Electrochemical insertion of magnesium in a mixed manganese–cobalt oxide

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The electrochemical insertion of Mg^{2+} into the cation-deficient mixed oxide $Mn_{2.15}Co_{0.37}O_4$ is studied in regard to its possible use as a positive electrode in magnesium ion-transfer batteries. The cation vacancies of the mixed oxide offer a pathway for Mg^{2+} insertion with a maximum uptake of 0.23 Mg per mole of oxide. Voltammetric and chronopotentiometric measurements indicate a single insertion step located near 2.9 V *vs* Li/Li^+. The strong polarizing effect of Mg^{2+} ions induces a more pronounced disordering process than for Li accommodation. This results in a limited stable specific capacity of 30 A h kg^{-1} when discharge–charge cycles are performed at a C/6 rate within the cycling limits 4.05–1.85 V *vs.* Li/Li^+.

The intercalation of divalent cations into transition-metal oxides has received little attention to date. However, the insertion of magnesium is of particular theoretical and practical interest both because of its similar size to lithium and because of its prospective application in ion-transfer battery systems. For ion-transfer batteries, magnesium exhibits attractive properties in comparison with Li, owing to its natural abundance, relatively low price and higher expected safety. The relevant literature dealing with Mg^{2+} insertion reactions mainly focuses on oxides. Our laboratory studied Mg^{2+} insertion into V_2O_5 at 150 °C in molten dimethyl sulfone.[1] Gregory *et al.*[2] screened about 15 compounds for their ability to insert Mg^{2+} ions. More recent works have shown the possibility of inserting Mg^{2+} species into V_2O_5 at room temperature,[3] and also into hydrated vanadium bronzes[4,5] as well as in orthorhombic molybdenum oxide.[6]

Chemical insertion of magnesium ions[2,7] has been carried out in various manganese oxides such as Mn_2O_3, Mn_3O_4 and γ-MnO_2, whereas electrochemical Mg insertion has not yet been reported. We sought to extend the Mg^{2+} insertion process to a related host lattice which belongs to a group of new cation-deficient mixed Mn–Co spinel oxides $Mn_yCo_zO_4$ ($2.5 < y+z \leqslant 2.62$), which are prepared *via* a solution technique. The carbonate precursor method used results in ultrafine materials and the simultaneous presence of manganese ions with valences of +4 and +3. A previous electrochemical investigation on Li intercalation,[8,9] has shown interesting properties with one reversible process located near 2.8 V involving a faradaic yield of 0.7–0.8 F (mol oxide)$^{-1}$. Moreover, because lithium ions are preferentially incorporated in vacant sites usually occupied by transition-metal ions, the magnitude of the Jahn–Teller effect is minimized as reduction proceeds.

The high oxidation state of Mn ($z = 3.17$) combined with the high content of cation vacancies (0.48) should also make this compound an attractive material for Mg intercalation. This paper reports on Mg insertion into the mixed oxide $Mn_{2.15}Co_{0.37}O_4$.

Experimental

The mixed manganese–cobalt carbonate was prepared by the addition of a 1 mol dm^{-3} solution of $NaHCO_3$ to a 0.5 mol dm^{-3} solution of the divalent ions Mn^{II} and Co^{II} under a continuous flow of CO_2. The composition homogeneity in carbonate and oxide samples was determined by electron microprobe energy dispersive X-ray analysis (EDXA) with a Philips SEM 501 B apparatus. The stoichiometry was confirmed by atomic absorption spectrometry.

The average oxidation states of the metal ions in the sample were determined by the following procedure. The sample (*ca.* 50 g) was dissolved in 5 ml of 0.1 mol dm^{-3} Fe^{2+}, 5 ml of conc. H_2SO_4, 5 ml of 35% HCl and 10 ml of H_2O under a continuous flow of argon and heated until complete dissolution. After cooling to 20–25 °C, 10 ml of H_3PO_4, 25 ml of H_2O and 1.5 ml of indicator (0.3% diphenylamine in ethanol) were added. The solution was titrated with standard 0.05 mol dm^{-3} K_2CrO_4. Previously, a blank titration was carried out under the same conditions. The difference between the titrations was assigned to the total content of oxidizing species and was used to calculate the oxygen to metal (O/M) ratios.

