SPINEL VERSUS LAYERED STRUCTURES FOR LITHIUM COBALT OXIDE SYNTHESISED AT 400°C

by

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ABSTRACT

Rietveld refinements of X-ray data of $LiCoO_2$ prepared at 400°C and a chemically-delithiated product $Li_{0.5}CoO_2$ using space group symmetries R$\overline{3}$m and Fd3m are reported. Refinements in both R$\overline{3}$m (layered-type structure) and Fd3m (spinel-type structure) give comparable fits to the data. This structural anomaly is discussed in terms of the refinements and electrochemical data obtained when lithium is extracted from $LiCoO_2$ in non-aqueous cells at room temperature. A spinel-related model for Li_xCoO_2 ($0.5 \leq x \leq 1$) is preferred.

MATERIALS INDEX: Lithium, cobalt, oxide, spinel, layered structure

Introduction

$LiCoO_2$, when synthesised at 900°C (in this paper referred to as HT-$LiCoO_2$) has a layered structure with R$\overline{3}$m symmetry [1]. It is an attractive electrode for rechargeable lithium cells because lithium can be extracted from, and reintroduced into the structure with a concomitant change in the oxidation state of the cobalt ions [2]. Although $LiCoO_2$ has a theoretical capacity of 273 mAh/g, in practice only about 50% of the capacity can be used because the structure is destabilized by the extraction of lithium at high cell voltages [3,4]. During lithium extraction from HT-Li_xCoO_2 the c/a ratio changes from 4.99 at x=1 to 5.12 at x=0.5 [5]. Recently it was demonstrated with neutron diffraction data that when $LiCoO_2$ is synthesised at 400°C a compound (referred to as LT-$LiCoO_2$) is formed which has a structure very similar to HT-$LiCoO_2$ but in which approximately 6% of the cobalt ions are located in the lithium layer [6,7]. However, unlike HT-$LiCoO_2$, LT-$LiCoO_2$ has an essentially ideal cubic-close-packed oxygen array (c/a=4.90) which surprisingly is maintained during lithium extraction. A profile refinement of the neutron diffraction pattern of LT-$Li_{0.49}CoO_2$ has revealed that approximately 80% of the remaining lithium ions are located in tetrahedral sites which gives the structure a spinel-like character [6].

The lithium spinels $Li[M_2]O_4$ (M=V,Ti,Mn) with prototypic symmetry Fd3m offer three-dimensional pathways for Li^+-ion diffusion through the face-shared 8a tetrahedra and interstitial 16c octahedra of the spinel structure. Evidence of $Li[Ni_2]O_4$, prepared by careful heating of $Li_{0.5}NiO_2$ (obtained by lithium extraction from the layered $LiNiO_2$ structure) to 250-300°C has been reported [8,9]. However, $Li[Ni_2]O_4$ is unstable and degrades when heated above 300°C. A cobalt analogue $Li[Co_2]O_4$ is not yet known although the $[Co_2]O_4$ spinel framework exists in several structures, for example, in Co_3O_4 and $Zn[Co_2]O_4$. Therefore, it seems feasible that it should be possible to synthesise $Li[Co_2]O_4$ under certain carefully-controlled conditions.

The structural refinements of LT-$Li_{0.49}CoO_2$ and LT-$LiCoO_2$ with neutron-diffraction data give strong evidence that the structures have a layered character. However, the X-ray diffraction patterns of these compounds are strikingly similar to those of lithium spinels $Li[M_2]O_4$ and their lithiated products $Li_2[M_2]O_4$ (M=Ti, V), respectively and, by analogy, to those of $Li[Co_2]O_4$ and $Li_2[Co_2]O_4$ [6]. This structural anomaly has been investigated in this paper and is discussed in terms of the electrochemical properties of these compounds. Attempts to synthesise a $Li[Co_2]O_4$ spinel by reaction of lithium carbonate with cobalt carbonate at moderate temperatures is described.

Experimental

LT-$LiCoO_2$ was prepared by the solid-state reaction of $CoCO_3$ and Li_2CO_3 and LT-$Li_{0.5}CoO_2$ by delithiation of LT-$LiCoO_2$ in acid as described elsewhere [6]. Lithium-cobalt-oxide samples containing a Li:Co ratio of 1:2 were also prepared by heating the following precursor materials in air at a rate of 1°C/min to 400°C, 1) an aqueous solution of $LiNO_3$ and $Co(NO_3)_2$ and 2) an intimate mixture of Li_2CO_3 and $CoCO_3$.

Powder X-ray diffraction data were recorded on an automated Rigaku X-ray powder diffractometer with CuKα radiation monochromated by a graphite single crystal. Simulated X-ray diffraction patterns were generated with an adapted version of the Lazy-Pulverix program [10]. Structures were refined with the Rietveld powder profile refinement program of D B Wiles, R A Young and A Sakthivel adapted to IBM-AT compatible microcomputers by J Schneider [11,12]. In the refinements of LT-$LiCoO_2$ the site occupancies of lithium and cobalt in crystallographically-equivalent octahedral sites were allowed to vary simultaneously, the sum of their occupancies being constrained to unity. In the refinement of LT-$Li_{0.5}CoO_2$ the occupancies of the Li^+ ions in the layered structure (R$\overline{3}$m) were taken directly from the previously reported neutron diffraction data [6]; in the refinement of the spinel model (Fd3m), the Li^+ ions were all assumed to be located in the 8a tetrahedral sites. Isotropic temperature factors obtained from the neutron-diffraction refinements of LT-$LiCoO_2$ and LT-$Li_{0.49}CoO_2$ were assigned to all atoms and were held constant during the refinement of the X-ray data. Figures of the structures were drawn with the aid of the ATOMS program [13].

