Electrochemical behaviour of $LiM_yMn_{2-y}O_4$ (M = Cu, Cr; $0 \leq y \leq 0\cdot4$)

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Abstract. Spinel lithium manganese oxide, $LiMn_2O_4$, is beset with problems of capacity fade upon repeated cycling. The loss in capacity upon cycling is attributable to Jahn–Teller distortion and manganese dissolution in the electrolyte in the charged state. One way to circumvent this capacity fade is to introduce other $3d$ transition metal ions in the $LiMn_2O_4$ lattice. In this paper, we report on the effect of partial substitution of manganese in the $LiMn_2O_4$ phase with copper (II) and chromium (III) ions. It has been shown that the higher octahedral stabilization energy of trivalent chromium imparts greater structural stability to chromium-doped $LiMn_2O_4$ spinels. Both copper and chromium reduce the capacity of the spinel in the 4 V region. In terms of its good reversible capacity and ability to sustain cycling with minimal capacity fade, $LiCr_{0\cdot1}Mn_{1\cdot9}O_4$ may be considered as a potential cathode material for lithium rechargeable cells.

Keywords. Chromium doped $LiMn_2O_4$; copper doped $LiMn_2O_4$; reversible capacity; cyclability; spinel structure.

1. Introduction

A theoretical specific capacity of 148 mAh/g, excellent electrochemical reversibility, good voltage regulation on cycling, low cost and eco-friendliness make $LiMn_2O_4$ an attractive cathode material in rechargeable lithium batteries. Although capacities of about 120 mAh/g have been realized even after 100 cycles in the 4 V region (Xia *et al* 1997), the commercial exploitation of $LiMn_2O_4$ has been hampered by capacity fade upon prolonged cycling especially at elevated temperatures (Gummow *et al* 1994; Amatucci *et al* 1997; Xia *et al* 1997). The capacity fade has been attributed to Jahn–Teller distortion (Gummow *et al* 1994; Thackeray *et al* 1996), lattice instability (Yamada 1996; Arora *et al* 1998), manganese dissolution (Gummow *et al* 1994; Jiang *et al* 1996; Thackeray *et al* 1996; Amatucci *et al* 1997), oxidation of the electrolyte (Gao and Dahn 1996; Jiang *et al* 1996), formation of oxygen-rich spinels (Xia *et al* 1997) and to lattice site exchange between lithium and manganese ions (Tarascon *et al* 1994). This deficiency was sought to be overcome by introducing extra lithium in the spinel, but with limited success (Gummow *et al* 1994; Tarascon *et al* 1994). Substitution of part of the manganese with another metal may increase the stability of the spinel structure (Sigala and Tournoux 1997; Spahr *et al* 1997) or may enhance the operating voltage of the system (Eli *et al* 1998) often at the expense of deliverable capacity (Sigala and Tournoux

1997; Spahr *et al* 1997; Eli *et al* 1998). A number of quaternary spinel oxides of the general formula $Li[M_yMn_{2-y}]O_4$, where M is a $3d$ transition metal ion, have been investigated with a view to enhance cyclability without capacity fading. In this paper we report the results of our studies with Cu(II) and Cr(III) doped $LiMn_2O_4$ as cathode materials in lithium rechargeable cells.

2. Experimental

The doped lithium manganese oxide spinels, $Li[M_yMn_{2-y}]O_4$ (M = Cr^{3+} or Cu^{2+}; $y = 0\cdot0$, $0\cdot1$, $0\cdot2$, $0\cdot3$ and $0\cdot4$), were prepared by a solid-state fusion method from stoichiometric amounts of the following precursors: Li_2CO_3 (E. Merck, India), $MnCO_3$ (Acros Organics, Belgium), $(NH_4)_2Cr_2O_7$ (E. Merck, India) and $CuCO_3$ (Ranbaxy, India). Finely powdered mixtures of the salts in the respective compositions were heated at 800ºC for 8 h. The product was then ground again and heat treated at 800ºC for another 18 h. Powder X-ray diffraction patterns were recorded on a Jeol 8030 X-ray diffractometer with a nickel filtered CuK_a radiation. Cathode-limited cells of the standard 2016 coin cell type were assembled using lithium metal as anode, Celgard 2400 separator and a 1 M solution of $LiPF_6$ in a 50 : 50 (v/v) mixture of ethylene carbonate and dimethyl carbonate. Cathodes were 1·8 cm diameter aluminium discs spread-coated with a 80 : 10 : 10 slurry of the cathode active powder, graphite and polyvinylidene fluoride in N–methyl–2–pyrrolidone. Cathode active material loadings in the case of chromium doped