XRD studies were performed on an INEL X-ray system using Cu-Kα radiation. The oxide $Mn_{2.15}Co_{0.37}O_4$ obtained from thermal decomposition of the corresponding mixed carbonate at 400 °C exhibits a tetragonal spinel structure with the following cell parameters: $a_t = 5.805$ Å, $c_t = 9.490$ Å (space group $I4_1/amd$). The chemical composition corresponds to the simultaneous presence of 0.43 Mn^{IV} and 1.72 Mn^{III} ions (mean oxidation state of metallic ions, $Z = 3.17$) and a ratio O/M = 1.587 which indicates the presence of 0.48 vacancies per mole of oxide.

The working electrode consisted of a stainless-steel grid on which the cathodic material was pressed. The cathode was made of a mixture of active material (80 mass%) with graphite (7.5 mass%), acetylene black (7.5 mass%) and PTFE (5 mass%). Anhydrous magnesium perchlorate was dried under vacuum at 190 °C for 15 h. Magnesium trifluoromethanesulfonate was dried under vacuum at 80 °C for 5 h. Either an $Mg(ClO_4)_2$ solution (0.1 mol dm^{-3}) in propylene carbonate (PC) (twice distilled, Fluka) or an $Mg(CF_3SO_3)_2$ solution (0.05 mol dm^{-3}) was used as the electrolyte while a magnesium rod served as the counter electrode. An Li/Li^+ couple in a separated compartment acted as the reference. A thin porosity frit was used to prevent any diffusion of lithium ions.

Results and Discussion

Typical voltammetric curves performed between the cycling limits 4.05–1.85 V *vs.* Li/Li^+ for the reduction–oxidation of $Mn_{2.15}Co_{0.37}O_4$ are reported in Fig. 1. Only one redox process is observed. The magnesium insertion process appears to be reversible over a few cycles with cathodic and anodic peaks located at 3.05 and 3.83 V, respectively.

The corresponding chronopotentiometric curves allow the clear quantification of the Mg insertion process (Fig. 2). A single reduction step centred near 2.9 V leads to a faradaic yield of 0.44 F (mol oxide)$^{-1}$ at a 1.8 V cut-off voltage. A more important hysteresis appears between the reduction and oxidation curves than in the case of Li insertion.[8,9]

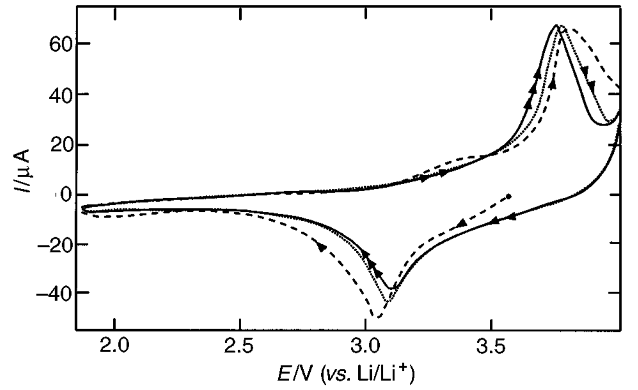

Fig. 1 Cyclic voltammetric curves of an $Mn_{2.15}Co_{0.37}O_4$ electrode in a 0.1 mol dm^3 $Mg(ClO_4)_2$ solution in propylene carbonate at 20 °C; sweep rate = 40 μV s^{-1}

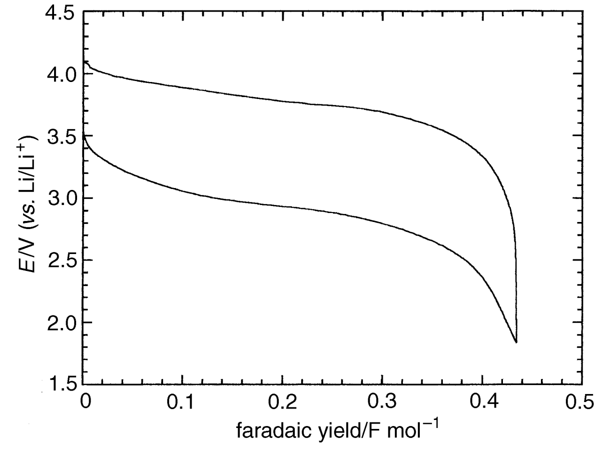

Fig. 2 Discharge–charge curves for $Mn_{2.15}Co_{0.37}O_4$ in 0.1 mol dm^{-3} $Mg(ClO_4)_2$/PC electrolyte ($j = 100$ μA cm^{-2})

