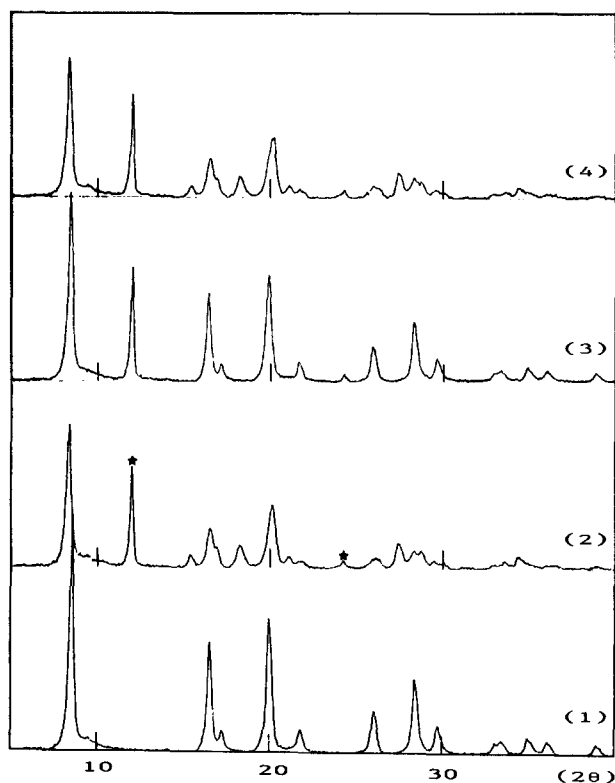
Fig. 10. X-ray diffraction patterns of $Li_{4/3}Mn_{5/3}O_4$ cathodes (*, graphite). (1) $Li_{4/3}Mn_{5/3}O_4$; (2) 1st discharge; (3) 1st charge; (4) 2nd discharge.

A spinel-type compound is obtained on extraction of half the lithium (Li/Mn = 0.40). A biphasic system is obtained for the ratio Li/Mn = 0.03 (a spinel-type phase and γ-MnO_2). γ-MnO_2 is obtained as a single phase on complete extraction.

The results obtained in button cells are presented in Fig. 9(a)–(c). As can be seen, the discharge capacity is not improved by earlier chemical extraction in the spinel framework. A cyclic voltammogram of $Li_{4/3}Mn_{5/3}O_4$ reveals the loss of electrochemical activity when cycling.

Considering the X-ray patterns, $Li_{4/3}Mn_{5/3}O_4$ (Fig. 10) seems to link the cubic–tetragonal transformation with the charge/discharge process. This result is surprising because of the +4 oxidation state of the manganese ions in $Li_{4/3}Mn_{5/3}O_4$. After charge, the cubic cell parameter is somewhat larger $[a_c = 8.209(6)$ Å] than that of $Li_{4/3}Mn_{5/3}O_4$ $[a_c = 8.174(2)$ Å]. Consideration of the spinel-type phase with the ratio Li/Mn = 0.40 (Fig. 11), and assuming a tetragonal phase for the reduced forms, indexing of the X-ray patterns leads to the results given in Table 3.
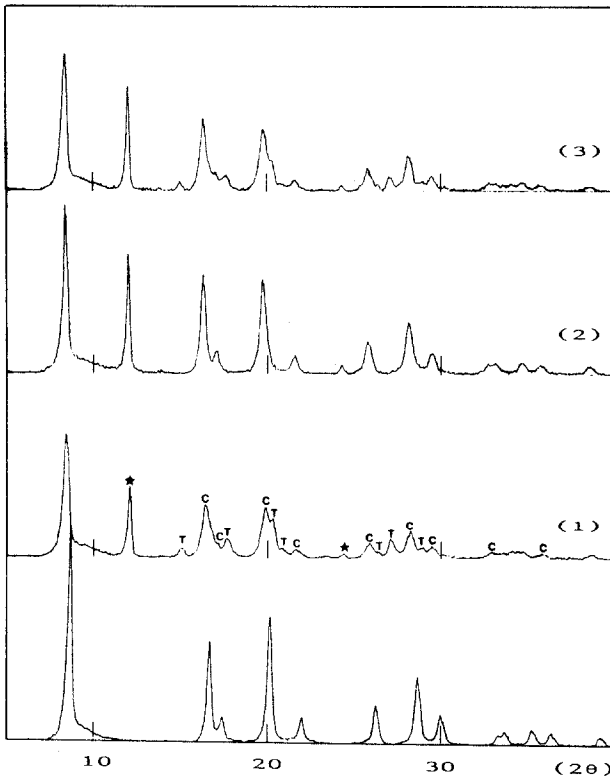
Fig. 11. X-ray diffraction patterns of spinel phase with Li/Mn = 0.40 (*, graphite). (1) 1st discharge; (2) 1st charge; (3) 2nd discharge. Lower trace — the spinel pattern.

TABLE 3

Cell parameters for spinel phase with Li/Mn = 0.40

	Cell parameters (Å)	
Spinel phase with Li/Mn = 0.40	$a_c = 8.112(1)$	
1st discharge	$a_c = 8.233(8)$	$a_t = 5.695(4)$ $c_t = 9.238(8)$
1st charge	$a_c = 8.255(7)$	
2nd discharge	$a_c = 8.263(7)$	$a_t = 5.688(8)$ $c_t = 9.28(1)$

a_c, cubic unit cell.
a_t, c_t, tetragonal unit cell.

Conclusions

From this study, it appears that compounds with a spinel framework are not suitable for lithium rechargeable applications in practical cells. The loss of discharge capacity for $LiMn_2O_4$ and $Li_{4/3}Mn_{5/3}O_4$ cannot be explained by a complete charge process. Further, previous chemical lithium extraction from these compounds does not significantly improve the discharge capacity. Thus, it appears that part of the electrochemically inserted Li^+ ions cannot be removed from the structure.

Compounds with the rocksalt structure — obtained by chemical lithium extraction from Li_2MnO_3 — are more attractive materials for lithium rechargeable applications.

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