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samples varied from 0·087 to 0·098 g while those of copper doped samples varied from 0·076 to 0·084 g. Charge–discharge studies were carried out using an in-house charging facility between 3 and 4·3 V.

3. Results and discussion

3.1 X-ray diffraction studies

The X-ray diffraction patterns of both the Cu^{2+} and Cr^{3+} doped samples show striking similarity to that of pure $LiMn_2O_4$ (space group $Fd3m$) in which the manganese ions occupy the $16d$ sites and the O^{2-} ions occupy the $32c$ sites (figures 1a, b). That the chromium-doped compounds also have cubic spinel structure has been demonstrated by several workers (Pistoia *et al* 1992; Baochen *et al* 1993; Guohua *et al* 1996). In fact, the lattice parameters of $Li[Cr_yMn_{2-y}]O_4$ are very close to those of $LiMn_2O_4$ (Mosbach *et al* 1983; Thackeray *et al* 1983, 1984; David *et al* 1984). It must, however, be mentioned here that some of the Cu^{2+} doped samples showed weak X-ray diffraction peaks, specifically one at around a $2q$ value of 44°, corresponding to CuO indicating small amounts of this impurity. The presence of these impurities may be related to the high stability of CuO. Additionally, a small but significant peak may be observed at a $2q$ value of 39°, which according to Eli *et al* (1998) indicates that a small amount of copper resides in the $8a$ tetrahedral site of the spinel. The similarity of the diffraction patterns suggests that they have structures similar to that of $LiMn_2O_4$.

Substitution of manganese with chromium should result in a shrinkage of the unit cell volume. This is because in the same oxidation state chromium ions have smaller ionic radii than manganese ions: Cr^{3+} (0·615 A), Mn^{3+} (0·68 A); Cr^{4+} (0·58 A), Mn^{4+} (0·60 A) (Borchardt-Ott 1993). The decrease in cell volume should increase the stability of the structure during insertion and deinsertion of lithium (Sigala *et al* 1995; Guohua *et al* 1996; Arora *et al* 1998). The stronger Cr–O bonds in the delithiated state (compare the binding energy of 1142 kJ/mole for CrO_2 with 946 kJ/mole for a-MnO_2 (Sigala *et al* 1995)) may also be expected to contribute to the stabilization of the octahedral sites. The higher stabilization energy of Cr^{3+} ions for octahedral coordination is well known (Wells 1962). Recently, Sigala *et al* (1995) demonstrated the structural stability imparted by Cr^{3+} ions to $LiMn_2O_4$ spinels while Zhang *et al* (1998) demonstrated a similar effect by a chemically modified Cr^{5+}–Cr^{6+} oxide. That the incorporation of Cr^{3+} greatly suppresses the dissolution of manganese ions in the electrolyte (one of the failure mechanisms of the $LiMn_2O_4$ cathode) has been shown by Iwata *et al* (1999).
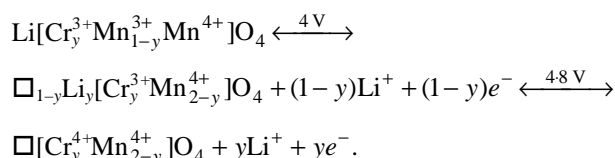
3.2 Charge–discharge studies