According to the following equation:

$$Mn_{2.15}Co_{0.37}O_4 + 2xe^- + xMg^{2+} \rightleftharpoons Mg_xMn_{2.15}Co_{0.37}O_4$$

the experimental faradaic balance, consistent with both the vacancies content (0.48) and the number of reducible Mn^{IV} ions (0.43), shows that *ca.* 0.22 Mg^{2+} ions reversibly enter the mixed oxide host lattice. Lower current densities (50–20 μA) did not enable this value to be exceeded significantly. However, this maximum uptake is lower than that found for Li insertion (*ca.* 0.62). In the latter case, Li ions were found to be incorporated preferentially in vacant octahedral sites, which are usually occupied by transition-metal oxides in cubic spinels of stoichiometric M_3O_4 but partially filled in the deficient oxide (8d sites of the space group $I4_1/amd$). Additional Li insertion of 0.14 ions in interstitial 8c octahedral sites associated with the reduction of some Mn^{3+} ions was considered to account for the Li content of 0.62.[8] Conversely, owing to its size and charge, the maximum content for magnesium insertion can be explained by the quantitative reduction of Mn^{4+} ions and the filling of only half of the available vacant 8d cationic sites. Strong coulometric interactions owing to the valence of the magnesium ions probably hinder further magnesium insertion and the correlative reduction of Mn^{3+}. In other respects, probably owing to the small size of magnesium ions, the voltage of the discharge curve is very close to that found for Li intercalation[8,9] with a coulombic capacity of 75% of the Li capacity. This indicates a high diffusivity of Mg^{2+} ions which easily enter the pathway offered by cation vacancies. Indeed, larger cation species such as sodium and potassium were shown to enter the same host lattice at around 2.5 and 2.2 V respectively.[8]

From chemical tests in a solution of dibutylmagnesium in heptane as insertion reagent, specific charges of *ca.* 150 and 220 A h kg^{-1} corresponding to stoichiometries of $Mg_{0.66}Mn_3O_4$ and $Mg_{0.8}Co_3O_4$ were estimated[2] without any data on reversibility. Our results on the cation-deficient Mn–Co mixed oxide in terms of maximum Mg content are lower than those obtained from chemical experiments with stoichiometric Mn and Co spinel oxides.

For host lattices, higher Mg contents are found from electrochemical experiments: 0.45 Mg^{2+} in V_2O_5,[1,3] 0.38/0.5 Mg^{2+} in MoO_3,[6] 1.8 Mg^{2+} in hydrated $Mg(V_3O_8)(H_2O)_y$.[3]

The XRD patterns obtained for the electrochemically formed $Mg_{0.23}Mn_{2.15}Co_{0.37}O_4$ show that the structure of the oxide is maintained, (Fig. 3). However, even when the main diffraction lines are well identified, a disordering process, more pronounced than that for $Li_{0.3}Mn_{2.15}Co_{0.37}O_4$, takes place.[8] This is probably related to the divalent charge, the strong polarizing effect and the larger size of Mg^{2+} radius (0.65 Å, *vs. ca.* 0.6 Å for Li ions).

In order to provide some information on the localization of Mg ions and their content in the cation-deficient mixed oxide $Mn_{2.15}Co_{0.37}O_4$, we investigate the chronopotentiometric properties of electrochemically formed samples $Mg_xMn_{2.15}Co_{0.37}O_4$ in a lithium-based electrolyte.

As shown in Fig. 4, the Mg-containing electrodes exhibit the typical behaviour expected for Li insertion in the parent oxide: two well defined insertion steps centred in the potential windows 3.5–2.0 and 2.0–1.0 V. However, the higher the Mg content, the shorter the transition time of the first step while the length of the second one remains unchanged. For Li and