Cathodes were prepared by intimately mixing 20mg of lithium-cobalt-oxide (80% by mass) with teflon-acetylene black (TAB). The electrolyte was a 1M solution of $LiClO_4$ in either propylene carbonate (PC) or a 1:1 PC/dimethoxyethane (DME) mixture. Three-electrode cells with pure lithium as the anode and reference electrode were used for the cyclic voltammetry experiments. Data were recorded on a Princeton Applied Research (PAR) Model 173 potentiostat linked to a PAR Model 175 Universal programmer. Two-electrode cells were employed for the cycling tests.

Lithium was inserted chemically into LT-$Li_{0.5}CoO_2$ by reaction with 1M n-butyllithium in hexane at 50°C for 24 hours. Samples were subsequently washed in hexane. The lithium

content in the chemically-prepared samples was determined by atomic-absorption methods.

Results and Discussion

Structural Considerations

The powder X-ray diffraction patterns of LT-LiCoO$_2$, LT-Li$_{0.5}$CoO$_2$, LT-LiCoO$_2$ obtained by lithiation of LT-Li$_{0.5}$CoO$_2$ with n-butyllithium at 50°C and the calculated patterns of a (Li$_2$)$_{16c}$[Co$_2$]$_{16d}$O$_4$ lithiated spinel structure and ideal spinel {Li}$_{8a}$[Co$_2$]$_{16d}$O$_4$ are shown in Fig.1(a-e), respectively. It is evident from the strong similarity of the diffraction patterns in Fig.1(a-c) that lithium can be extracted from LT-LiCoO$_2$ to a composition LT-Li$_{0.5}$CoO$_2$ and reintroduced into the structure without any apparent modification or damage to the CoO$_2$ subarray, at least for the initial lithium extraction/insertion cycle. Fig.1 shows the strikingly strong similarity of the X-ray diffraction pattern of LT-LiCoO$_2$ (Fig.1a) with the calculated X-ray pattern of a lithiated spinel Li$_2$[Co$_2$]O$_4$ (Fig.1d) and of LT-Li$_{0.5}$CoO$_2$ (Fig.1b) with the calculated X-ray pattern of an ideal spinel Li[Co$_2$]O$_4$ (Fig.1e).

Two Theta
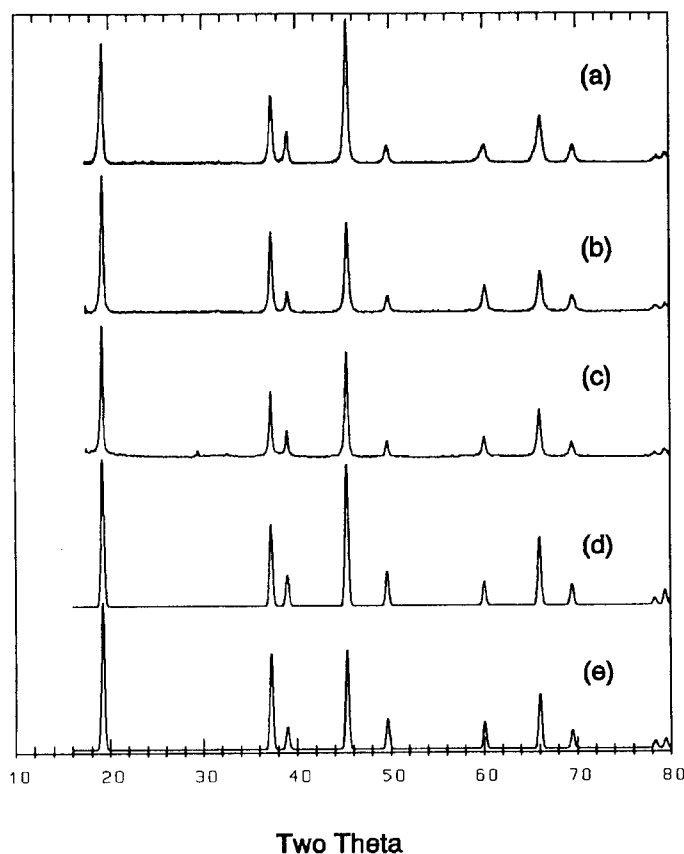
FIG. 1

Powder X-ray diffraction patterns of (a) LT-LiCoO$_2$ (b) LT-Li$_{0.5}$CoO$_2$, acid leached (c) LT-LiCoO$_2$ obtained by lithiation of LT-Li$_{0.5}$CoO$_2$ with n-butyllithium (d) spinel (Li$_2$)$_{16c}$[Co$_2$]$_{16d}$O$_4$ (calculated pattern) (e) spinel {Li}$_{8a}$[Co$_2$]$_{16d}$O$_4$ (calculated pattern).