$Li/LiM_yMn_{2-y}O_4$ cells were cycled between 3 and 4·3 V at 100 μA rate. Capacities above 4·3 V were not tapped for
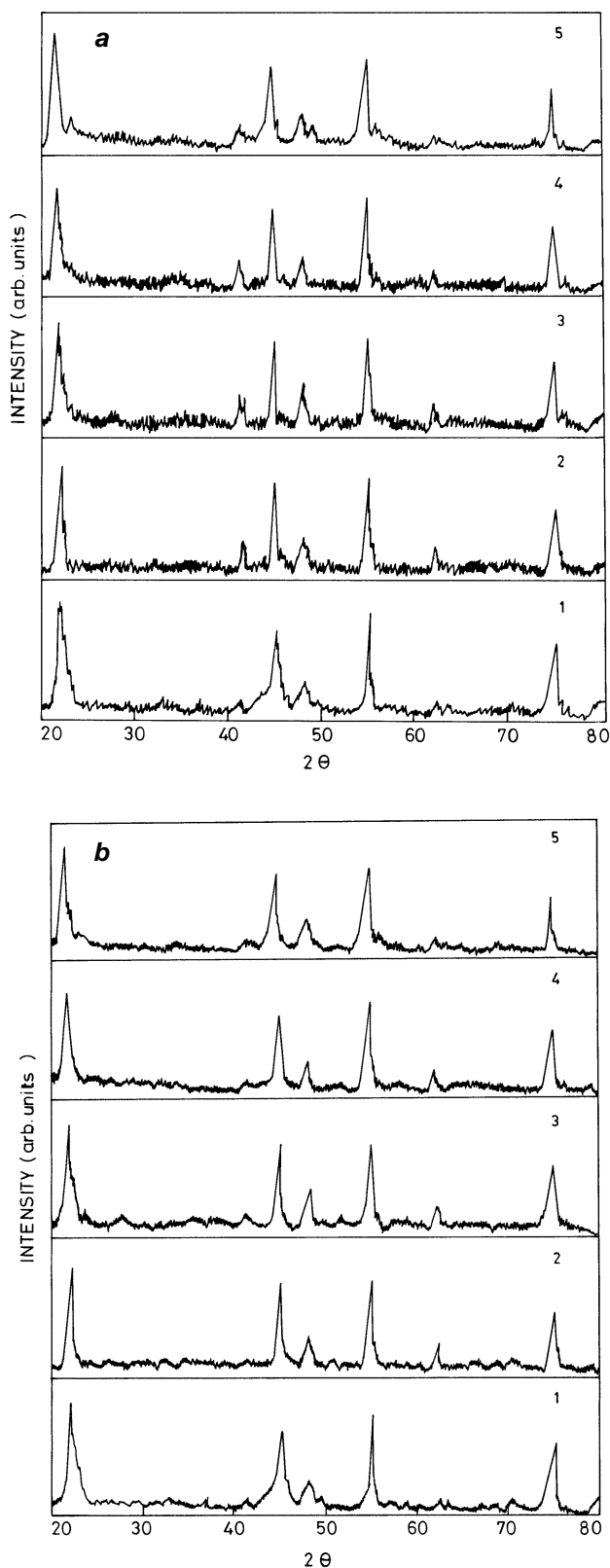
Figure 1. Powder XRD patterns of **a.** $Li[Cu_yMn_{2-y}]O_4$ and **b.** $Li[Cr_yMn_{2-y}]O_4$. 1. $y = 0$; 2. $y = 0·1$; 3. $y = 0·2$; 4. $y = 0·3$ and 5. $y = 0·4$.

fear of electrolyte decomposition at such voltages. The capacities obtained correspond to the oxidation of Mn^{3+} to Mn^{4+}. Capacities corresponding to the Cr^{4+}/Cr^{3+} or Cu^{3+}/Cu^{2+} couple may also be tapped if stable electrolytes are employed. The oxidation of Cr^{3+} to Cr^{4+} occurs at 4·8 V (Sigala *et al* 1995; Sigala and Tournoux 1997; Kawai *et al* 1999) while that of Cu^{2+} to Cu^{3+} occurs at 4·9 V (Eli *et al* 1998). The two-step intercalation/deintercalation process in the case of chromium-doped LiMn$_2$O$_4$ may, for example, be represented as follows

