

DEFECT SPINELS IN THE SYSTEM $\text{Li}_{2.0.y}\text{MnO}_2$ ($y > 2.5$):
A NEUTRON-DIFFRACTION STUDY AND ELECTROCHEMICAL CHARACTERIZATION
OF $\text{Li}_2\text{Mn}_4\text{O}_9$

A de Kock, M H Rossouw, L A de Picciotto and M M Thackeray*
Division of Materials Science and Technology, CSIR, P O Box 395,
Pretoria 0001, South Africa

and

W I F David and R M Ibberson
Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire
OX11 0QX, UK

(Received February 19, 1990; Communicated by J.B. Goodenough)

ABSTRACT

The structure of the defect spinel $\text{Li}_2\text{Mn}_4\text{O}_9$ which is a component of the system $\text{Li}_{2.0.y}\text{MnO}_2$ ($y = 4.0$) has been determined by neutron diffraction analysis; it has the spinel notation $(\text{Li}_{0.89} \square_{0.11})[\text{Mn}_{1.78} \square_{0.22}]_4\text{O}_4$. The electrochemical properties of $\text{Li}_2\text{Mn}_4\text{O}_9$ when used as an insertion electrode in rechargeable room-temperature lithium cells have been evaluated.

MATERIALS INDEX: lithium, manganese, oxides, spinels

Introduction

There has recently been much interest in reactions of manganese- and lithium salts at moderately high temperatures (350-450°C) for synthesising lithium-manganese-oxide electrodes for rechargeable lithium cells [1-4]. A previous report has shown that these reactions produce an electrochemically inactive rock salt phase Li_2MnO_3 and an electrochemically active spinel phase in the system $\text{Li}_x\text{Mn}_{2-z}\text{O}_4$ ($0 \leq x \leq 1.33$, $0 \leq z \leq 0.33$) the composition of which depends on the Li:Mn ratio used and the temperature of preparation [5]. At temperatures below 400°C spinel phases are produced in which the manganese ions are all tetravalent; these phases may be defined by the solid-solution system $\text{Li}_{2.0.y}\text{MnO}_2$ where $y \geq 2.5$. The end members of this system are $\text{Li}_4\text{Mn}_5\text{O}_{12}$ [6] and the defect spinel phase $\lambda\text{-MnO}_2$ [7]; they have the general stoichiometries M_3O_4 and MO_2 , respectively, where M represents the total lithium- and manganese-ion content in the compounds. This paper presents structural, chemical, electrochemical and physical properties of an intermediate phase of the system, $\text{Li}_2\text{Mn}_4\text{O}_9$ ($y = 4$), which has the stoichiometry M_2O_3 .

*To whom correspondence should be addressed.

Experimental

Single-phase $\text{Li}_2\text{Mn}_4\text{O}_9$ was prepared by reaction of Li_2CO_3 and MnCO_3 powder, intimately mixed in a 1:4 molar ratio, at 400°C in air for five hours. The reaction conditions were strictly controlled to prevent the loss of oxygen from $\text{Li}_2\text{Mn}_4\text{O}_9$ that occurs when higher temperatures and longer reaction times are used.

$\text{Li}_2\text{Mn}_4\text{O}_9$ was lithiated chemically with 1M n-butyllithium in hexane at 40°C under an argon atmosphere, and electrochemically at room temperature (22°C). Li_2O was removed from $\text{Li}_2\text{Mn}_4\text{O}_9$ by acid digestion in 0.4M H_2SO_4 for 20 hours at room temperature. For the electrochemical experiments the working electrode consisted of 20-60 mg $\text{Li}_2\text{Mn}_4\text{O}_9$ compacted on to a stainless-steel gauze disc. A 20 wt/o mixture of acetylene black and teflon (2:1 ratio) was added to the electrode to enhance its electrical conductivity and mechanical strength. A 1M solution of LiClO_4 in dimethoxyethane/propylene carbonate (1:1 mixture) was employed as electrolyte in all the electrochemical tests. Cyclic voltammetry experiments were carried out in three electrode cells using lithium-foil counter- and reference electrodes. The voltage limits and scan rate, typically 1mV/s, were controlled by a Princeton Applied Research (PAR) Model 173 Potentiostat coupled to a PAR Model 175 Universal Programmer. The electrode capacity utilization and cycling efficiency of $\text{Li}/\text{Li}_2\text{Mn}_4\text{O}_9$ cells were determined in two-electrode cells; initial discharge capacities of cells, when discharged at 0.1 mA/cm^2 , were calculated to a cut-off voltage of 2.0V. Cycling of cells was carried out at charge and discharge current rates of 0.125 mA/cm^2 and 0.250 mA/cm^2 , respectively, between voltage limits of 3.6V and 2.0V.