Refinement of LT-LiCoO$_2$ and LT-Li$_{0.5}$CoO$_2$ with the X-ray data using a layered model with trigonal symmetry (R$\bar{3}$m) yielded structural parameters that were in excellent agreement with those obtained from time-of-flight neutron data [6] as shown in Tables 1a and 1b. The observed and calculated X-ray diffraction profiles are given in Figs.2a and 2b, respectively. With this model, the X-ray data of LT-LiCoO$_2$ confirm that a small fraction (5%) of the cobalt ions are located in the octahedral sites (3a) of the lithium layer. In LT-Li$_{0.5}$CoO$_2$ it was apparent that during the acid-leaching process the cobalt ions had been removed from the lithium-rich layer to yield a structure in which all the cobalt ions completely fill the 3b octahedral sites. The refinement showed that there was a small amount of scattering from the tetrahedral (6c) sites of the original lithium-rich layer and from the octahedral (3a) sites; this was attributed to the residual lithium, consistent with the analysis of the neutron data. The presence of lithium in the 6c sites is surprising because of the short intersite distance, 1.73 Å, between the lithium in 6c tetrahedra and cobalt in face-sharing 3a octahedra. If, however, some of the cobalt ions are displaced to the lithium layer, such that some 6c tetrahedra are surrounded by vacant 3a and 3b octahedra, it would be possible to stabilize some lithium in the tetrahedral sites of the lithium layer. Such a situation has been reported on delithiating layered LiVO$_2$ to a composition Li$_{0.22}$VO$_2$ [14]; in this instance there is clear evidence of vanadium-ion migration from the 3b octahedra to the 3a octahedra via face-shared 6c tetrahedra. However, this process which generates a defect rocksalt phase with a 2:1 ratio of vanadium in alternate layers changes the relative intensities of the peaks in the X-ray diffraction pattern significantly.

Refinement of LT-LiCoO$_2$ using the spinel model (Fd3m) resulted in a fit to the data that was comparable to that obtained from the layered model as shown in Table 2a. The observed and calculated X-ray diffraction profiles are given in Figs.3a and 3b, respectively.

It is therefore evident that it is difficult to distinguish unequivocally between the two models with the available X-ray data; this structural anomaly has recently been addressed [15,16]. From a structural viewpoint, if LT-LiCoO$_2$ adopted an ideal layered structure (R$\bar{3}$m), delithiation would result in a change in the c/a ratio. In practice, the c/a ratio remains constant at the ideal value for a cubic-close-packed lattice (4.90) which favours the spinel model. However, unlike the spinels Li$_x$[V$_2$]O$_4$ and Li$_x$[Ti$_2$]O$_4$ that expand and contract isotropically over the range 1≤x≤2 [17,18], there is no significant expansion nor contraction in LT-Li$_x$CoO$_2$ over this compositional range, the lattice parameter of the cubic unit cell (a = 7.994(1)Å) remaining surprisingly constant.

Idealized structures of the layered and spinel LT-Li$_x$CoO$_2$ (x=0.5 and x=1.0) compounds are shown in Figs.4(a-d). In the [Co$_2$]O$_4$ framework of ideal Li$_x$[Co$_2$]O$_4$ spinel-related structures (1≤x≤2) the cobalt ions are distributed in a 3:1 ratio between alternate layers. In view of the energetically unfavourable arrangement of the cations in the layered (R$\bar{3}$m) model for Li$_{0.5}$CoO$_2$ and the necessity to displace a significant proportion of cobalt ions in a transition from layered LT-LiCoO$_2$ to spinel LT-Li$_{0.5}$CoO$_2$, it is concluded that the spinel model is preferred. However, the electrochemical data at hand suggest that LT-LiCoO$_2$ and LT-Li$_{0.5}$CoO$_2$ prepared for our investigations have structures in which the distribution of the cobalt ions in alternate layers deviates from the ideal spinel arrangement.

