The intercalation compound Li($Mn_{0.9}Co_{0.1}$)O_2 as a positive electrode for rechargeable lithium batteries

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By replacing only 10% of the Mn by Co in the layered lithium intercalation compound $LiMnO_2$ the amount of lithium that can be removed and reinserted is increased by 50% corresponding to an increase in the ability to store charge from 130 to 200 mA h g^{-1} at 100 µ A cm^{-2} and rendering this low cost/toxicity material of potential interest as a positive electrode in rechargeable lithium batteries; furthermore the cooperative Jahn–Teller distortion due to localised high spin Mn^{3+}($3d^4$) in $LiMnO_2$ appears to be suppressed for $Li_x(Mn_{0.9}Co_{0.1})O_2$; $x < 0.9$ (80% Mn^{3+} assuming Co^{3+}).

First generation rechargeable lithium batteries are now a major commercial success.[1] They utilise the layered intercalation compound, $LiCoO_2$, as the positive electrode from which lithium is removed on charging the cell and reinserted on discharge.[2,3] Only half the lithium may be removed and reinserted reversibly (Li_xCoO_2; $0.5 < x < 1$) limiting the practical capacity to store charge to *ca.* 130 mA h g^{-1}. In order to develop much needed second generation batteries, new lithium intercalation hosts are essential. The challenge facing solid state chemistry is to synthesise lithium intercalation compounds that possess a higher capacity to cycle lithium in a host which is cheaper and less toxic than $LiCoO_2$.[2] Several systems have been extensively investigated including those based on layered $LiNiO_2$ and the spinel $LiMn_2O_4$.[4–11] The former offers improved capacity of *ca.* 170 mA h g^{-1} while the latter (110 mA h g^{-1}) is cheaper and less toxic than $LiCoO_2$. Recently we reported the first synthesis of layered $LiMnO_2$, isostructural with $LiCoO_2$.[12–14] Key to the preparation was the use of a low temperature ion exchange route. Being a manganese oxide it has the potential to deliver a low cost/toxicity electrode. Most of the lithium may be removed on initial charging (> 200 mA h g^{-1} at 100 µA cm^{-2}) but only a proportion of this can be reinserted (*ca.* 130 mA h g^{-1}) rendering this otherwise attractive cathode of less interest. By replacing only 10% of the Mn by Co, a material is obtained, the cost and toxicity of which remain sufficiently low to be of industrial interest and for which the ability to sustain a high capacity on cycling (200 mA h g^{-1} on cycling at 100 µA cm^{-2}) is enhanced.

Synthesis of Li($Mn_{0.9}Co_{0.1}$)O_2 employed the ion exchange method reported previously.[12] Na($Mn_{0.9}Co_{0.1}$)O_2 was synthesised by mixing Na_2CO_3, $Mn(CH_3CO_2)_2\cdot 4H_2O$ and $Co(CH_3CO_2)_2\cdot 4H_2O$ in water, drying by rotary evaporation then heating initially at 250 °C for 3 h then 670 °C for 1 h in air. The resulting solid was subjected to ion exchange by refluxing in a 5–10 fold excess of LiBr in hexanol at 150 °C for 8 h. Rietveld refinement using powder neutron data collected on POLARIS (ISIS, RAL, Oxfordshire) confirmed that the structure is layered and isostructural with $LiCoO_2$ (α-$NaFeO_2$ structure). A good fit was obtained between the observed and calculated powder diffraction profiles [R_{wp} = 0.026, rhombohedral cell with lattice parameters a = 2.8750(2) Å and c = 14.3930(8) Å, c/a = 5.006], Fig. 1. The structure is composed of close packed oxide ion layers stacked to yield a cubic close packed arrangement, a sheet of octahedral sites is located between each pair of oxide layers and alternate sheets are occupied by transition metal and lithium ions. The very different scattering lengths of Mn and Co made it possible to refine their occupancies on the shared transition metal sites. Values for Mn and Co of 0.93(1) and 0.07(1) were obtained. We have also synthesised Co substituted compounds up to Li($Mn_{0.5}Co_{0.5}$)O_2 and refinement with neutrons shows a continuous increase of the Co content on the transition metal sites and an associated contraction of the a-axis corresponding to shortening of the TM-O distances (TM = transition metal), as expected for a continuous solid solution. The a-axis contracton is consistent with replacement of Mn^{3+} by Co^{3+} rather than Co^{2+}/Mn^{4+}. Atomic emission analysis revealed a slightly lithium deficient composition of $Li_{0.85}(Mn_{0.9}Co_{0.1})O_2$ which agrees well with the amount of lithium that can be removed and inserted electrochemically and with the neutron refinement of the Li site occupancy.

