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A REINVESTIGATION OF THE STRUCTURES OF LITHIUM-COBALT-OXIDES WITH NEUTRON-DIFFRACTION DATA

R J Gummow, D C Liles and M M Thackeray
Division of Materials Science and Technology, CSIR,
P O Box 395, Pretoria 0001, South Africa
and
W I F David
Rutherford Appleton Laboratory, Chilton
Didcot, Oxfordshire OX11 OQX, UK

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ABSTRACT

The structures of LT-$LiCoO_2$ (synthesised by reaction of Li_2CO_3 and $CoCO_3$ at 400°C) and its delithiated product LT-$Li_{0.4}CoO_2$ have been reinvestigated by neutron powder diffraction. Despite an unusually close similarity between diffraction profiles that makes it difficult to determine whether the structures are layered or spinel-like, the data confirm that the preferred structure of the LT-$LiCoO_2$ sample made for this study is one that has a cobalt distribution which is intermediate between an ideal layered and an ideal lithiated spinel structure. On the other hand, refinement of the data of LT-$Li_{0.4}CoO_2$ prepared by reacting LT-$LiCoO_2$ with acid shows, unequivocally, that a spinel-type structure is formed. These structures are discussed in relation to previously reported electrochemical data obtained from Li/LT-$LiCoO_2$ cells.

MATERIALS INDEX: lithium, cobalt, oxides, spinels

Introduction

$LiCoO_2$, when prepared at 800°C-900°C, (in this paper referred to as HT-$LiCoO_2$) has a layered rock salt structure with trigonal symmetry, $R\bar{3}m$ [1,2]. The layers of lithium and cobalt ions are sandwiched between sheets of close-packed oxygen ions. The oxygen-ion array in this structure is not ideally cubic-close-packed; the c/a ratio of 4.989 is significantly larger than that of an ideal ccp lattice ($c/a = 2\sqrt{6} = 4.899$). Delithiation of HT-$LiCoO_2$ to a composition $Li_{0.5}CoO_2$ increases the c/a ratio to 5.13 [3].

It was recently reported that when $LiCoO_2$ is prepared at 400°C (referred to as LT-$LiCoO_2$), a structure was generated that had an almost ideal cubic-close-packed oxygen array [4].

Various refinements of the lattice constants of the trigonal unit cell of LT-$LiCoO_2$ with X-ray and neutron diffraction data have yielded *c/a* ratios of:

1. 4.903(3) (X-ray data, refinement of individual peak positions (d-spacings) [4]),
2. 4.918(2) (X-ray data, profile refinement [5]), and
3. 4.9142(7) (time-of-flight neutron data, profile refinement) [4]

The refinement of the structure with time-of-flight neutron diffraction data is regarded to be the most accurate set of data obtained thus far; the calculated *c/a* ratio (4.9142(7)) is in good agreement with that obtained by profile refinement of X-ray data (4.918(2)). The refinement of the neutron data provided strong evidence that LT-$LiCoO_2$ had a layered-type structure, in which approximately 6% of the cobalt ions resided in the lithium layer.

Delithiation of LT-$LiCoO_2$ to a composition LT-$Li_{0.4}CoO_2$ resulted in little change to the X-ray and neutron diffraction patterns; however, all refinements of the lattice parameters of the trigonal unit cell showed that the oxygen array of the delithiated structure was essentially ideally cubic-close-packed. The *c/a* ratios were:

1. 4.899(1) (X-ray data, refinement of individual peak positions (d-spacings) [4]),
2. 4.901(2) (X-ray data, profile refinement [5]), and
3. 4.899(2) (time-of-flight neutron data, profile refinement) [4]

In these studies of LT-Li_xCoO_2 it was pointed out that LT-$LiCoO_2$ and its delithiated compounds had diffraction patterns that strongly resembled those of spinel compounds. Unfortunately, the structural refinements of LT-$LiCoO_2$ with X-ray data have demonstrated that it is difficult to determine unequivocally whether the structure is layered or spinel. However, the refinements of LT-$Li_{0.4}CoO_2$ have shown that the lithium ions are located predominantly in tetrahedral sites, which in the layered model necessitates an unacceptably short lithium to cobalt distance (1.73Å) in the structure. A spinel model for the delithiated compounds is therefore preferred [5].

The structural anomaly of LT-$LiCoO_2$ and its significantly different electrochemical properties compared to HT-$LiCoO_2$ have been discussed in several recent papers [4-8]. Dahn *et al*, in particular, have shown that the calculated X-ray and neutron diffraction patterns of **ideal** layered and lithiated spinel LT-$LiCoO_2$ structures are equivalent [7]. In order to explain the marked difference in electrochemical properties between LT-$LiCoO_2$ and HT-$LiCoO_2$, these authors therefore believe that LT-$LiCoO_2$ adopts the ideal lithiated spinel structure.