Although a single-phase LT-LiCoO$_2$ compound could be synthesised at 400°C, attempts to prepare a single-phase LT-Li$_{0.5}$CoO$_2$ compound from Li$_2$CO$_3$ and CoCO$_3$ at moderate temperatures in air have been unsuccessful. This is not surprising because of the difficulty in synthesising cobalt oxides containing Co^{4+} at elevated temperatures. The X-ray pattern of a typical product synthesised at 400°C is shown in Fig.5a; the pattern is characteristic of a two-phase material consisting of Co$_3$O$_4$ with a lattice parameter a =8.081(4)Å and a compound that resembles LT-LiCoO$_2$. Heat-treatment at 900°C results
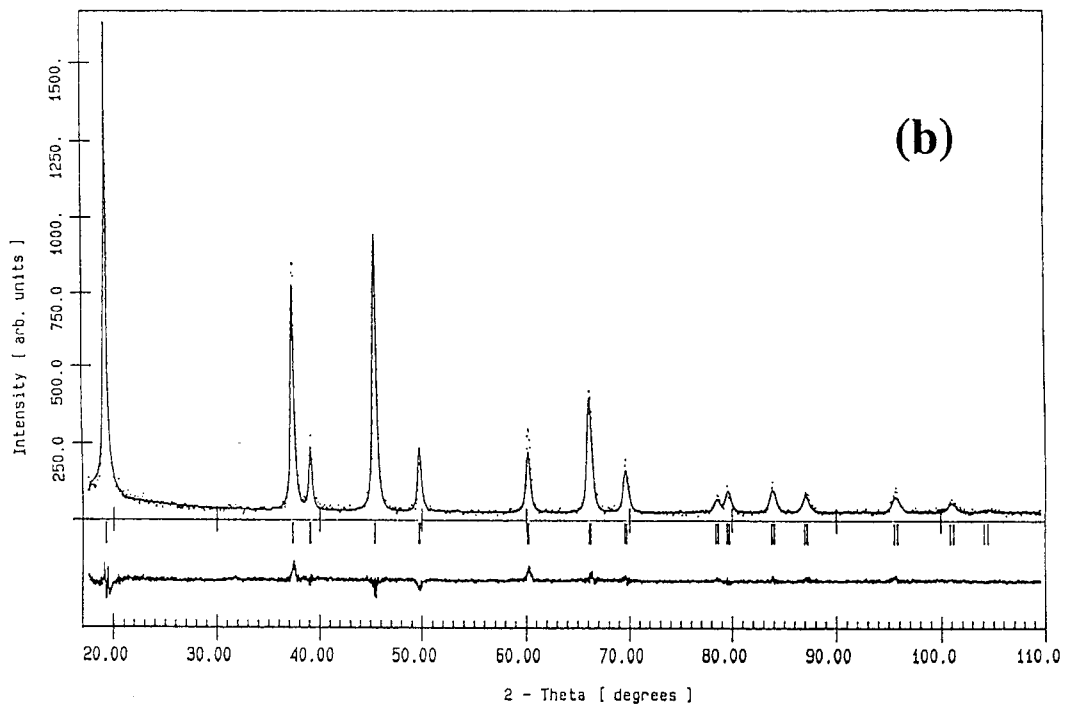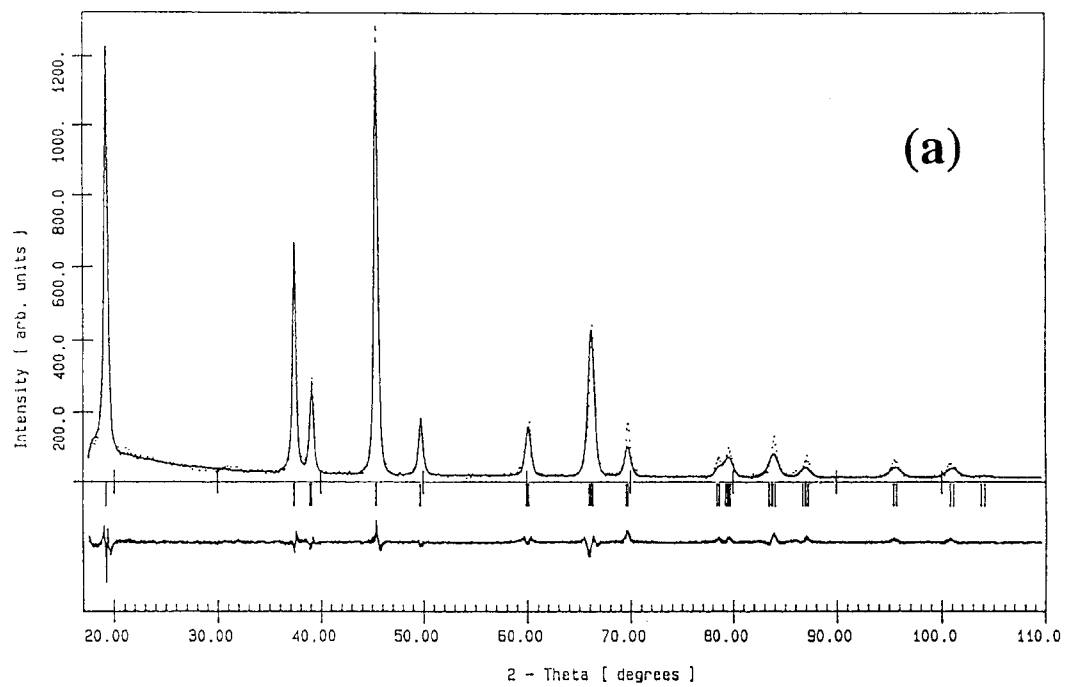
FIG. 2