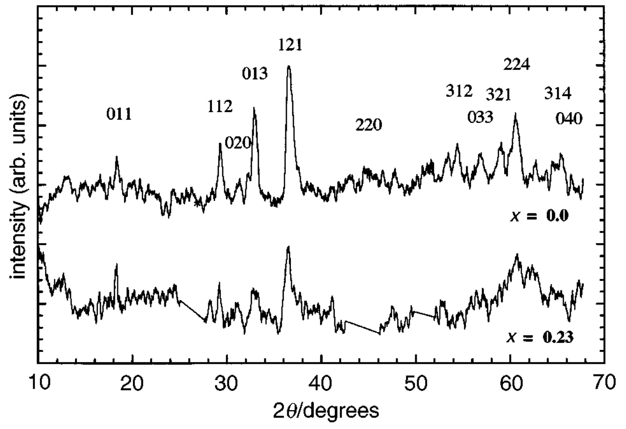

Fig. 3 X-Ray diffraction pattern of $Mg_{0.23}Mn_{2.15}Co_{0.37}O_4$ in reflection geometry

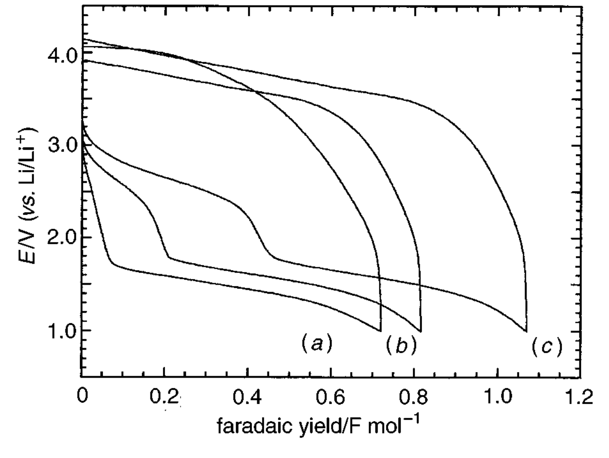

Fig. 4 Discharge–charge curves for $Mg_xMn_{2.15}Co_{0.37}O_4$ in 1 mol dm^{-3} $LiClO_4$/PC electrolyte ($j = 100$ μA cm^{-2}). (*a*) $x = 0.27$; (*b*) $x = 0.23$; (*c*) $x = 0.1$.

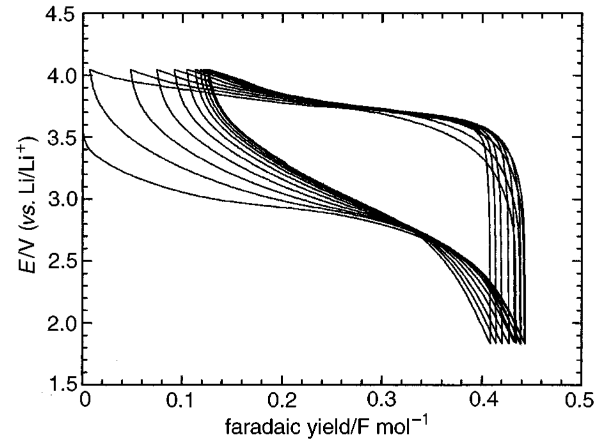

Fig. 5 Discharge–charge cycles of $Mn_{2.15}Co_{0.37}O_4$ within the potential range 4.05–1.85 V (C/6 rate)

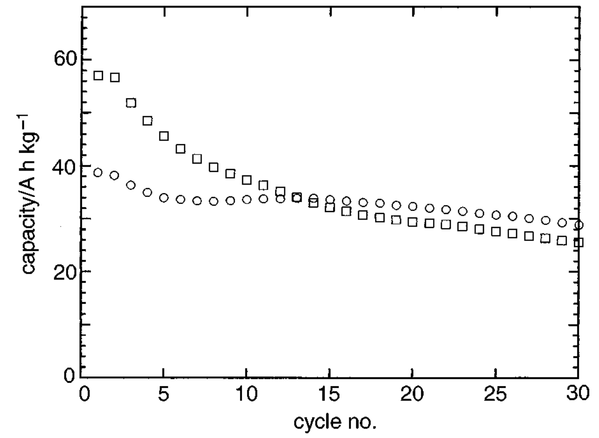

Fig. 6 Evolution of the specific capacity for $Mn_{2.15}Co_{0.37}O_4$ during cycling galvanostatic experiments in 0.1 mol dm^{-3} $Mg(ClO_4)_2$/PC electrolyte. Voltage range: (○) 4.05–2.8 V; (□) 4.05–1.85 V (j= 100 μA cm^{-2}).