Time of flight (TOF) neutron-diffraction data of $\text{Li}_2\text{Mn}_4\text{O}_9$ were collected on the high-resolution powder diffractometer (HRPD) at the spallation neutron source (ISIS) at the Rutherford Appleton Laboratory, UK. The structures were refined with a profile-refinement program modified to describe peak shape by a double decay exponential convoluted with a Voigt function [8, 9]. Neutron-scattering amplitudes used in the structure refinement were $b(\text{Li}) = -0.203 \times 10^{-12} \text{ cm}$, $b(\text{Mn}) = -0.3730 \times 10^{-12} \text{ cm}$, and $b(\text{O}) = 0.5804 \times 10^{-12} \text{ cm}$ [10]. Initial unit cell parameters were obtained from powder X-ray diffraction data of the sample. During structure refinement, 15 profile and 8 structural parameters were refined simultaneously.

X-ray diffraction data of $\text{Li}_2\text{Mn}_4\text{O}_9$, an acid-treated $\text{Li}_2\text{Mn}_4\text{O}_9$ sample and lithiated products $\text{Li}_{2+x}\text{Mn}_4\text{O}_9$ ($0 < x \leq 2.4$) were collected in South Africa on an automated Rigaku powder diffractometer with $\text{CuK}\alpha$ radiation monochromated by a graphite single crystal. The particle-size distribution in $\text{Li}_2\text{Mn}_4\text{O}_9$ samples was determined on a Malvern Instruments Master Particle Sizer M3.0. Surface areas were obtained by the BET method using nitrogen gas. The lithium content in the various samples was determined by atomic absorption spectroscopy.

Results and Discussion

Stoichiometric spinels have the general formula $\text{A}[\text{B}_2]\text{X}_4$ where A and B refer to cations on tetrahedral and octahedral sites, respectively, and X to the anions that form a cubic-close-packed array. The structure of $\text{Li}_2\text{Mn}_4\text{O}_9$ was refined with neutron-diffraction data using the prototypic cubic spinel space group, $\text{Fd}3\text{m}$. The lithium ions were positioned on the A

sites (the 8a crystallographic positions), the manganese ions on the B sites (the 16d crystallographic positions) and the oxygen ions on the crystallographic 32e positions. The final crystallographic parameters are listed in Table 1. The observed and calculated neutron-diffraction profiles of $\text{Li}_2\text{Mn}_4\text{O}_9$ are shown in Fig. 1.