The observed and calculated X-ray diffraction profiles of (a)LT-$LiCoO_2$ and (b) LT-$Li_{0.5}CoO_2$ refined in space-group R3m.
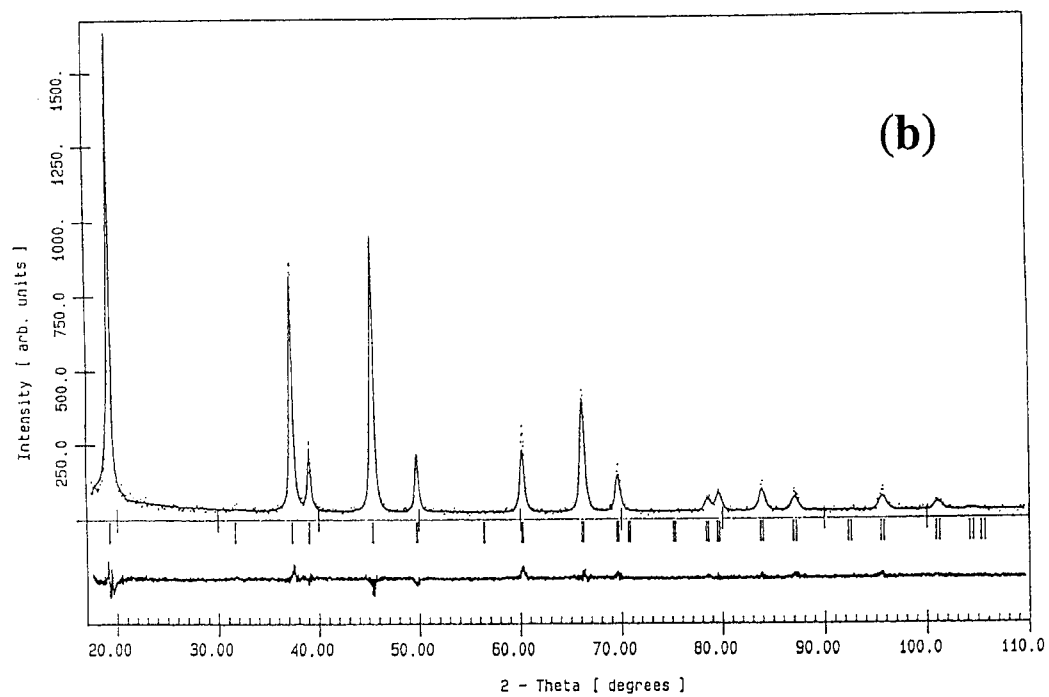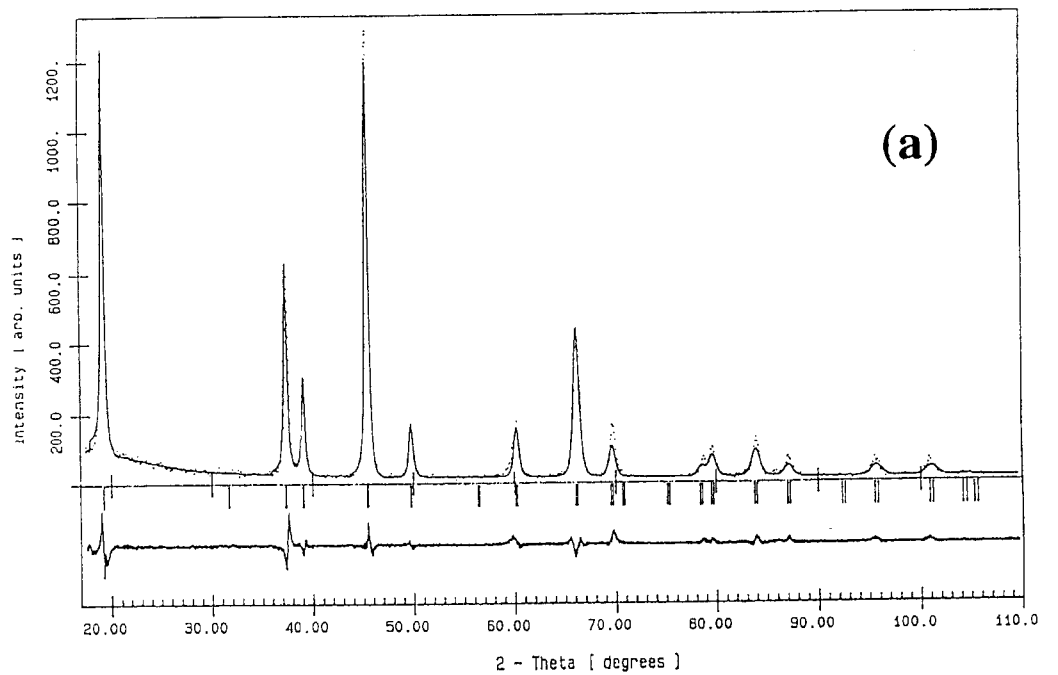
FIG. 3

The observed and calculated X-ray profiles of (a) LT-$Li_2Co_2O_4$ and (b) LT-$LiCo_2O_4$ refined in space-group Fd3m.

TABLE 1 (a)

Crystallographic parameters for the Rietveld refinement of LT-LiCoO$_2$

$a = 2.824(1)$Å $c = 13.888(1)$Å Space Group R$\overline{3}$m

| Atom	X Y Z	n (X-rays)	B-factor	n (neutrons)
Li(3a)	0 0 0	0.95(1)	1.6	0.94(1)
Li(3b)	0 0 0.5	0.05(1)	0.9	0.04(2)
Co(3a)	0 0 0	0.05(1)	1.6	0.06(1)
Co(3b)	0 0 0.5	0.95(1)	0.9	0.96(2)
O(6c)	0 0 0.2459	1.0	1.13	1.0

R-factors: X-rays $R_p = 13.60\%$ $R_{wp} = 17.97\%$ $R_{exp} = 18.03\%$ $R_{Bragg} = 10.74\%$
               Neutrons $R_p = 4.92\%$ $R_{wp} = 4.67\%$ $R_{exp} = 1.61\%$ $R_{Bragg} = 24.46\%$

TABLE 1 (b)

Crystallographic parameters for the Rietveld refinement of LT-Li$_{0.5}$CoO$_2$

$a = 2.825(1)$Å $c = 13.846(1)$Å Space Group R$\overline{3}$m

Atom	X Y Z	n (X-rays)	B-factor	n (neutrons)
Li(3a)	0 0 0	0.09	0.96	0.09(1)
Co(3a)	0 0 0	0.02(1)	0.96	0.01(1)
Co(3b)	0 0 0.5	1.07(1)	0.96	0.99(1)
Li(6c)	0 0 0.375	0.20	0.96	0.20(1)
O(6c)	0 0 0.2437(3)	1.0	1.63	1.0

R-factors : X-rays $R_p = 12.40\%$ $R_{wp} = 15.88\%$ $R_{exp} = 16.98\%$ $R_{Bragg} = 10.82\%$
               Neutrons $R_p = 3.49\%$ $R_{wp} = 3.21\%$ $R_{exp} = 1.65\%$ $R_{Bragg} = 24.70\%$

in a two-phase product of Co$_3$O$_4$ and HT-LiCoO$_2$ (Fig.5b) according to the reaction:

$$3\ Li_2CO_3 + 12\ CoCO_3 \xrightarrow[900°C]{^5/_2O_2} 2\ Co_3O_4 + 6\ HT\text{-}LiCoO_2 + 15\ CO_2$$
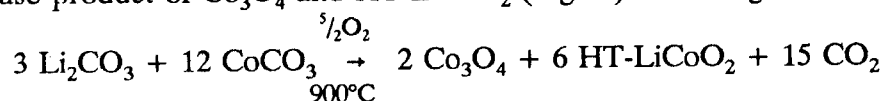
Electrochemical Considerations

