Influence of ion exchange conditions on the defect chemistry and performance of cobalt doped layered lithium manganese oxide based intercalation compounds†

Alastair D. Robertson, A. Robert Armstrong and Peter G. Bruce*

School of Chemistry, University of St. Andrews, North Haugh, St. Andrews, Fife, UK KY16 9ST.
E-mail: p.g.bruce@st-andrews.sc.uk

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It is shown that by varying the conditions used to exchange Na by Li in layered sodium manganese oxide based compounds, not only are the guest ions exchanged but the defect chemistry of the host is modified and this has an important effect on the reversibility of lithium intercalation; in particular, defect 2.5% Co doped layered lithium manganese oxide exhibits a capacity to store lithium equivalent to 200 mA h g^{-1} which fades by only 0.08% per cycle on cycling at 25 mA g^{-1}.

One of the greatest challenges in the field of rechargeable lithium batteries is to replace the $LiCoO_2$ positive electrode with an alternative lithium intercalation compound that is safer, cheaper and less toxic, such as a lithium manganese oxide. The spinel, $LiMn_2O_4$, has been widely studied in this regard.[1–4] Recently, we reported the first synthesis of the layered intercalation compound, $LiMnO_2$, which involved the low temperature ion exchange of Na by Li in $NaMnO_2$.[5,6] The present interest in layered $LiMnO_2$ based materials is significant.[5–12] When doped with Co, high capacities to store Li are obtained but reversibility on cycling is insufficient. Here, we report that varying the ion exchange conditions has an important effect on the defect chemistry in these layered materials, and this has a critical influence on the all-important reversibility of the lithium intercalation reaction.

The layered sodium manganese cobalt oxide phases, $Na_xMn_{1-y}Co_yO_2$, were prepared as described previously.[11] The initial reaction mixture contained 1 mol of Na per transition metal ion, *i.e.* $x = 1$. Ion exchange was carried out using an 8-fold excess of LiBr in either ethanol at 80 °C for 48 h or hexanol at 160 °C for 8 h. Following ion exchange the materials were washed with ethanol and water. Powder X-ray diffraction was carried out on a Stoe STADI/P diffractometer in transmission mode and using an Fe-Kα_1 source (λ = 1.936 Å). Neutron diffraction data were collected on the GEM diffractometer at RAL. Chemical analysis was carried out using well established methods; for Li and Na this was conducted by flame emission whereas atomic absorption spectroscopy was employed for Mn and Co. Oxidation states were obtained by $KMnO_4$/iron(II) ammonium sulfate titration.[13] BET measurements indicated that the surface areas were between 5 and 10 m^2 g^{-1}.

Powder X-ray diffraction patterns of the as-prepared Na materials revealed that they contain two phases, one may be indexed based on the layered phase whereas the other exhibits the characteristic peaks of Na_2CO_3. Evidently the Na_2CO_3 has not reacted completely and by implication the layered sodium phase is Na deficient, *i.e.* $x < 1$. The Na_2CO_3 is removed during the ion exchange and subsequent washing in ethanol–water. Focussing on the layered lithium phases, powder neutron diffraction patterns for these phases prepared in either hexanol or ethanol exhibit a single phase that may be indexed based on the layered O3 structure of $LiCoO_2$ (space group $R\bar{3}m$, structure type α-$NaFeO_2$). For the Co doped materials prepared in hexanol, full structure refinements have been reported previously.[11] Before discussing further Rietveld refinement of the ethanol samples it is instructive to consider the results of chemical analysis (Table 1). Several conclusions may be drawn from these results. First the sodium phase is alkali metal deficient ($x < 1$), consistent with the XRD data, and this is carried through to the Li phases after ion exchange. There is evidence of a somewhat greater alkali metal content after ion exchange than before indicating that some lithium intercalation accompanies the ion exchange process. Table 1 also reveals that the Na phase contains vacancies on the transition metal sites, these vacancies are retained in ethanol samples prepared at 80 °C whereas ion exchange in hexanol at 160 °C eliminates almost all the vacancies. The transition metal vacancies in the Na phase will be associated with negative effective charges which are likely to trap some of the Na^+ ions; this can explain the retention of a small amount of Na during the ethanol exchange. The ion exchange conditions used here are somewhat reducing, and this is sufficient to result in some lithium intercalation in ethanol and hexanol. The more aggressive conditions of reflux in hexanol at 160 °C cause, in addition, reduction of the host with the associated elimination of the transition metal vacancies, without the transition metal vacancies to trap Na^+, the ion exchange process is more complete. Overall it is evident that the ion exchange process is not