$$\text{Li}[\text{Cr}_y^{3+}\text{Mn}_{1-y}^{3+}\text{Mn}^{4+}]\text{O}_4 \xleftrightarrow{\ 4\,\text{V}\ }$$

$$\square_{1-y}\text{Li}_y[\text{Cr}_y^{3+}\text{Mn}_{2-y}^{4+}]\text{O}_4 + (1-y)\text{Li}^+ + (1-y)e^- \xleftrightarrow{\ 4\cdot8\,\text{V}\ }$$

$$\square[\text{Cr}_y^{4+}\text{Mn}_{2-y}^{4+}]\text{O}_4 + y\text{Li}^+ + ye^-.$$

While in the case of Cr^{3+} doped LiMn$_2$O$_4$ the Cr^{3+} ions would replace the Mn^{3+} ions reducing the 4 V capacity of the compound, in the case of Cu^{2+} doped spinels a corresponding amount of Mn^{3+} would be oxidized to the inactive Mn^{4+} species resulting in much reduced capacities. Thus the composition of LiMn$_2$O$_4$ spinels doped with 0·2 moles of Cu^{2+} and Cr^{3+} be represented as Li[Cu$_{0.2}^{2+}$Mn$_{0.6}^{3+}$Mn$_{1.2}^{4+}$]O$_4$ and Li[Cu$_{0.2}^{3+}$Mn$_{0.8}^{3+}$Mn^{4+}]O$_4$, respectively. Because the capacity is determined by the amount of the oxidizable Mn^{3+} species, the copper doped LiMn$_2$O$_4$ spinels would deliver lower capacities than the chromium-doped spinels.
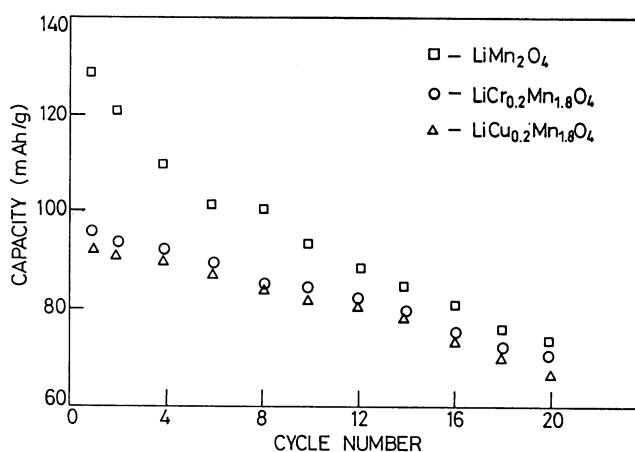
The 4 V discharge capacities of the cathodes of various compositions obtained in the first cycle (figure 2) along with the theoretical values are shown in table 1. The theoretical capacities were calculated on the premise that Cu^{2+} and Cr^{3+} ions replace the Mn^{3+} ions in the octahedral sites. Such a replacement in the case of the copper doped spinels would lead to the oxidation of Mn^{3+} to Mn^{4+} in order to balance the charge in the spinel. However, it appears that the cation distribution in the copper doped spinel is extremely complex because the stability and rela-