Previous reports have shown that lithium is extracted electrochemically from LT-LiCoO$_2$ in a two-phase reaction at an open-circuit-voltage of 3.61V vs pure lithium [6]; this contrasts strongly with the extraction of lithium from HT-LiCoO$_2$, most of which occurs above 4V [2]. The two-phase region in Li/LT-Li$_x$CoO$_2$ cells is consistent with the coexistence of a lithiated spinel Li$_2$[Co$_2$]O$_4$ which is a rocksalt phase and a stoichiometric spinel phase Li[Co$_2$]O$_4$. A typical profile of an initial charge (lithium extraction) to 3.9V and discharge (lithium insertion) to 3.2V of a Li/LT-LiCoO$_2$ cell is shown in Fig.6a. The charge reaction

TABLE 2 (a)

Crystallographic parameters for the Rietveld refinement of $Li_2Co_2O_4$

$a = 7.994(1)$Å   Space Group Fd3m

Atom	X Y Z	n (X-rays)	B-factor
Li(16d)	0.5 0.5 0.5	0.06(1)	0.9
Li(16c)	0 0 0	0.95(1)	1.6
Co(16d)	0.5 0.5 0.5	0.94(1)	0.9
Co(16c)	0 0 0	0.05(1)	1.6
O(32e)	0.2538 0.2538 0.2538(3)	1.0	1.13

R-factors: X-rays $R_p = 15.29\%$ $R_{wp} = 19.86\%$ $R_{exp} = 18.76\%$ $R_{Bragg} = 9.55\%$

TABLE 2 (b)

Crystallographic parameters for the Rietveld refinement of $LiCo_2O_4$

$a = 7.992(1)$Å   Space Group Fd3m

Atom	X Y Z	n (X-rays)	B-factor
Li(8a)	0.125 0.125 0.125	1.0	0.96
Co(16d)	0.5 0.5 0.5	0.99(1)	0.96
Co(16c)	0 0 0	0.03(1)	0.96
O(32e)	0.2566 0.2566 0.2566(3)	1.0	1.63

R-factors: X-rays $R_p = 11.74\%$ $R_{wp} = 15.53\%$ $R_{exp} = 17.71\%$ $R_{Bragg} = 8.35\%$

corresponds to the removal of approximately 0.45 Li^+ ions from the LT-$LiCoO_2$ structure and the discharge reaction to the reinsertion of 0.24 Li^+. Fig.6b shows the first discharge and charge cycle of a Li/LT-$Li_{0.5}CoO_2$ (acid-leached) cell which is almost 100% efficient on the first cycle. However, Li/LT-$LiCoO_2$ and Li/LT-$Li_{0.5}CoO_2$ cells do not cycle well. Further effort is required to stabilize the LT-$LiCoO_2$ structure if it is to be used successfully in rechargeable lithium battery applications. A very recent announcement by Sony Energytec disclosing a Li-ion rechargeable cell that delivers 3.6V suggests that this is possible by doping LT-$LiCoO_2$ with nickel and manganese [19].

The cyclic voltammograms of Li/LT-Li_xCoO_2 cells are shown in Fig.7(a-e); a cyclic voltammogram of a $Li/Li_x[Mn_2]O_4$ cell is given in Fig.7f for comparison. In the $Li_x[Mn_2]O_4$ spinel system which has been characterised in detail [20-22], the anodic peaks correspond to removal of lithium from octahedral (16c) sites (peak 1) and to a two-stage extraction of lithium from the tetrahedral (8a) sites (peaks 2 and 3); these processes are reversible. Lithium extraction from the tetrahedral sites occurs at a voltage approximately 1V higher than the extraction of lithium from the octahedral sites; this phenomenon has also been observed in the $Li_x[V_2]O_4$ system [23]. Of interest is the small anodic peak at about 3.8V (peak 4) in Fig. 7f which has been attributed to lithium extraction from the octahedral 16d sites of the spinel structure [20].

By contrast, the anodic scan in the cyclic voltammogram of LT-Li_xCoO_2 (Fig.7a)

