Electrochemical behaviour of LiM_yMn_{2-y}O_4 (M = Cu, Cr; 0 ≤ y ≤ 0.4)

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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_yMn_{1-y}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,Mn_{2-x}]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,Mn_{2-x}]O_4 (M = Cr^{3+} or Cu^{2+}; y = 0.0, 0.1, 0.2, 0.3 and 0.4), 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 800°C for 8 h. The product was then ground again and heat treated at 800°C for another 18 h. Powder X-ray diffraction patterns were recorded on a Jeol 8030 X-ray diffractometer with a nickel filtered CuKα 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 slurry of the cathode active powder, graphite and polyvinylidene fluoride in N-methyl-2-pyrrolidone. Cathode active material loadings and the case of chromium doped...
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$_2$O$_4$ (space group Fd$ar{3}$m) 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$_y$Mn$_{2-y}$]O$_4$ are very close to those of LiMn$_2$O$_4$ (Mossbach 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 2$\theta$ value of 44º, 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 2$\theta$ value of 39º, 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$_2$O$_4$.

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 Å), Mn$^{3+}$ (0.68 Å); Cr$^{4+}$ (0.58 Å), Mn$^{4+}$ (0.60 Å) (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 α-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$_2$O$_4$ spinels while Zhang et al. (1998) demonstrated a similar effect by a chemically modified Cr$^{4+}$–Cr$_{3+}$ 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$_2$O$_4$ cathode) has been shown by Iwata et al. (1999).

3.2 Charge–discharge studies

Li/Li$_x$M$_{2-x}$Mn$_2$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[Cr$_y$Mn$_{2-y}$]O$_4$ and b. Li[Cr$_y$Mn$_{2-y}$]O$_4$. 1. $y = 0$; 2. $y = 0.1$; 3. $y = 0.2$; 4. $y = 0.3$ and 5. $y = 0.4$. 
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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$^{3+}$/Cr$^{4+}$ or Cu$^{2+}$/Cu$^{3+}$ 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$^{4+}$ 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:

$$\text{Li}[\text{Cr}^{3+}\text{Mn}^{3+}_{1-y}\text{Mn}^{4+}_y]\text{O}_4 \leftrightarrow \text{Li}^+ + \text{Mn}^{3+}_{1-y}\text{Mn}^{4+}_y\text{O}_3 + (1-y)\text{Li}^+ + (1-y)e^-$$

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$^{4+}$ 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 LiCu$_{0.5}Mn_{0.5}Mn_{1-y}^{3+}\text{O}_4$ and LiCu$_{0.5}Mn_{0.5}Mn^{4+}\text{O}_4$, 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-