Because of the current debate about the structures of LT-Li_xCoO_2 compounds which are technologically significant for lithium batteries [2,9-11], neutron-diffraction data obtained previously have been reinvestigated. This paper compares the structurally-refined layered models of LT-$LiCoO_2$ and LT-$Li_{0.4}CoO_2$ with spinel models.

Experimental

The structures of LT-$LiCoO_2$ and LT-$Li_{0.4}CoO_2$ were refined using space group symmetries $R\bar{3}m$ (layered models) and Fd3m (spinel models) with time-of-flight neutron-diffraction data collected previously on the Polaris diffractometer at the Rutherford Appleton Laboratory, UK [4]. The LT-$LiCoO_2$ sample was prepared by reaction of $CoCO_3$ and Li_2CO_3 at 400°C, and LT-$Li_{0.4}CoO_2$ by the acid-treatment of LT-$LiCoO_2$ at room temperature, as previously described [4].

Structures were refined with a profile-refinement program that had been modified to describe the peak shape by a double-decay exponential, convoluted with a Voigt function [12,13]. The neutron scattering amplitudes used in the structure refinements were b(Li) = -0.2030×10^{-12}cm, b(Co)=0.2530×10^{-12}cm and b(O)=0.5805×10^{-12}cm [14].

Results and Discussion

LT-$LiCoO_2$

The superimposed observed and calculated neutron diffraction profiles of LT-$LiCoO_2$, when refined with space group symmetries $R\bar{3}m$ and Fd3m, are shown in Figs.1(a) and 1(b), respectively. The crystallographic parameters obtained from these refinements are provided in Tables 1(a) and 1(b).

A visual inspection of Figs.1(a) and 1(b) indicates that both the layered and spinel models give excellent fits to the data. The crystallographic parameters obtained from the re-refinement of the layered model (Table 1(a)) confirm the data that have been reported previously [4]. These data provide evidence of a LT-$LiCoO_2$ structure that is not ideally layered, and in which 6% of the cobalt ions reside in the octahedral (3a) sites of the lithium layer. The cation distribution in the structure was determined to be $(Li_{.94}Co_{.06})_{3a}(Li_{.04}Co_{0.96})_{3b}O_2$; the overall composition $Li_{0.98}Co_{1.02}O_2$ is in excellent agreement with the expected stoichiometry. There was no evidence of any significant scattering from the tetrahedral (6c) sites, which is to be expected for a rock salt-type structure. Of significance in this refinement is the *c/a* ratio of 4.9142(7) which indicates that the oxygen-ion array is not ideally cubic-close-packed, *c/a* (ideal cubic) = $2\sqrt{6}$ = 4.8990. The deviation from ideal cubic-close-packing, although small, is statistically highly significant, *c/a*(calc) = 1.00310(14) *c/a*(obs).

The structural refinement of the lithiated spinel model of LT-$LiCoO_2$ provided a fit which was marginally inferior to that obtained with the layered model. This is to be expected because the unit cell was constrained to adopt cubic symmetry; the refined *a* parameter was 8.002(1)Å. Furthermore, although the refined composition of the rock salt phase $Li_{1.98}Co_{2.02}O_4$ or in spinel notation, $(Li_{.98}Co_{.02})_2[Co_{.99}Li_{.01}]_2O_4$ is also in good agreement with the chemically-determined composition, this refinement indicated a small amount of positive scattering from the tetrahedral 8a sites; the possibility of an additional .06 cobalt ions on these sites is discounted, firstly, because the simultaneous occupation of face-shared tetrahedral and octahedral sites in a rock salt phase is energetically unfavourable, and secondly, because it necessitates a significant deviation from the expected stoichiometry of the compound.

The superior fit of the layered model as reflected by the slightly lower R-factors (R_p=4.91%, R_{wp}=4.66%) and Chi-squared value (χ^2 = 8.35) compared to those obtained with the spinel model (R_p=5.44%, R_{wp}=5.48% and χ^2=11.5) therefore endorses earlier reports that propose that LT-$LiCoO_2$ has a rock salt structure with a cobalt distribution which is intermediate between the ideal layered arrangement as in HT-$LiCoO_2$ and the ideal spinel arrangement