FIG. 4
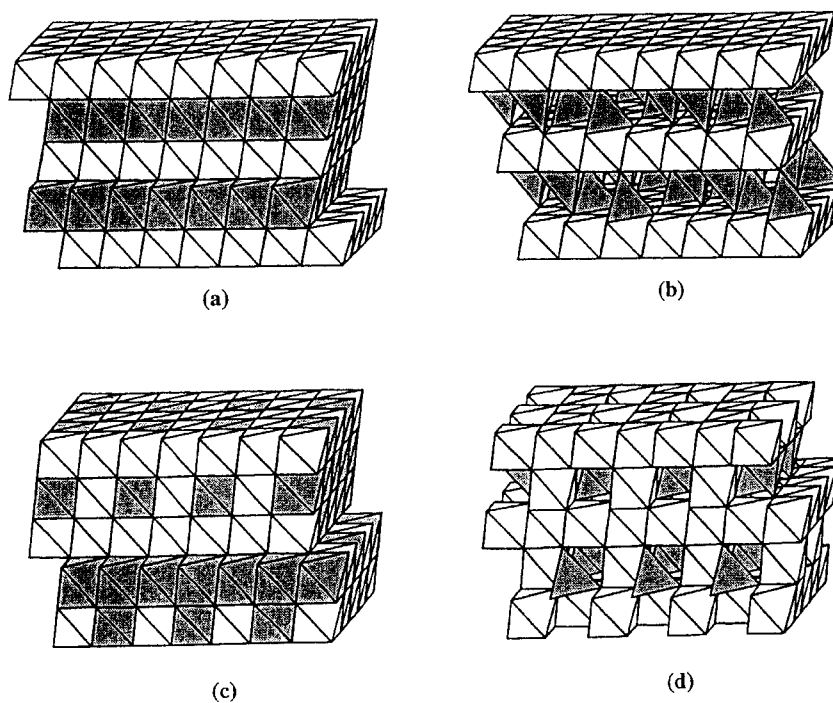
Idealized structures of (a) LiCoO$_2$ layered, (b) Li$_{0.5}$CoO$_2$ layered, (c) Li$_2$Co$_2$O$_4$ spinel and (d) LiCo$_2$O$_4$ spinel. Unshaded and shaded polyhedra contain Co and Li, respectively.
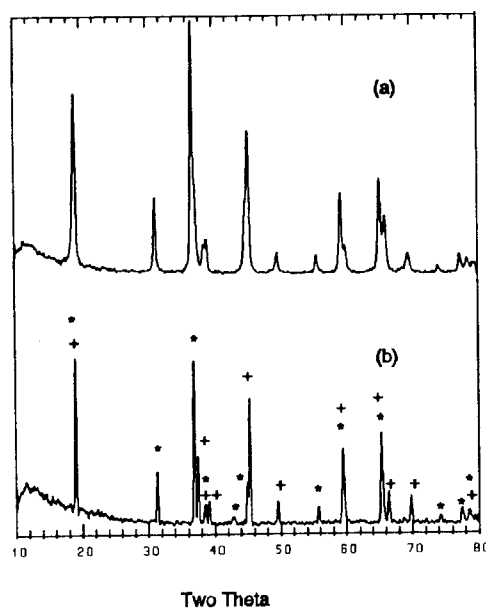

Two Theta

FIG. 5

Powder X-ray diffraction profiles of the reaction product of Li$_2$CO$_3$ and CoCO$_3$, Li:Co=1:2 at (a) 400°C and (b) 900°C, * = Co$_3$O$_4$, + = HT-LiCoO$_2$.
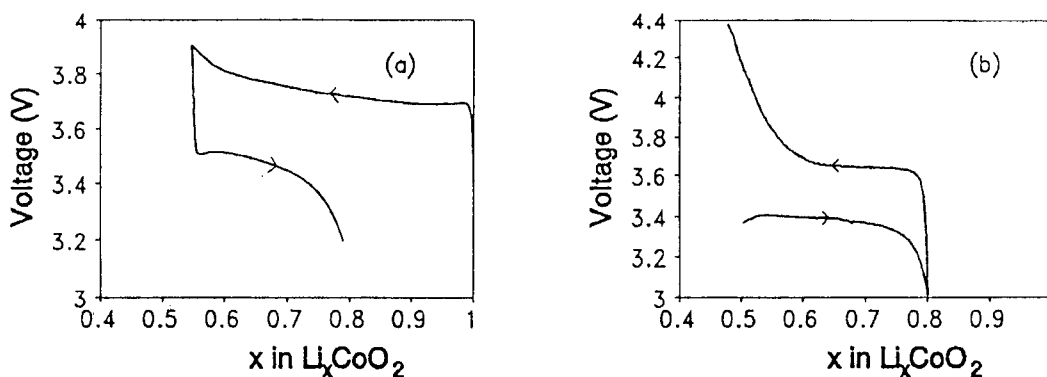
FIG. 6

(a) Initial charge and discharge curves of a Li/LT-LiCoO$_2$ cell (Charge current = 0.1 mA/cm^2, discharge current = 0.2 mA/cm^2) and (b) initial discharge and charge of a Li/LT-Li$_{0.5}$CoO$_2$ cell (Discharge and charge current = 0.02 mA/cm^2). Electrolyte for both cells = 1M LiClO$_4$ in PC/DME.

indicates that lithium is probably extracted from the octahedral sites in a two-step process between 3.6V and 4V; these peaks are not resolved in the corresponding reduction peak at 3.2V. Moreover, a reduction peak at 3.7V in Fig.7a (which previously has been attributed to the insertion of lithium ions into tetrahedral sites of the structure [6]) is separated from the peak associated with lithium insertion into octahedral sites by only 0.5V. These data therefore suggest, in the absence of a second phase, a non-idealized spinel-type structure. On cycling, the reduction peak at 3.2V shifts to a slightly lower voltage, indicative of a change in the site energy of the octahedral sites. A two-stage reduction process is clearly visible in the cyclic voltammogram of LT-Li$_{0.5}$CoO$_2$ (Fig.7e) on the second and third cycles. This is attributed to lithium insertion into two crystallographically non-equivalent octahedral sites. The instability of the spinel-like structure which is evident from a decrease in the peak intensities on cycling is consistent with the rapid drop in cell capacity that has been observed on cycling Li/LT-Li$_x$CoO$_2$ cells [6,7]. Fig.7(b-d) show the cyclic voltammograms of LT-LiCoO$_2$ for various upper voltage limits between 3.7 V and 4.0 V. These data indicate that capacity loss effects are more pronounced at the higher voltages and that optimum cycling of Li/LT-Li$_x$CoO$_2$ cells with a 1M LiClO$_4$ PC:DME electrolyte can be expected if the upper voltage limit is restricted to about 3.7V.

Finally, it is of interest to note that the absence of a second anodic peak in the cyclic voltammogram of Li$_{0.5}$CoO$_2$ (prepared by acid-leaching of lithium from LT-LiCoO$_2$ at room temperature) shows that no lithium is extracted from the tetrahedral sites of the structure below 4.6V (Fig. 7e). With this evidence it seems unlikely that spinel-related LT-Li$_x$CoO$_2$ (0≤x≤0.5) compounds would be stable in known organic electrolytes because of their highly-oxidising character.