Mg insertion, the overall faradaic yield never exceeds the expected value of *ca.* 0.6–0.65 F mol^{-1} at a 2.0 V cut-off voltage. These results seem to indicate the partial occupancy of 8d octahedral vacant sites by Mg^{2+} ions with retention of the structural integrity.[8] Because there is no change in voltage, it can be suggested that subsequent Li insertion occurs in a similar manner by filling the remaining 8d sites and also some interstitial 8c sites, as suggested previously for an Li insertion process.[8] This requires the additional reduction of Mn^{3+} ions. Assuming each Mg^{2+} ion occupies one site, these experiments show that the faradaic yield for Mg insertion is mainly controlled by the initial content of Mn^{4+}, but also by high Coulombic repulsive interactions which prevent achievement of the maximum value of 0.3 for the degree of insertion of a divalent cation. In all cases, the charging process does not reveal any reversibility, as is known for stoichiometric oxides. When a deeper discharge is performed to obtain $Mg_{0.27}Mn_{2.15}Co_{0.37}O_4$, its further reduction in 1 mol dm^{-3} $LiClO_4$/PC gives rise to a single voltage plateau at 1.5 V.

In order to further characterize the properties relevant to the prospective use of the mixed Mn–Co oxide for secondary battery electrodes, we investigated the cycling behaviour of $Mn_{2.15}Co_{0.37}O_4$. Results obtained for two cycling limits are reported in Fig. 5 and 6. During the first five cycles, it can be seen that a significant fraction of the inserted Mg^{2+} ions remains bonded in the crystal lattice of the cation-deficient mixed oxide and cannot be extracted from the material (Fig. 5). The specific charge decreases from 60 to 40 A h kg^{-1} by the fifth cycle and slowly decreases thereafter to reach 30 A h kg^{-1} by the 30th cycle (Fig. 6). This may be explained by the disordering process induced by the magnesium insertion as indicated by XRD experiments. It is possible to obtain a more stable specific capacity by cycling within the limited voltage range 4.05–2.8 V (Fig. 5). The initial Coulombic capacity of 40 A h kg^{-1} decreases in the early cycles to stabilize at *ca.* 30 A h kg^{-1} after 20 cycles. These first results are noteworthy as compared with the fairly irreversible behaviour exhibited by the stoichiometric Co_3O_4 oxide with low Coulombic capacities (5 A h kg^{-1}). It is the first time that reversible magnesium insertion into a manganese oxide has been reported. For the sake of comparison, only a few cathodic materials have been proved to reversibly accommodate Mg ions. For instance, vanadium pentoxide[3] can be utilized after 20 cycles with an appreciable Coulombic capacity (50 A h kg^{-1}) while *ca.* 60–80 and 50 A h kg^{-1} can be attained with hydrated vanadium bronzes[5] and MoO_3 in a liquid inorganic molten salt electrolyte at 80 °C, respectively.[6]

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References

1 J. P. Pereira-Ramos, R. Messina and J. Perichon, *J. Electroanal. Chem.*, 1987, **2–8**, 241.
2 T. D. Gregory, R. J. Hoffman and R. C. Winterton, *J. Electrochem. Soc.*, 1990, **137**, 775.
3 P. Novak and J. Desilvestro, *J. Electrochem. Soc.*, 1993, **140**, 140.
4 P. Novak, W. Scheifele and O. Hass, *J. Power Sources*, 1995, **54**, 479.
5 P. Novak, W. Scheifele, F. Joho and O. Hass, *J. Electrochem. Soc.*, 1995, **142**, 2544.
6 M. E. Spahr, P. Novak, O. Hass and R. Nesper, *J. Power Sources*, 1995, **54**, 346.
7 P. G. Bruce, F. Krok, J. Nowinski, V. C. Gibson and K. Tavakkoli, *J. Mater. Chem.*, 1991, **1**, 705.
8 J. Farcy, J. P. Pereira-Ramos, L. Hernán, J. Morales and J. L. Tirado, *Electrochim. Acta*, 1994, **39**, 339.
9 L. Sánchez, J. Farcy, J. P. Pereira-Ramos, L. Hernán, J. Morales and J. L. Tirado, *J. Mater. Chem.*, 1996, **6**, 37.

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