Table 1 Compositional analysis of as-prepared 2.5% Co Na phase[a] and ion exchanged Li phases for layered $A_xMn_{1-y}Co_yO_2$ materials

Nominal Co content	A = Na or Li; Ion exchange conditions	Composition	Average TM oxidation state	No. of TM vacancies	Mn^{3+} occupancy of TM sites
0.025	Na	$Na_{0.53}Mn_{0.92}Co_{0.025}O_2$[a]	3.672+	5.5%	28.5%
0.025	Li; Ethanol, 80 °C	$Na_{0.048}Li_{0.58}Mn_{0.91}Co_{0.025}O_2$	3.610+	6.5%	33.8%
0.025	Li; Hexanol, 160 °C	$Na_{0.009}Li_{0.62}Mn_{0.96}Co_{0.028}O_2$	3.412+	1.2%	55.3%
0.1	Li; Ethanol, 80 °C	$Na_{0.035}Li_{0.54}Mn_{0\cdot87}Co_{0.087}O_2$	3.579+	4.3%	31.5%
0.1	Li; Hexanol, 160 °C	$Na_{0.012}Li_{0.64}Mn_{0\cdot90}Co_{0.094}O_2$	3.368+	0.6%	53.4%

[a] Content of Na determined by CHN analysis, thereby allowing the amount of Na_2CO_3 and Na in the main phase to be calculated.

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† Electronic supplementary information (ESI) available: powder neutron diffraction profile for $Li_x(Mn_{0.975}Co_{0.025})O_2$ prepared in ethanol. See http://www.rsc.org/suppdata/cc/b0/b002552f/

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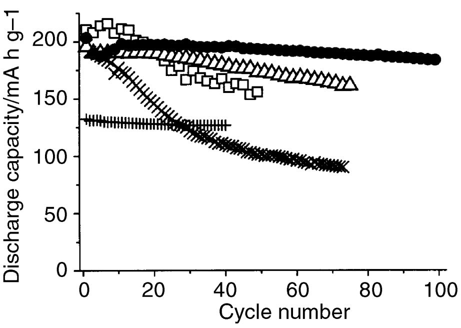

Fig. 1 Discharge capacities as a function of the number of charge–discharge cycles carried out at 25 mA g^{-1} (C/7) and 30 °C between potential limits of 2.4 and 4.6 V for; (●) 2.5% Co prepared in ethanol: (△) 2.5% Co prepared in hexanol: (□) 10% Co prepared in hexanol: (X) $Li_{1.07}(Mn_{1.78}Co_{0.05})O_4$ spinel and (+) $LiCoO_2$ cycled between 3.3 and 4.2 V.

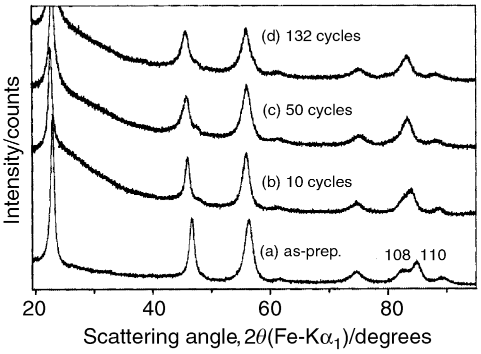

Fig. 2 Powder X-ray diffraction patterns collected on Li_x-$(Mn_{0.975}Co_{0.025})O_2$, prepared in ethanol at 80 °C, (a) before cycling, (b) after 10 cycles, (c) after 50 cycles and (d) after 132 cycles. Cycling was carried out at 25 mA g^{-1} and over the range 2.4–4.6 V.

restricted to the anticipated simple exchange of Na by Li, instead it plays a critical role in controlling the defect chemistry/non-stoichiometry of the transition metal host.