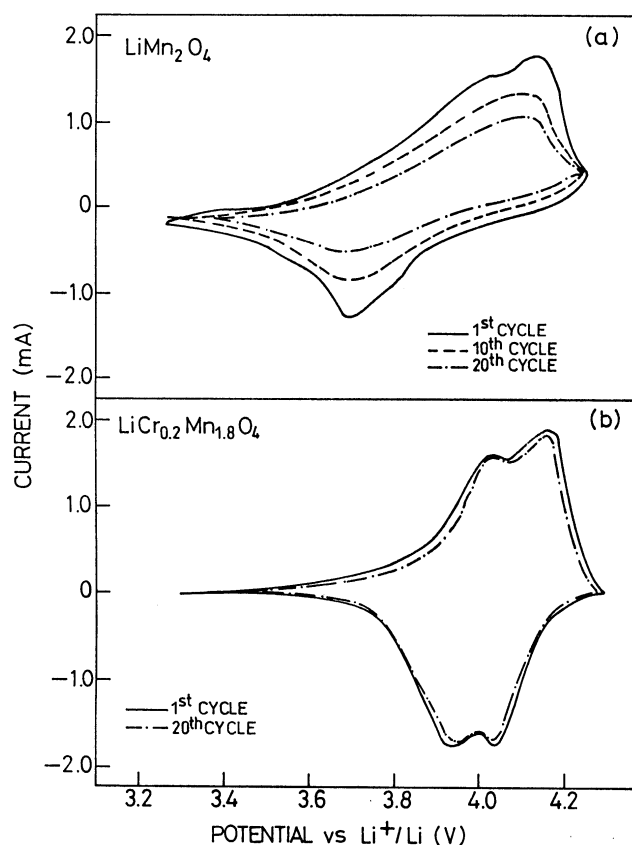**Table 1.** 4 V capacities of various compositions (mAh/g).

Formula	Practical capacity	Theoretical capacity
LiMn$_2$O$_4$[Li]$_{8a}$[Mn^{3+}Mn^{4+}]$_{16d}$[O$_4$]$_{32c}$	128·0	148·2
LiCr$_{0.1}$Mn$_{1.9}$O$_4$[Li]$_{8a}$[Cr$_{0.1}^{3+}$Mn$_{0.9}^{3+}$Mn$_{1.0}^{4+}$]$_{16d}$[O$_4$]$_{32c}$	109·5	133·6
LiCr$_{0.2}$Mn$_{1.8}$O$_4$[Li]$_{8a}$[Cr$_{0.2}^{3+}$Mn$_{0.8}^{3+}$Mn$_{1.0}^{4+}$]$_{16d}$[O$_4$]$_{32c}$	96·4	118·9
LiCr$_{0.3}$Mn$_{1.7}$O$_4$[Li]$_{8a}$[Cr$_{0.3}^{3+}$Mn$_{0.7}^{3+}$Mn$_{1.0}^{4+}$]$_{16d}$[O$_4$]$_{32c}$	80·1	104·3
LiCr$_{0.4}$Mn$_{1.6}$O$_4$[Li]$_{8a}$[Cr$_{0.4}^{3+}$Mn$_{0.6}^{3+}$Mn$_{1.0}^{4+}$]$_{16d}$[O$_4$]$_{32c}$	70·5	89·5
LiCu$_{0.1}$Mn$_{1.9}$O$_4$[Li]$_{8a}$[Cu$_{0.1}^{2+}$Mn$_{0.8}^{3+}$Mn$_{1.1}^{4+}$]$_{16d}$[O$_4$]$_{32c}$	108·7	118·0
LiCu$_{0.2}$Mn$_{1.8}$O$_4$[Li]$_{8a}$[Cu$_{0.2}^{2+}$Mn$_{0.6}^{3+}$Mn$_{1.2}^{4+}$]$_{16d}$[O$_4$]$_{32c}$	92·4	88·1
LiCu$_{0.3}$Mn$_{1.7}$O$_4$[Li]$_{8a}$[Cu$_{0.3}^{2+}$Mn$_{0.4}^{3+}$Mn$_{1.3}^{4+}$]$_{16d}$[O$_4$]$_{32c}$	76·0	58·5
LiCu$_{0.4}$Mn$_{1.6}$O$_4$[Li]$_{8a}$[Cu$_{0.4}^{2+}$Mn$_{0.2}^{3+}$Mn$_{1.4}^{4+}$]$_{16d}$[O$_4$]$_{32c}$	59·5	29·1
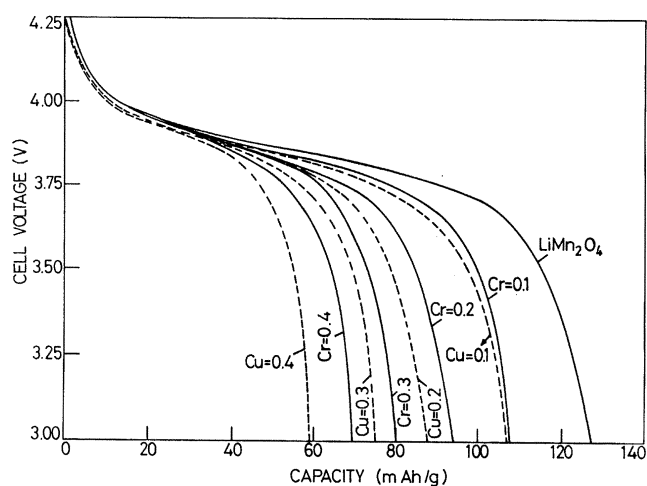
Figure 2. Discharge curves of LiCu$_y$Mn$_{2-y}$O$_4$ and LiCr$_y$Mn$_{2-y}$O$_4$ (Drain rate: 100 μA).