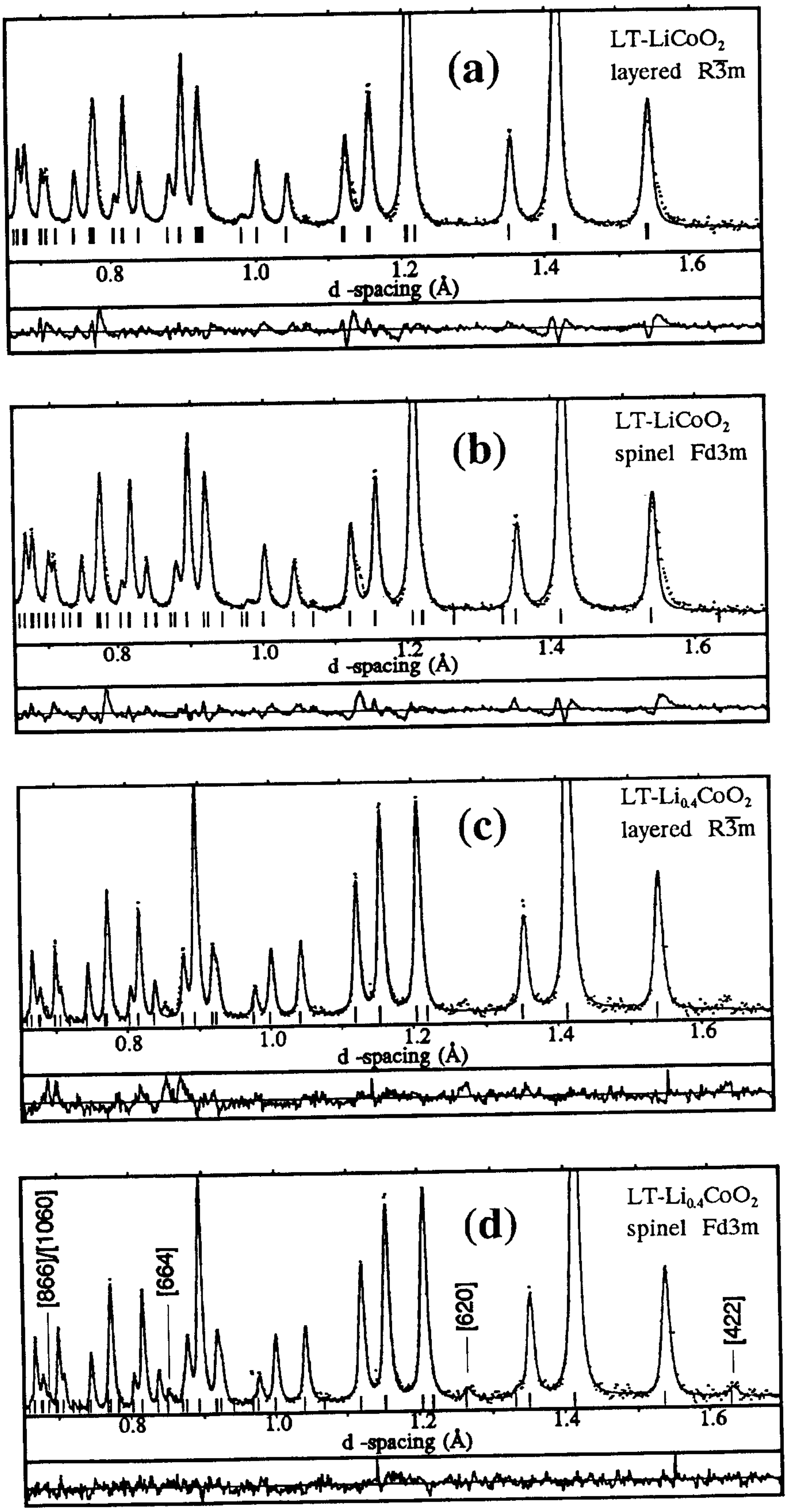

Figure 1. Superimposed observed (••••) and calculated (——) powder t.o.f. neutron diffraction profiles of LT-LiCoO$_2$: layered, R$\bar{3}$m (**a**) and spinel, Fd3m (**b**); and LT-Li$_{0.4}$CoO$_2$: layered, R$\bar{3}$m (**c**) and spinel, Fd3m (**d**).

