Synthesis of layered $LiMnO_2$ as an electrode for rechargeable lithium batteries

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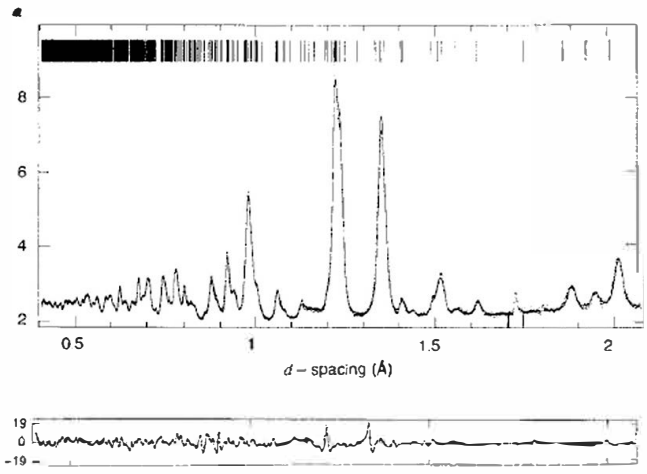
RECHARGEABLE lithium batteries can store more than twice as much energy per unit weight and volume as other rechargeable batteries[1,2]. They contain lithium ions in an electrolyte, which shuttle back and forth between, and are intercalated by, the electrode materials. The first commercially successful rechargeable lithium battery[3], introduced by the Sony Corporation in 1990, consists of a carbon-based negative electrode, layered $LiCoO_2$ as the positive electrode, and a non-aqueous liquid electrolyte. The high cost and toxicity of cobalt compounds, however, has prompted a search for alternative materials that intercalate lithium ions. One such is $LiMn_2O_4$, which has been much studied as a positive electrode material[4-7]; the cost of manganese is less than 1% of that of cobalt, and it is less toxic. Here we report the synthesis and electrochemical performance of a new material, layered $LiMnO_2$, which is structurally analogous to $LiCoO_2$. The charge capacity of $LiMnO_2$ ($\sim$270 mA h g^{-1}) compares well with that of both $LiCoO_2$ and $LiMn_2O_4$, and preliminary results indicate good stability over repeated charge–discharge cycles.

Many attempts have been made to prepare layered $LiMnO_2$, mainly involving the use of aqueous solutions[8-10]. The resulting products, though interesting, have stoichiometries which differ from $LiMnO_2$, contain water or protons, are of poor crystallinity or do not maintain their structure during cycling. In contrast we have succeeded in preparing layered, anhydrous and stoichiometric $LiMnO_2$ which is analogous to $LiCoO_2$ and may be cycled in a rechargeable battery; it is obtained by ion exchange from $NaMnO_2$. The sodium compound was synthesized by solid-state reaction between stoichiometric quantities of Na_2CO_3 and manganese (III) oxide at 700–730 °C for 18–72 hours under flowing argon[11]. $LiMnO_2$ was obtained by refluxing $NaMnO_2$ with an excess of LiCl or LiBr in *n*-hexanol at 145–150 °C for 6–8 hours. After cooling to room temperature the product was filtered under suction and washed, first with *n*-hexanol and then with ethanol, and dried[12]. Phase purity was established by powder X-ray diffraction.

The layered structure of $LiMnO_2$ was confirmed by powder neutron diffraction carried out on the POLARIS diffractometer at the ISIS pulsed source (Rutherford Appleton Laboratory) (Fig. 1*a*). The structure was refined by the Rietveld method using the program TF12LS based on the Cambridge Crystallographic Subroutine Library[13]. Adoption of a layered model yielded a final agreement factor, $R_{\text{weighted profile}}$, of 2.06% compared with an R_{expected} of 0.60%. A common structure obtained when attempts are made to prepare compounds with the $LiMnO_2$ composition is that of tetragonally distorted spinel $Li_2Mn_2O_4$ (ref. 4). This structure was tested in the refinement process; however, the fit obtained using the layered model was far superior to the fit assuming a tetragonal spinel structure for which $R_{wp} = 4.79\%$. The layered structure of $LiMnO_2$ is shown in Fig. 1*b*. The oxide ions are arranged in close-packed layers which are stacked in an ABC repeat sequence, that is, cubic close packing. Manganese ions are located in each octahedral site between the first and second oxide layers (Fig. 1*b*). Between the second and third layers the Li^+ ions reside also in octahedral sites. Refinement was carried out permitting the Li^+ and Mn^{3+} ions to occupy their