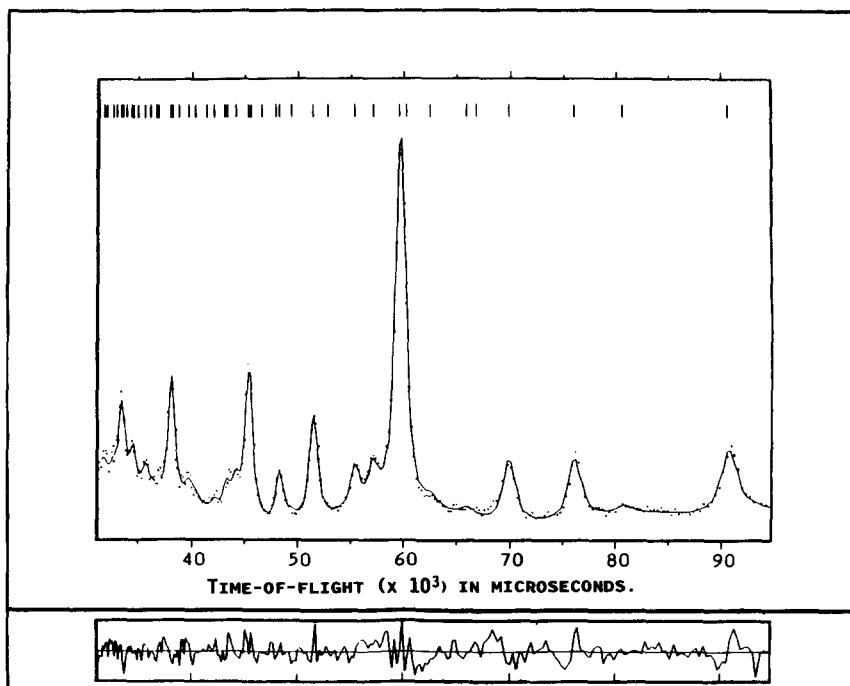


FIG. 1

The observed (dots) and calculated (solid line) neutron diffraction powder patterns for $\text{Li}_2\text{Mn}_4\text{O}_9$. The difference between observed and calculated profiles is plotted below. Note that for time of flight data, TOF = 48276.6 d (Å).

The structure analysis yielded a defect spinel composition $(\text{Li}_{0.83}\square_{0.17})_{8a}[\text{Mn}_{1.76}\square_{0.24}]_{16d}\text{O}_4$. The lithium and manganese ions partially occupy the A and B sites, respectively. The average calculated valency of the manganese ions is 4.07 which slightly exceeds the maximum allowed value of 4.0. It was therefore assumed that the most likely composition was $(\text{Li}_{0.89}\square_{0.11})_{8a}[\text{Mn}_{1.78}\square_{0.22}]_{16d}\text{O}_4$ (or $\text{Li}_2\text{Mn}_4\text{O}_9$), the stoichiometry of which is well within the limits of experimental error. In $\text{Li}_2\text{Mn}_4\text{O}_9$ the Li:Mn ratio of 1:2 of the initial reaction mixture is maintained; all the manganese ions are tetravalent.

$\text{Li}_2\text{Mn}_4\text{O}_9$ is a component of the spinel system $\text{Li}_2\text{O} \cdot y\text{MnO}_2$ ($y = 4.0$). The end members of this solid solution system are the stoichiometric spinel $\text{Li}_4\text{Mn}_5\text{O}_{12}$, at $y = 2.5$, $(\text{Li}[\text{Li}_{0.33}\text{Mn}_{1.67}]\text{O}_4)$ [6] and the defect spinel $\lambda\text{-MnO}_2$ ($\square_{1.0}[\text{Mn}_2]\text{O}_4$) in which all the tetrahedral

TABLE 1

Crystallographic Parameters of $\text{Li}_2\text{Mn}_4\text{O}_9$ from neutron-diffraction data.Space group: $\text{Fd}3\text{m}$; $a = 8.174(1)\text{\AA}$

Atom	Position	x	y	z	B ₁₁ *	B ₁₂ *	n
Li	8a	0.1250	0.1250	0.1250	0.4(8)	0	0.83
Mn	16d	0.5000	0.5000	0.5000	1.2(3)	0.3(2)	0.88
O	32e	0.2634(2)	0.2634(2)	0.2634(2)	1.1(1)	0.2(1)	1.0

R Factors:

$$R_p = 2.05\%; R_{wp} = 2.36\%, R_E = 1.53\%$$

where

$$R_p = \frac{\sum |Y_{\text{obs}} - Y_{\text{calc}}|}{\sum Y_{\text{obs}}}; R_{wp}^2 = \frac{\sum w |Y_{\text{obs}} - Y_{\text{calc}}|^2}{\sum w |Y_{\text{obs}}|^2}; R_E^2 = \frac{N - P + C}{\sum |Y_{\text{obs}}|^2}$$

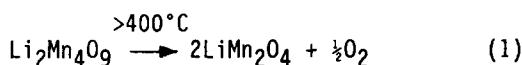
and

Y_{obs} = observation at time of flight, t_{obs} ; w = weights and $N - P + C$ = number of observations - number of variables + number of constraints.