TABLE 1(a)
Crystallographic Parameters of LT-$LiCoO_2$ ($R\bar{3}m$)
$a=2.8265(1)$Å, $c=13.890(1)$Å, $c/a=4.9142(7)$

Atom	Site	Position			Occupancy	B_{11}	B_{22}	B_{33}	B_{12}
		x	y	z					
Li(1)	3a	0	0	0	0.94(1)	1.6(1)			
Li(2)	3b	0	0	0.5	0.04(2)	0.9(1)			
Co(1)	3a	0	0	0	0.06(1)	1.6(1)			
Co(2)	3b	0	0	0.5	0.96(2)	0.9(1)			
Co(3)	6c	0	0	0.375	0.01(1)	0.9(1)			
Co(4)	6c	0	0	0.125	0.00(1)	0.9(1)			
O	6c	0	0	0.2402(1)	1.00	1.10(1)	1.10(1)	1.21(5)	0.55(1)

$R_p=4.91\%$, $R_{wp}=4.66\%$, $R_E=1.61\%$.
$\chi^2=8.35$ for 1559 observations and 25 variables.

TABLE 1(b)
Crystallographic parameters of LT-$LiCoO_2$ ($Fd3m$)
$c=8.002(1)$Å

Atom	Site	Position			Occupancy	B_{11}	B_{22}	B_{33}
		x	y	z				
Li(1)	16c	0	0	0	0.98(3)	1.7(1)		
Li(2)	16d	0.5	0.5	0.5	0.01(2)	0.8(1)		
Co(1)	16d	0.5	0.5	0.5	0.99(2)	0.8(1)		
Co(2)	16c	0	0	0	0.02(3)	1.7(1)		
Co(3)	8a	0.125	0.125	0.125	0.06(3)	1.7(1)		
O	32e	0.2588(1)	0.2588	0.2588	1.00	1.15(1)	1.15(1)	1.15(1)

$R_p=5.44\%$, $R_{wp}=5.48\%$, $R_E=1.62\%$.
$\chi^2=11.5$ for 1559 observations and 19 variables.

in which the cobalt ions occupy alternate layers in a 3:1 ratio. Furthermore, by analogy with the lithiated spinels $Li_2[V_2]O_4$ and $Li_2[Ti_2]O_4$ which have cubic symmetry, the *c*/*a* ratio of 4.9142(7) indicates that LT-$LiCoO_2$ probably does not have the ideal $[Co_2]O_4$ spinel framework. Because the cation distribution in LT-$LiCoO_2$ is intermediate between layered and spinel-type structures and because of the strong resemblance of the X-ray and neutron diffraction patterns to that of a lithiated spinel structure ($Li_2[Co_2]O_4$), LT-$LiCoO_2$ is therefore referred to in this paper as a *quasi-spinel* phase.

LT-$Li_{0.4}CoO_2$

The observed and calculated neutron-diffraction patterns of LT-$Li_{0.4}CoO_2$, when refined with space group symmetries $R\bar{3}m$ and Fd3m are shown in Figs. 1(c) and (d), respectively. Crystallographic parameters of the corresponding layered and spinel structures are provided in Tables (2a) and (2b). In the layered model (Table (2a)), the cobalt ions were found to be located in essentially one layer as in the parent compound; the lithium ions were found to be distributed over both the tetrahedral and octahedral sites of the original lithium layer, but predominantly in the tetrahedral sites; these data are consistent with earlier refinements of this structure [4,5]. The composition of the delithiated compound determined from this refinement was $Li_{.49}CoO_2$ with the cation distribution $\{Li_{.40}\}_{6c}(Li_{.09}Co_{.01})_{3a}[Co_{0.99}]_{3b}O_2$. In the spinel model (Table (2b)) the cobalt ions were located in the octahedral sites (16d); the lithium ions predominantly occupied the tetrahedral sites (8a), with a minor concentration occupying the (16c) and (16d) octahedral sites. This refinement yielded the composition $Li_{0.47}Co_{0.97}O_2$, or in spinel notation $\{Li_{.83}\}_{8a}(Li_{.06})_{16c}[Co_{1.94}Li_{.06}]_{16d}O_4$. An important observation is that, unlike LT-$LiCoO_2$, the neutron-diffraction profile of LT-$Li_{0.4}CoO_2$ contains several weak, but clearly defined, peaks that are accounted for only by the spinel model, for example the [4 2 2], [6 2 0], [6 6 4] and overlapping [8 6 6] and [10 6 0] peaks as shown in Fig. 1(d). Although both models give good fits to the data, the lower R and Chi-squared values for the spinel model (R_p=3.14, R_{wp}=2.45, χ^2=2.21) compared to the layered model (R_p=3.49, R_{wp}=3.21, χ^2=3.78) are significant; they confirm, unequivocally, the preference for the spinel model.