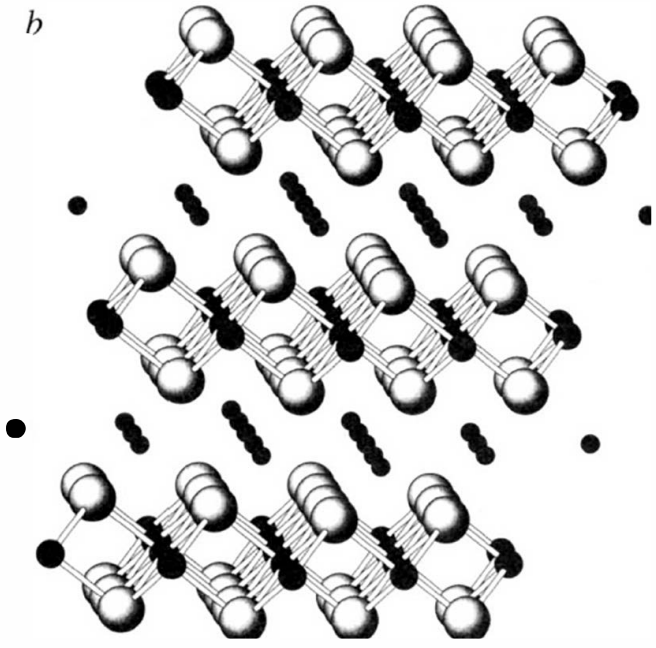


FIG. 1 *a*, Observed (dots) and calculated (solid line) neutron-diffraction profiles for monoclinic $LiMnO_2$. The lower plot shows the difference/estimated standard deviation *b*, Structure of $LiMnO_2$ emphasising the layered nature of the material. Mn, large dark circles; Li, smaller dark circles;/ O, pale circles.

TABLE 1 Crystallographic parameters of $LiMnO_2$

Atom	Wyckoff symbol	*x*	*y*	*z*	B_{eq}	Site occupancy
Li1/Mn1	2d	0	0.5	0.5	2.4(2)	0.91/0.09(4)
Li2/Mn2	2a	0	0	0	0.72(6)	0.10/0.90(3)
O1	4i	0.2723(3)	0	0.7706(2)	0.68(4)	1

Monoclinic, space group *C*2/*m* (no. 12). Unit-cell dimensions: $a = 5.4387(7)$ Å, $b = 2.80857(4)$ Å, $c = 5.3878(6)$ Å, $\beta = 116.006(3)°$. $\chi^2 = 11.83$. $R_{exp} = 0.60\%$, $R_p = 1.86\%$, $R_{wp} = 2.06\%$, $R_I = 3.98\%$.)

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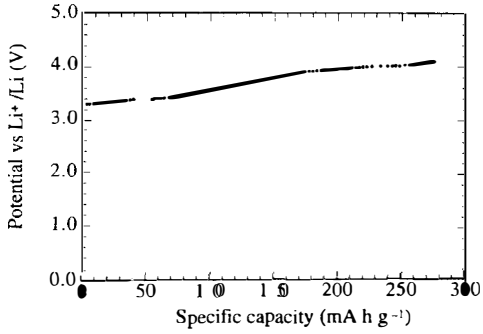

FIG. 2 Variation of electrode potential with capacity on charging $LiMnO_2$ at a current density of 10 μA cm $^{-2}$.

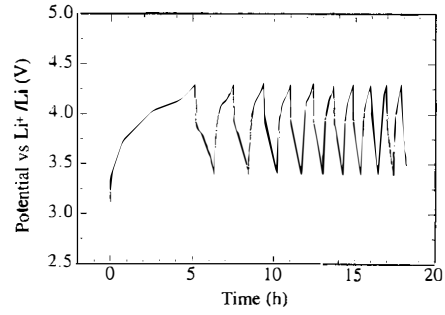

FIG. 3 Cycling of the $LiMnO_2$ electrode at a current density of 0.5 mA cm^{-2} and between voltage limits of 3.4 to 4.3 V vs Li^+/Li.

own sites and those of each other. The Li^+ and Mn^{3+} ion occupancies were free to refine on both sites, the only constraint being that the total occupancy of each site was set to equal one. The total lithium and manganese contents were respectively 1.02(7) and 0.98(7), consistent with the $LiMnO_2$ stoichiometry. Atomic absorption analysis was carried out (Unicam PU9400X) and provided further confirmation of the stoichiometry. The maximum occupancies of Li on the Mn sites (2a) and Mn on the Li (2d) sites were respectively 0.10(3) and 0.09(4), demonstrating that the lithium and manganese ions reside predominantly on their own sites. Due to the strong Jahn–Teller nature of high-spin $Mn^{3+}(3d^4)$, the local site symmetry around the Mn^{3+} ions is distorted somewhat from a regular octahedron and the crystal structure is not rhombohedral but monoclinic (space group $C2/m$). The crystallographic data are given in Table 1.