Chi-squared = 2.38 for 280 observations and 23 basic variables.

*Note: $B_{11} = B_{22} = B_{33}$ and $B_{12} = B_{23} = B_{13}$

sites are unoccupied [7]. The stability of the spinel phases of this system at 400°C decreases as the concentration of the MnO_2 component, y , increases; it has been established that spinel structures can be synthesised at this temperature for compositions from $\text{Li}_4\text{Mn}_5\text{O}_{12}$ ($y = 2.5$), through $\text{Li}_2\text{Mn}_3\text{O}_7$ ($y = 3$), [11] to at least $\text{Li}_2\text{Mn}_4\text{O}_9$ ($y = 4$). If $\text{Li}_2\text{Mn}_4\text{O}_9$ is heated above 400°C , particularly for long periods of time, oxygen is lost and defects are removed from the structure to leave LiMn_2O_4 , according to the reaction:



The thermal stability of phases for $y > 4$ is still to be determined. It is known, however, that $\lambda\text{-MnO}_2$ which is usually prepared at room temperature by oxidation of LiMn_2O_4 in an acidic medium [7], is stable only to $\sim 250^\circ\text{C}$ at which temperature it transforms to $\beta\text{-MnO}_2$.

The powder X-ray diffraction patterns of $\text{Li}_2\text{Mn}_4\text{O}_9$, two chemically lithiated products $\text{Li}_{3.7}\text{Mn}_4\text{O}_9$ and $\text{Li}_{4.4}\text{Mn}_4\text{O}_9$, and an acid-treated $\text{Li}_2\text{Mn}_4\text{O}_9$ sample are shown in Fig. 2(a-d). Lithiation of $\text{Li}_2\text{Mn}_4\text{O}_9$ (Fig. 2a) to the composition $\text{Li}_{3.7}\text{Mn}_4\text{O}_9$ (Fig. 2b) reduces the average valency of the manganese ions from 4.00 to 3.56. At this composition the lithiated spinel structure retains its cubic symmetry. Lattice constants determined from the X-ray patterns show that the lattice

parameter of $\text{Li}_2\text{Mn}_4\text{O}_9$ ($a = 8.162\text{\AA}$) expands only marginally to $a = 8.171\text{\AA}$ at a composition $\text{Li}_{3.7}\text{Mn}_4\text{O}_9$. A powder X-ray diffraction pattern of a sample with overall composition $\text{Li}_{4.4}\text{Mn}_4\text{O}_9$ (average Mn valency is 3.40) (Fig. 2c) was dominated by peaks of the cubic phase, but contained, in addition, a few weak peaks of a second phase which has not yet been characterized, but which is believed to be a highly lithiated $\text{Li}_{2+x}\text{Mn}_4\text{O}_9$ phase with $x > 2.4$.

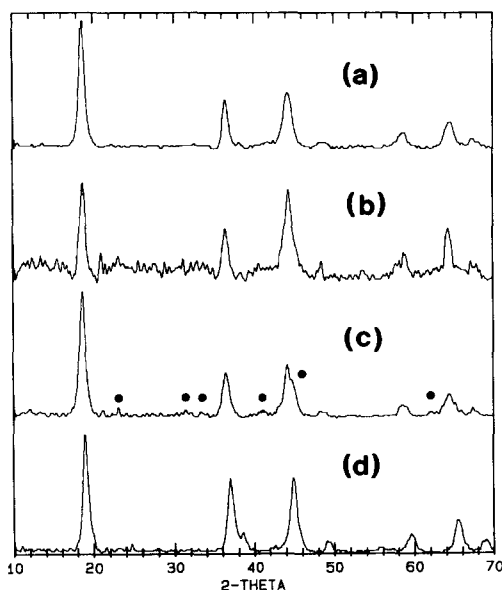
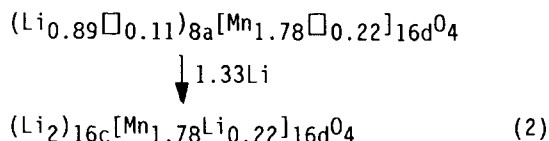