Figure 3. Capacity of cells employing LiMn$_2$O$_4$, LiCu$_{0.2}$Mn$_{1.8}$O$_4$ and LiCr$_{0.2}$Mn$_{1.8}$O$_4$ as a function of cycle number.

Figure 4. Cyclic voltammograms of cells containing (a) $LiMn_2O_4$ and (b) $LiCr_{0.2}Mn_{1.8}O_4$ (scan rate: 1 mV/s).

compositions studied, $LiCr_{0.1}Mn_{1.9}O_4$ qualifies as a potential cathode material for lithium rechargeable cells.

3. Conclusions

Both chromium and copper doped $LiMn_2O_4$ spinels exhibited reduced capacities in the 4 V range, the reduction in capacity being higher in the case of copper. However, the practical capacities obtained with copper doped $LiMn_2O_4$ spinels were inconsistent with the simple spinel structure that may be assigned to the $LiCu_yMn_{2-y}O_4$ compositions. The higher octahedral stabilization energy of trivalent chromium bestows greater structural stability to chromium-doped $LiMn_2O_4$ spinels. The reduced reversibility of the pure spinel as compared to the doped ones as seen from cyclic voltammetric behaviour is vindicated by our charge–discharge studies which show reduced fade of capacity upon repeated cycling for chromium-doped cathodes. Both the dopants reduced capacity fade during cycling. In terms of its appreciable reversible capacity and extended cyclability, $LiCr_{0.1}Mn_{1.9}O_4$ qualifies as a potential cathode material for lithium rechargeable cells.

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tively low reactivity of copper oxide restrict the complete incorporation of copper into the spinel structure (Xia *et al* 1997). This is reflected in the increased capacity obtained for samples with $y = 0.2$, 0.3 and 0.4 as observed by Eli *et al* (1998). These results are inconsistent with the simple spinel structure that we have ascribed to the product of reaction obtained from Li_2CO_3, $MnCO_3$ and $CuCO_3$. Both the copper doped and chromium doped cathode materials exhibited reduced capacity fades upon cycling (figure 3). However, the effect of chromium is more pronounced in reducing the capacity fade.

Cyclic voltammograms (sweep rate: 1 mV/s) of the cells employing $LiMn_2O_4$ and $LiCr_{0.2}Mn_{1.8}O_4$ are presented in figures 4a and b, respectively. It can be seen that the added chromium reduces the separation between the anodic and cathodic peaks. Further, the peak currents in the case of $LiMn_2O_4$ decrease more rapidly than those for $LiCr_{0.2}Mn_{1.8}O_4$ as the cycling continues. The results suggest improved rechargeability upon chromium substitution. In fact, the specific capacities observed at the end of the 20th cycle for the cathode materials are 76 mAh ($LiMn_2O_4$); 90.6 mAh ($LiCr_{0.1}Mn_{1.9}O_4$); 72.9 mAh ($LiCr_{0.2}Mn_{1.8}O_4$); and 52.5 mAh ($LiCr_{0.4}Mn_{1.6}O_4$). The percentage capacity fades for the above compounds are 1.46, 0.86, 1.22 and 1.28, respectively. Thus among the

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