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<tr>
<th>Formula</th>
<th>Practical capacity</th>
<th>Theoretical capacity</th>
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<tbody>
<tr>
<td>LiMn$<em>2$O$<em>4$[Li]$</em>{0.6}$[Mn$^{3+}$Mn$^{4+}$]$</em>{1.6}$O$_{4}$</td>
<td>128.0</td>
<td>148.2</td>
</tr>
<tr>
<td>LiCr$<em>{0.5}$Mn$</em>{1.5}$O$<em>4$[Li]$</em>{0.6}$[Cr$^{3+}$Mn$^{3+}$Mn$<em>{1-y}^{4+}$]$</em>{1.6}$O$_{4}$</td>
<td>109.5</td>
<td>133.6</td>
</tr>
<tr>
<td>LiCr$<em>{0.2}$Mn$</em>{1.8}$O$<em>4$[Li]$</em>{0.6}$[Cr$^{3+}$Mn$^{3+}$Mn$<em>{1-y}^{4+}$]$</em>{1.6}$O$_{4}$</td>
<td>96.4</td>
<td>118.9</td>
</tr>
<tr>
<td>LiCr$<em>{0.5}$Mn$</em>{1.5}$O$<em>4$[Li]$</em>{0.6}$[Cr$^{3+}$Mn$^{3+}$Mn$<em>{1-y}^{4+}$]$</em>{1.6}$O$_{4}$</td>
<td>80.1</td>
<td>104.3</td>
</tr>
<tr>
<td>LiCr$<em>{0.4}$Mn$</em>{1.6}$O$<em>4$[Li]$</em>{0.6}$[Cr$^{3+}$Mn$^{3+}$Mn$<em>{1-y}^{4+}$]$</em>{1.6}$O$_{4}$</td>
<td>70.5</td>
<td>89.5</td>
</tr>
<tr>
<td>LiCu$<em>{0.5}$Mn$</em>{1.5}$O$<em>4$[Li]$</em>{0.6}$[Cu$^{2+}$Mn$^{3+}$Mn$<em>{1-y}^{4+}$]$</em>{1.6}$O$_{4}$</td>
<td>108.7</td>
<td>118.0</td>
</tr>
<tr>
<td>LiCu$<em>{0.5}$Mn$</em>{1.5}$O$<em>4$[Li]$</em>{0.6}$[Cu$^{2+}$Mn$^{3+}$Mn$<em>{1-y}^{4+}$]$</em>{1.6}$O$_{4}$</td>
<td>92.4</td>
<td>88.1</td>
</tr>
<tr>
<td>LiCu$<em>{0.5}$Mn$</em>{1.5}$O$<em>4$[Li]$</em>{0.6}$[Cu$^{2+}$Mn$^{3+}$Mn$<em>{1-y}^{4+}$]$</em>{1.6}$O$_{4}$</td>
<td>76.0</td>
<td>58.5</td>
</tr>
<tr>
<td>LiCu$<em>{0.4}$Mn$</em>{1.6}$O$<em>4$[Li]$</em>{0.6}$[Cu$^{2+}$Mn$^{3+}$Mn$<em>{1-y}^{4+}$]$</em>{1.6}$O$_{4}$</td>
<td>59.5</td>
<td>29.1</td>
</tr>
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</table>

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

**Figure 2.** Discharge curves of LiCu$_{0.5}$Mn$_{1.5}$O$_4$ and LiCr$_{0.5}$Mn$_{1.5}$O$_4$ (Drain rate: 100 µA).

**Figure 3.** Capacity of cells employing LiMn$_2$O$_4$, LiCu$_{0.5}$Mn$_{1.5}$O$_4$ and LiCr$_{0.5}$Mn$_{1.5}$O$_4$ as a function of cycle number.
tively low reactivity of copper oxide restricts 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$_2$CO$_3$, 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$_2$O$_4$ 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$_2$O$_4$ 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$_2$O$_4$); 90.6 mAh (LiCr$_{0.2}$Mn$_{1.8}$O$_4$); 72.9 mAh (LiCr$_{0.3}$Mn$_{1.7}$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 compositions studied, LiCr$_{0.3}$Mn$_{1.9}$O$_4$ qualifies as a potential cathode material for lithium rechargeable cells.

3. Conclusions

Both chromium and copper doped LiMn$_2$O$_4$ 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$_2$O$_4$ spinels were inconsistent with the simple spinel structure that may be assigned to the LiCu$_{x}$Mn$_{2-y}$O$_4$ compositions. The higher octahedral stabilization energy of trivalent chromium bestows greater structural stability to chromium-doped LiMn$_2$O$_4$ 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$_{0.3}$Mn$_{1.9}$O$_4$ qualifies as a potential cathode material for lithium rechargeable cells.

References


Baocben W, Yongyao X, Li F and Dongjinang Z 1993 J. Power Sources 43-44 539

Borchardt-Ott W 1993 Crystallography (New York: Springer)


Gao Y and Dahn J R 1996 Solid State Ionics 84 33


Iwata E, Takahashi K, Maeda T and Mouri T 1999 J. Power Sources 81–82 430


Kawai H, Nagata M, Tukamoto H and West A R 1999 J. Power Sources 81–82 67


Sigala C and Tournoux M 1997 J. Solid State Chem. 132 372


Figure 4. Cyclic voltammograms of cells containing (a) LiMn$_2$O$_4$ and (b) LiCr$_{0.2}$Mn$_{1.8}$O$_4$ (scan rate: 1 mV/s).
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Spahr M E, Novak P, Haas O and Nespar R 1997 *J. Power Sources* **68** 629


Xia Y, Zhou Y and Yoshio M 1997 *J. Electrochem. Soc.* **144** 2593


Zhang D, Popov B N and White R E 1998 *J. Power Sources* **76** 81