Mn^{3+} is a Jahn–Teller active ion and in pure $LiMnO_2$ it results in a distortion from the ideal rhombohedral structure to monoclinic symmetry.[12] The cooperative Jahn–Teller distortion persists on deintercalation giving rise to a two phase mixture of monoclinic $LiMnO_2$ and rhombohedral $Li_{0.5}MnO_2$ until the $Li_{0.5}MnO_2$ composition is reached at which the structure becomes a single rhombohedral phase. At this point only 50% of the transition metal sites are occupied by the Jahn–Teller active Mn^{3+} ion. It appears that a combination of cobalt substitution and slight lithium deficiency is enough in the case of $Li_{0.85}(Mn_{0.9}Co_{0.1})O_2$ to suppress the cooperative Jahn–Teller distortion despite 75% of the transition metal sites being occupied by Mn^{3+} (assuming Co^{3+}). We have inserted lithium into $Li_{0.85}(Mn_{0.9}Co_{0.1}O_2)$ and find that even for $Li_{0.9}(Mn_{0.9}Co_{0.1}O_2)$ (80% Mn^{3+} if Co^{3+}) there is no evidence for a cooperative distortion in the X-ray or neutron data. The Jahn–Teller distortion in $LiMnO_2$ is driven by the localised high spin $3d^4$ configuration of Mn^{3+}. It is interesting that such a low level of Co^{3+} suppresses the distortion. Understanding the electronic structure in detail and particularly investigating the origin of the suppression of the cooperative Jahn–Teller distortion is beyond the scope of this paper and necessitates a subsequent study,

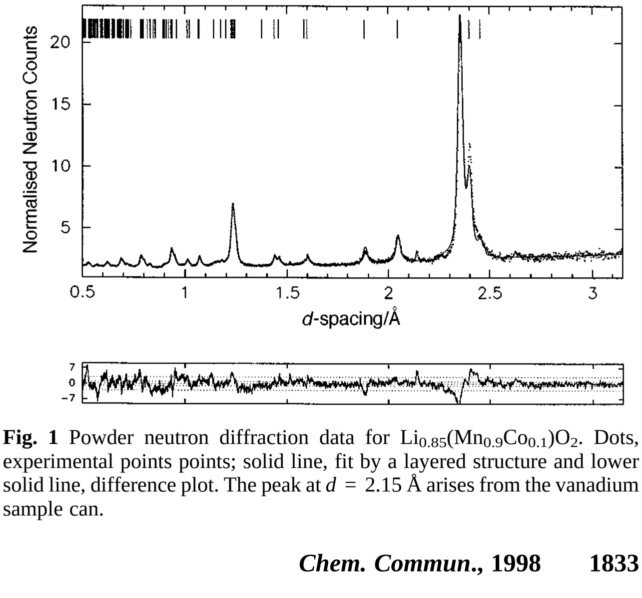

Fig. 1 Powder neutron diffraction data for $Li_{0.85}(Mn_{0.9}Co_{0.1})O_2$. Dots, experimental points points; solid line, fit by a layered structure and lower solid line, difference plot. The peak at d = 2.15 Å arises from the vanadium sample can.

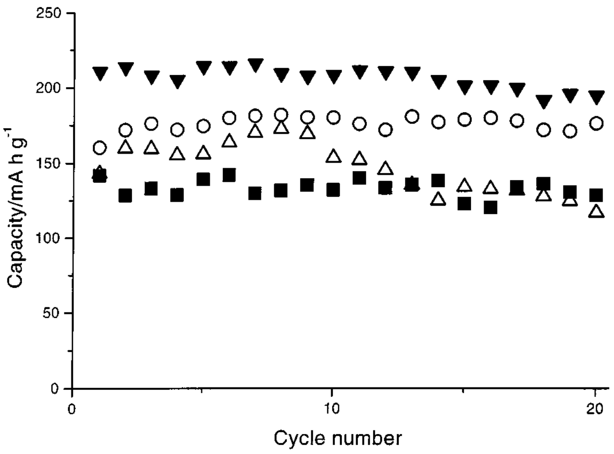

Fig. 2 Variation of specific discharge capacity with cycle number at 100 μA cm^{-2} and 2.6–4.8V; for layered $LiMnO_2$ and three Co doped samples. (△) $Li(Mn_{0.95}Co_{0.05})O_2$, (▼) $Li(Mn_{0.90}Co_{0.10})O_2$, (○) $Li(Mn_{0.85}Co_{0.15})O_2$, (■) $LiMnO_2$.

already underway, which will include establishing the oxidation states of Mn and Co.