FIG. 2

The powder X-ray diffraction patterns of
 a) $\text{Li}_2\text{Mn}_4\text{O}_9$
 b) $\text{Li}_{3.7}\text{Mn}_4\text{O}_9$
 c) $\text{Li}_{4.4}\text{Mn}_4\text{O}_9$ (dots indicate peaks of an unidentified phase)
 d) an acid-treated $\text{Li}_2\text{Mn}_4\text{O}_9$ sample.

Reaction of $\text{Li}_2\text{Mn}_4\text{O}_9$ with 0.4M H_2SO_4 for 20 hours at room temperature, leaches out the Li_2O component from the structure. The product contained 0.1% Li, which corresponds to a phase of composition $\text{Li}_{0.05}\text{Mn}_4\text{O}_{8.025}$; it has a lattice parameter of $a = 8.069\text{\AA}$. The powder X-ray diffraction pattern of this phase [Fig. 2d] is essentially that of $\lambda\text{-MnO}_2$ ($a = 8.03\text{\AA}$) [7].

The discharge curve of a $\text{Li}/\text{Li}_2\text{Mn}_4\text{O}_9$ cell which represents the electrochemical insertion of lithium into $\text{Li}_2\text{Mn}_4\text{O}_9$ at a low current rate of 0.1 mA/cm^2 is shown in Fig. 3. At this discharge rate, the $\text{Li}_2\text{Mn}_4\text{O}_9$ structure accommodates 3Li^+ ions per formula unit, to a cut-off voltage of 2.0V. Although no detailed structure refinement of $\text{Li}_5\text{Mn}_4\text{O}_9$ has been undertaken, the similarity of the peak intensities in the powder X-ray diffraction patterns of $\text{Li}_2\text{Mn}_4\text{O}_9$ and the lithiated product $\text{Li}_{3.7}\text{Mn}_4\text{O}_9$ (Fig. 2a & b) indicate that the manganese ions remain on the B-sites of the spinel framework structure during the lithiation process. A likely reaction for complete lithiation of $\text{Li}_2\text{Mn}_4\text{O}_9$ to a rock salt composition $\text{Li}_5\text{Mn}_4\text{O}_9$, in spinel notation, is therefore:



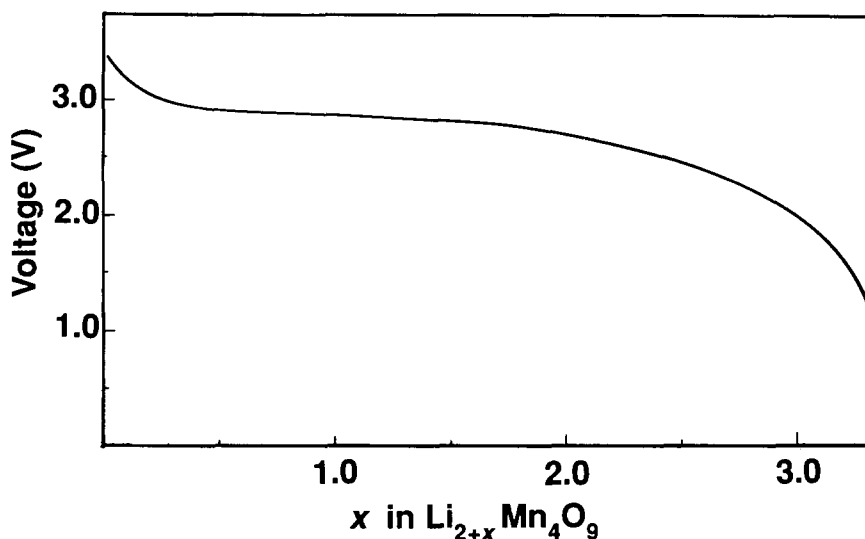


FIG. 3

The electrochemical discharge curve of a $\text{Li}/\text{Li}_2\text{Mn}_4\text{O}_9$ cell representing the insertion of lithium into $\text{Li}_2\text{Mn}_4\text{O}_9$ at a current rate of $0.1\text{mA}/\text{cm}^2$.