Interest in layered $LiMnO_2$ as a positive electrode in rechargeable lithium batteries stems from the fact that Li^+ ions and electrons may be removed and reinserted into this compound, that is, it is an intercalation host for lithium. The electrochemical performance of $LiMnO_2$ was investigated with a three-electrode cell composed of lithium metal counter and reference electrodes, the working electrode being fabricated by compressing powdered $LiMnO_2$ (80%), carbon black (13.3%) and PTFE (6.7%) on to a metal grid. The electrolyte consisted of a 1 M solution of $LiClO_4$ dissolved in propylene carbonate. The salt was rigorously dried by heating under vacuum at 150 °C and the solvent was distilled as described elsewhere[14]. The cell was subjected to charging at a current density of 10 μA cm^{-2}. The resulting voltage curve is shown in Fig. 2. These data confirm that up to 0.95 lithiums per formula unit may be extracted from $LiMnO_2$ on initial charging, corresponding to a capacity of 270 mA h g^{-1}. Preliminary measurements at the much higher current density of 0.5 mA cm^{-2} suggest that a capacity approaching 200 mA h g^{-1} may be obtained up to a cut-off potential of 4.3 V.

The earliest lithium batteries, introduced in the 1980s, used lithium metal as the negative electrode. Despite some problems with flammability, there is still interest in using such cells for electric-vehicle applications because of their high gravimetric energy density. For such cells cathodes with a potential of 3 V are sufficient. When combined with carbon-based anodes in 'rocking-chair' cells (in which both electrodes form intercalation compounds), cathodes with potentials of more than 3 V are required; however the move from petroleum coke to graphite has resulted in an anode with a potential closer to that of lithium metal over a greater range of composition. A practical capacity of $\sim$150 mA h g^{-1} is obtainable from the cathode used in the present generation of commercially available rechargeable lithium batteries, that is, $LiCoO_2$. A slightly smaller practical capacity may be obtained at 3 and 4 volts from $LiMn_2O_4$. The capacities of 200 and 270 mA h g^{-1} obtained on intially charging $LiMnO_2$ and already mentioned above, demonstrate that this compound is both scientifically interesting and potentially attractive as a cathode for rechargeable lithium batteries. However a full analysis of the utility of this cathode in comparisson with others will require extensive measurements of the capacity variation on cycling at different current densities and over different voltage ranges. Some preliminary cycling data are presented below.

X-ray diffraction data reveal that for $(1-x) \approx 0.5$ in $Li_{1-x}MnO_2$ the structure is rhombohedral. On removal of lithium from $LiMnO_2$, the Jahn–Teller active Mn^{3+} ion is oxidized to Mn^{4+} with the resulting loss of the monoclinic distortion. The layered compound also exhibits a voltage transition at a composition of $\sim Li_{0.5}MnO_2$. This is the same composition ($LiMn_2O_4$) at which lithium manganese oxide with the spinel structure transforms from a 3 - V to 4 - V cathode, suggesting that the voltage transition is not related specifically to the spinel structure. However, a full discussion of these more detailed aspects must await the availability of further structural data.

Some preliminary cycling data are presented in Fig. 3. The cell was cycled at a constant current density of 0.5 mA cm^{-2} between the potential limits 3.4 and 4.3 V. Previous studies using cyclic voltammetry indicated that the electrolyte was stable in contact with this electrode up to at least 4.4 V. X-ray diffraction carried out on the layered material at different stages of cycling indicate that the layered structure, is retained during lithium removal and reinsertion. Although the capacity declines on cycing, it must be stressed that the voltage range has not been opitimized and includes both voltage plateaux. In the case of the $LiMn_2O_4$ spinel, cycling over both plateaux results in a greater capacity fade than if confined to just one plateau. It should also be recalled that the early spinel materials showed very poor cyclability, and only later optimization yielded satisfactory results. □

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