The performance of the material as an intercalation electrode in a cell was investigated by forming a composite between the intercalation compound, super S carbon and Kynar Flex 2801 binder (a copolymer based on PVDF) in the weight ratios 85 : 10 : 5. The electrode was cast onto Al foil. Cycling was performed in three-electrode cells (Li counter and reference) in 1 M $LiPF_6$ in EC–DMC (2 : 1) as electrolyte and at a constant current density of 100 μA cm^{-2} (14 mA g^{-1}) within the potential range 2.6–4.8 V, Fig. 2. The discharge capacity on the first cycle is 210 mA h g^{-1} and ranges between this value and 200 mA h g^{-1} up to twenty cycles (the variation between different cells is $< 5\%$), demonstrating a substantial improvement in capacity compared with $LiMnO_2$ and eliminating the capacity loss on the first cycle. Why might this be so?

Cycling lithium in the spinel host $LiMn_2O_4$ over the range $Li_{1+x}Mn_2O_4 (0 < x < 1)$, involves a two phase reaction between cubic $LiMn_2O_4$ and tetragonal $Li_2Mn_2O_4$, arising from the Jahn–Teller distortion which occurs when more that 50% of the octahedral 16d sites in spinel are occupied by Mn^{3+}.[6] As a result, there is an abrupt change in the unit cell volume on Li cycling as one phase converts to the other, leading to disconnection of the particles and the formation of isolated regions in the electrode incapable of storing lithium.[15] A similar first order phase change occurs in the case of layered $LiMnO_2$ within the first cycle. We also know from extensive X-ray and neutron diffraction studies, HREM and electrochemical data that $LiMnO_2$ converts to a spinel phase on cycling.[16] The absence of a Jahn–Teller distortion in $Li_{0.85}(Mn_{0.9}Co_{0.1})O_2$ may be related to the elimination of the abrupt capacity loss suffered by $LiMnO_2$ within the first cycle. Further work will be carried out, including longer term cycling, to better understand the mechanism of intercalation in the Co doped materials and to understanding how a small proportion of Co modifies the process compared with pure $LiMnO_2$.

Results from compositions which neighbour $Li_{0.85}(Mn_{0.9}Co_{0.1})O_2$ are also shown in Fig. 2. The data indicate that the capacity retention is even better for compositions with more than 10% Co, however the overall capacity is somewhat reduced.

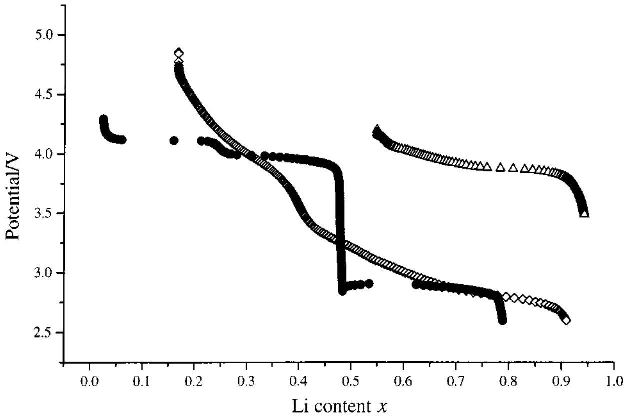

Fig. 3 Discharge curves for: (◇) layered $LiMn_{0.9}Co_{0.1}O_2$, (●) $LiMn_2O_4$ spinel and (△) layered $LiCoO_2$

Only a proportion of the capacity is delivered above 4 V *vs.* Li^+/Li, Fig. 3. However, the move to 2.3 V electronics in mobile communications and other portable applications coupled with the use of graphite anodes which deliver a large proportion of their capacity at a voltage near that of lithium metal, makes 3 V electrodes attractive for future lithium-ion batteries. The intense current interest in α-MnO_2 and its derivatives, which operate at 3 V, bears witness to this.[17]

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