Returning to the neutron data for the 2.5% Co doped ethanol sample (ESI†), Rietveld refinement was carried out based on the O3-$LiCoO_2$ structure, which possesses cubic close packed oxide ions. Li and Na were placed in the octahedral sites (3b) of the alkali metal layers and Mn and Co in the octahedral sites (3a) of the transition metal layers. The Na and Co occupancies were fixed at values obtained from the chemical analysis ($Na_{0.048}Li_{0.58}Mn_{0.91}Co_{0.025}O_2$). The Li and Mn occupancies were allowed to vary freely. The refined occupancies are in good agreement with the chemical analysis. A good fit to the observed data was obtained and the crystallographic data are presented in ref. 14. $LiMnO_2$ is monoclinic owing to a cooperative Jahn–Teller distortion promoted by the high spin Mn^{3+} ions. For the Co doped materials it has been shown that cobalt is in the trivalent state.[11] The presence of Co^{3+} along with the alkali metal deficiency and, in the case of the ethanol samples, vacancies on the transition metal sites conspire to reduce the occupancy of the octahedral sites by Mn^{3+} to a level where they can no longer promote a cooperative distortion which typically occurs at *ca.* 50% occupancy of the transition metal octahedral sites by Mn^{3+}. As a result none of the samples exhibit a monoclinic distortion.

What effect does the presence of transition metal vacancies have on the behaviour of these materials as intercalation electrodes? The variation of discharge capacity with cycle number is shown in Fig. 1. Considering first the hexanol samples, reducing the Co content from 10 to 2.5% improves the capacity retention on cycling. However the highest degree of reversibility is obtained from the 2.5% Co doped sample prepared in ethanol; this corresponds to a capacity fade of only 0.08% per cycle. High capacities to store Li are of no value for application in rechargeable lithium batteries unless accompanied by a high degree of reversibility of the intercalation reaction. This is now becoming recognised as a key feature that must be built into the chemistry of intercalation compounds for rechargeable lithium battery electrodes. The capacity of $LiCoO_2$, used as the positive electrode in the current generation of rechargeable lithium batteries, is also shown for comparison. The layered manganese based materials may be particularly relevant to the market in sub 3 V electronics for which high capacity cathodes delivering their charge above 2.4 V could be combined with graphite anodes to yield high capacity low voltage cells for such electronic applications. This is one of the most rapidly growing markets for rechargeable lithium batteries.

We have shown previously that Co doped materials prepared in hexanol convert to spinel on cycling.[11] This is also the case for the samples prepared in ethanol. The merging of the 108 and 110 peaks is indicative of the transformation (Fig. 2). It is interesting to compare the capacity fade of the layered compounds prepared in hexanol and ethanol which convert to spinel *in situ*, with a directly prepared cobalt doped lithium manganese spinel cycled over the same voltage range. The chosen spinel, which was prepared by conventional solid state reaction, has a very similar composition to the 2.5% Co doped material prepared in ethanol containing, as it does, a similar concentration of vacancies on the transition metal sites. Whereas spinels are known to cycle well when confined to a potential range around 4 V, the irreversibility of the intercalation process on cycling over the wider voltage range is clearly severe even for Co doped samples (Fig. 1), yet this is not the case for the *in situ* spinels.

The results presented here show that by changing the mild ion exchange conditions, it is possible to modify the defect chemistry/stoichiometry of the host. In particular, by forming a layered lithium manganese oxide based spinel with Co and vacancies on the transition metal sites it is possible to improve significantly the reversibility of the intercalation process which is a critical property for applications as an electrode material.

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14 *Crystallographic data* for $Li_xMn_{0.975}Co_{0.025}O_2$ prepared by ion exchange under reflux in ethanol: space group $R\bar{3}m$, $a = 2.86605(2)$, $c = 14.5752(5)$ Å, Li/Na (3b) (0.0, 0.0, 0.5), $B_{iso} = 0.23(13)$, occupancies: Li = 0.595(14), Na = 0.048 (fixed from analysis). Mn/Co (3a) (0.0, 0.0, 0.0), $B_{11} = B_{22} = 0.95(8)$, $B_{33} = 1.7(2)$, $B_{12} = 0.48(4)$, occupancies: Mn = 0.897(10), Co = 0.025 (fixed from analysis). O1 (6c) (0.0, 0.0, 0.2624(1)), $B_{11} = B_{22} = 0.70(2)$, $B_{33} = 1.01(3)$, $B_{12} = 0.351(8)$. *R*-factors: $R_{exp} = 1.2\%$, $R_{wp} = 3.4\%$, $R_p = 2.9\%$, $R_I = 3.4\%$.