Conclusions

The structural and electrochemical properties of LiCoO$_2$ synthesised at 400°C and a delithiated derivative Li$_{0.5}$CoO$_2$ have been discussed. Despite a structural anomaly that makes it difficult to distinguish between ideal layered Li$_x$CoO$_2$ (0.5≤x≤1) and spinel-related Li$_y$[Co$_2$]O$_4$ (1≤y≤2) structures, refinements of X-ray data and electrochemical information
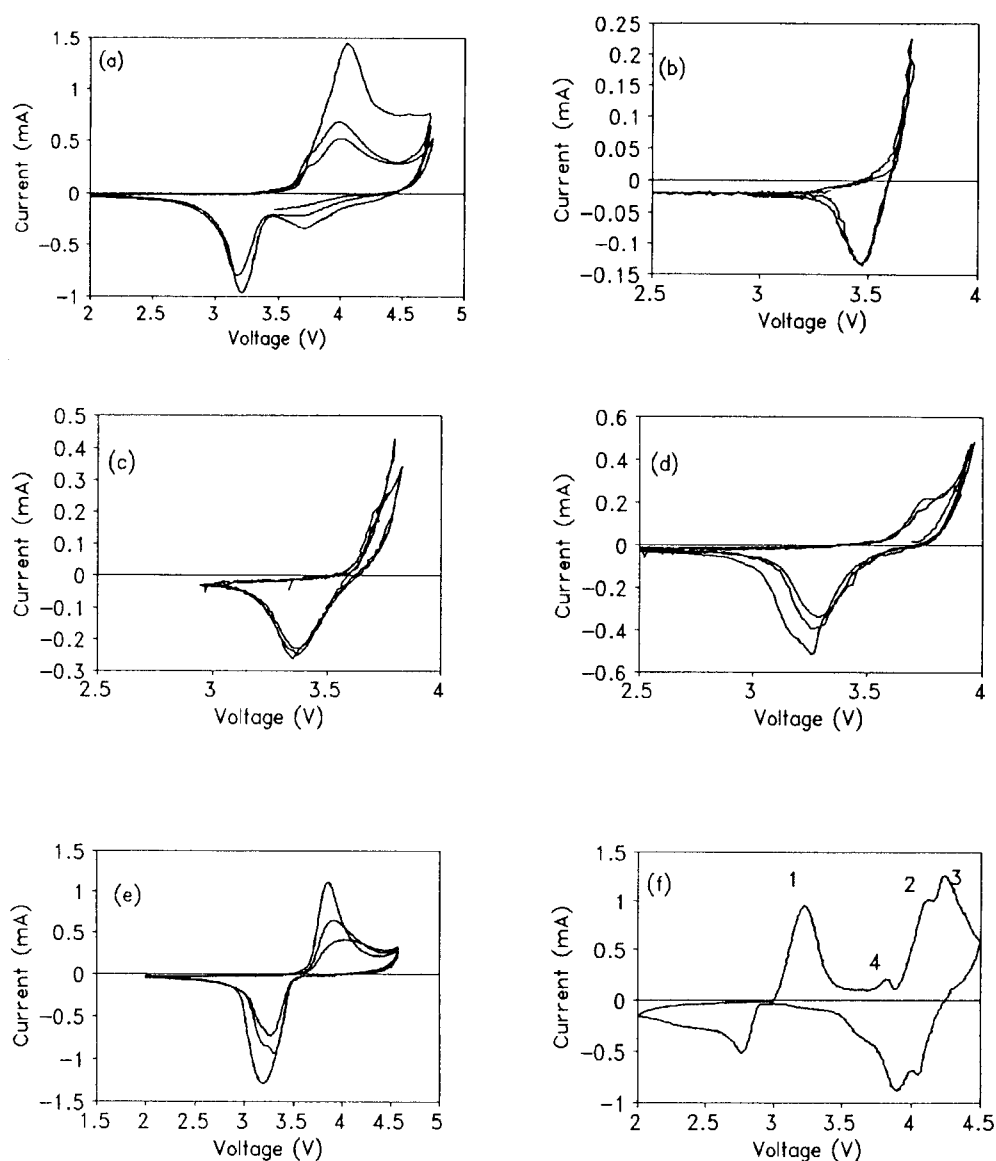
FIG. 7

Cyclic voltammograms of (a) LT-LiCoO$_2$ (b) LT-LiCoO$_2$, cycles 1 and 2 to an upper limit of 3.7V (c) LT-LiCoO$_2$, cycle 3 to 3.75V, cycles 4 and 5 to 3.8V (d) LT-LiCoO$_2$, cycles 6, 7 and 8 to 4.0V (e) LT-Li$_{0.5}$CoO$_2$ (acid-leached) and (f) Li$_x$Mn$_2$O$_4$. Electrolyte for (a-d) = 1M LiClO$_4$ in PC:DME. Electrolyte for (e and f) = 1M LiClO$_4$ in PC. Scan rate for (a-d) = 0.5 mV/s, (e and f) = 0.1 mV/s.

provide evidence of Li$_x$CoO$_2$ compounds that are spinel-like in character, in which the cobalt distribution deviates from the ideal spinel arrangement. In principle, under carefully-selected processing conditions it should be possible to synthesise ideal Li[Co$_2$]O$_4$ spinel and lithiated Li$_2$[Co$_2$]O$_4$ spinel structures.

Acknowledgements

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