During this reaction the lithium ions on the tetrahedral 8a sites are initially displaced into neighbouring face-shared octahedra (the crystallographic 16c positions); in the fully lithiated structure all the octahedral sites are occupied by lithium and manganese ions. However, the possibility that a fraction of lithium ions remain on the 8a sites cannot be discounted as evidence for this phenomenon was observed in the related lithiated spinel phase $\text{Li}_2[\text{Mn}_2]\text{O}_4$ [12].

The cyclic voltammogram of an $\text{Li}/\text{Li}_2\text{Mn}_4\text{O}_9$ cell, cycled between limits of 4.6V and 1.8V, illustrates that the lithiation process of $\text{Li}_2\text{Mn}_4\text{O}_9$ is reversible (Fig. 4a). With reference to reaction (2) it would appear that 1.33 Li^+ ions are inserted into the defect spinel structure during the initial cathodic scan to form the rock salt phase $\text{Li}_5\text{Mn}_4\text{O}_9$ (peak 1). However, during the anodic scan lithium extraction occurs in three stages which can be attributed to (i) removal of 75% of the inserted lithium ions from the octahedral sites 16c, (peak 2), which occurs with a simultaneous migration of the remaining lithium ions from the 16c sites to the tetrahedral 8a sites to generate a stoichiometric spinel phase $(\text{Li})_{8a}[\text{Mn}_{1.78}\text{Li}_{0.22}]\text{O}_4$ and (ii) removal of the remaining 25% of the inserted lithium ions in a two-step process (peaks 3 and 4). Further structural data is required to determine whether this two-step process can be attributed to lithium extraction from only the 8a tetrahedral sites as has been observed for the system $\text{Li}_{1-x}[\text{Mn}_2]\text{O}_4$ [5, 13] or whether a fraction of the lithium ions is also removed from the 16d octahedral sites. Peaks 5 and 6 correspond to the reverse process of 4 and 3, respectively, whereas peak 7 in the second cycle corresponds to the insertion of only one lithium ion per spinel unit to form the rock salt phase. Fig. 4b is the cyclic voltammogram of $\text{Li}_2\text{Mn}_4\text{O}_9$ when cycled between 3.75V and 1.80V; it shows excellent rechargeable characteristics.

Data of early cycling characteristics of $\text{Li}/\text{Li}_{2+x}\text{Mn}_4\text{O}_9$ electrochemical cells have shown that at discharge and charge rates of 0.3 mA/cm^2 and 0.15 mA/cm^2 , respectively, 2.2 Li^+ ions per 4 Mn (0.55 Li/Mn) can be cycled in and out of the spinel framework structure between voltage limits of 3.5 V and 2.0 V ; this cycling efficiency, which corresponds nicely with the mechanism proposed for interpreting peaks 2 and 7 of the cyclic voltammogram in Fig. 4a, is comparable to that reported for a heat-treated $\gamma\text{-MnO}_2$ electrode [14].

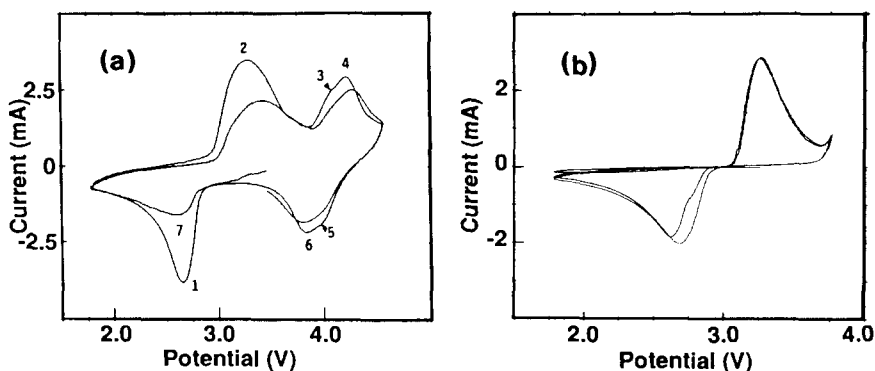


Fig. 4
Cyclic voltammograms of $\text{Li}/\text{Li}_2\text{Mn}_4\text{O}_9$ cells cycled between limits of
a) 4.6 V and 1.8 V , and b) 3.75 V and 1.8 V .

Conclusions

In conclusion, there are several properties of $\text{Li}_2\text{Mn}_4\text{O}_9$ that are worth highlighting, particularly when compared to LiMn_2O_4 .

- (i) $\text{Li}_2\text{Mn}_4\text{O}_9$ can be regarded as an oxygen-rich spinel with notation $\text{LiMn}_{2.5}\text{O}_{4.5}$. The additional oxygen concentration which creates defects on the A and B sites (in LiMn_2O_4 the A and B sites are fully occupied) gives $\text{Li}_2\text{Mn}_4\text{O}_9$ a significantly greater theoretical electrode capacity (213 mAh/g) than LiMn_2O_4 (148 mAh/g) when the electrodes are discharged to the rock salt compositions $\text{Li}_5\text{Mn}_4\text{O}_9$ and $\text{Li}_2\text{Mn}_2\text{O}_4$, respectively.
- (ii) Electrochemical lithiation of $\text{Li}_2\text{Mn}_4\text{O}_9$ to $\text{Li}_5\text{Mn}_4\text{O}_9$ reduces the average manganese-ion valency from 4.00 to 3.25 ; the cubic symmetry of the electrode structure is maintained, at least to a composition $\text{Li}_{3.7}\text{Mn}_4\text{O}_9$ in which the average Mn valency is 3.56 . By contrast, during the electrochemical reduction of LiMn_2O_4 to $\text{Li}_2\text{Mn}_2\text{O}_4$ the average valency of the manganese ions is lowered from 3.50 to 3.00 . During this reaction the higher concentration of the $d^4 \text{ Mn}^{3+}$ ions induces a Jahn Teller distortion which reduces the crystal symmetry from cubic to tetragonal symmetry, and results in a two-phase electrode over the compositional range $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ ($0.08 < x < 2$) [15]. However, data in this paper suggest that a similar process occurs in extensively lithiated $\text{Li}_{2+x}\text{Mn}_4\text{O}_9$ samples for $x > 2$ (i.e. when the average Mn valency is < 3.5 as evidenced by the appearance of a second phase in the X-ray diffraction pattern of $\text{Li}_{4.4}\text{Mn}_4\text{O}_9$).

- (iii) $\text{Li}_2\text{Mn}_4\text{O}_9$ electrodes exhibit a voltage of $\sim 3.5\text{V}$ against pure lithium whereas the lithium-deficient spinel electrodes in the system $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$ exhibit significantly higher voltages ($\sim 4.0\text{V}$); the latter electrodes are considered to be too highly oxidizing for the electrolytes currently employed which limits their usefulness in lithium cells.
- (iv) High surface areas ($78\text{ m}^2/\text{g}$) and small average particle size ($\sim 3\mu\text{m}$) characterize $\text{Li}_2\text{Mn}_4\text{O}_9$ electrodes when made by the method described in this paper. These properties account for the good electrochemical activity of this electrode. By contrast, LiMn_2O_4 electrodes, which are synthesised typically above 600°C , yield much lower surface areas ($2\text{--}10\text{ m}^2/\text{g}$). Consequently, $\text{Li}/\text{LiMn}_2\text{O}_4$ cells show inferior electrochemical performance in terms of both discharge capacity and Li^+ -ion diffusion rate when discharged at the same current density as $\text{Li}/\text{Li}_2\text{Mn}_4\text{O}_9$ cells.

Acknowledgements

Mr H Lachmann and Mr J Stander of the CSIR are thanked for the chemical analyses and particle-size and surface area determinations of the samples.

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