It must be stressed that the LT-$Li_{0.4}CoO_2$ sample used in this investigation was prepared at room temperature by acid-treatment of LT-$LiCoO_2$, not by electrochemical methods. Because lithium extraction occurs by distinctly different processes in these two methods, it is highly probable that the chemically- and electrochemically delithiated products will have different cation distributions within their structures. For example, electrochemical delithiation takes place according to the reaction:

$$LiCoO_2 \longrightarrow Li_{1-x}CoO_2 + xLi$$

By contrast, chemical delithiation to produce the ideal spinel composition occurs by the disproportionation reaction:

$$6LiCoO_2 \longrightarrow 2Li[Co_2]O_4 + 2CoO + 2Li_2O$$

In the latter process both CoO and Li_2O dissolve in the acidic environment; this reaction is believed to occur via a mechanism similar to that which occurs in the formation of λ-MnO_2 from $Li[Mn_2]O_4$ [15,16]. The transformation of the *quasi-spinel* structure to the ideal-spinel phase in acid, which necessitates the diffusion of both cobalt and lithium ions through the oxygen-ion array is rapid; the electrochemical transformation of the *quasi-spinel* phase to the ideal-spinel phase at room temperature during which only lithium ions are removed from the structure is not expected to occur as easily. It is therefore necessary that further work is carried out to determine the structures of electrochemically-delithiated samples of LT-Li_xCoO_2 ($0<x<1$).

TABLE 2(a)
Crystallographic Parameters of LT-$Li_{0.4}CoO_2$ ($R\bar{3}m$)
a=2.8253(1)Å, c=13.840(1)Å, c/a=4.899(1)

Atom	Site	Position x	y	z	Occupancy	B_{11}	B_{22}	B_{33}	B_{12}
Li(1)	3a	0	0	0	0.09(1)	0.96			
Li(2)	6c	0	0	0	0.20(1)	0.96			
Co(1)	3a	0	0	0	0.01(1)	0.96			
Co(2)	3b	0	0	0.5	0.99(1)	0.96(5)			
O	6c	0	0	0.2377(1)	1.00	1.96(4)	1.96(4)	0.96(3)	0.98(2)

R_p=3.49%, R_{wp}=3.21%, R_E=1.65%.
χ^2=3.78 for 1559 observations and 22 variables.

TABLE 2(b)
Crystallographic Parameters of LT-$LiCo_{0.4}O_2$ ($Fd3m$)
a=7.991(1)Å

Atom	Site	Position x	y	z	Occupancy	B_{11}	B_{22}	B_{33}
Li(1)	8a	0.125	0.125	0.125	0.83(3)	1.7(1)		
Li(2)	16c	0	0	0	0.03(1)	1.7(1)		
Li(3)	16d	0.5	0.5	0.5	0.03(1)	0.9(1)		
Co	16d	0.5	0.5	0.5	0.97(1)	0.9(1)		
O	32e	0.2629(1)	0.2629	0.2629	1.00	1.35(2)	1.35(2)	1.35(2)

R_p=3.14%, R_{wp}=2.45%, R_E=1.65%.
χ^2=2.21 for 1559 observations and 22 variables.

Electrochemical Considerations

Electrochemical extraction of lithium from LT-$LiCoO_2$ takes place on a constant voltage plateau at 3.6V (on open-circuit) against pure lithium [4]. This behaviour contrasts markedly with that of a Li/HT-$LiCoO_2$ cell in which the open-circuit voltage varies between 3.2V and 4.5V over the compositional range $0.1<x<1.0$ [10]. The two-phase behaviour of the LT-$LiCoO_2$ electrode is consistent with a phase transition between a rock salt structure in which the cations occupy only octahedral sites and a spinel-type structure in which the cations occupy both octahedral and tetrahedral sites. Unfortunately, Li/LT-Li_xCoO_2 cells lose capacity on cycling; this poor performance is attributed to the structural instability of the *quasi-spinel* LT-$LiCoO_2$ structure on repeated extraction and re-insertion of lithium. It is believed that if the ideal lithiated spinel arrangement $Li_2[Co_2]O_4$ could be synthesised, then improved cycling from Li/LT-Li_xCoO_2 cells can possibly be expected, at least over the compositional range $0.5<x<1.0$ over which the $[Co_2]O_4$ spinel framework is expected to be stable.

Work is in progress to evaluate the electrochemical performance of $Li_x[Co_2]O_4$ spinel compounds prepared by acid-treatment of LT-$LiCoO_2$ and to compare their cycling ability against that of *quasi-spinel* LT-$LiCoO_2$ electrodes.

Conclusions

This study has confirmed earlier reports that LT-$LiCoO_2$ synthesised by reaction of Li_2CO_3 and $CoCO_3$ at 400°C results in a compound that adopts a structure which is intermediate between the ideal layered and spinel structure types. Acid-leaching of LT-$LiCoO_2$ results in compounds that are predominantly spinel in character.

State-of-the-art LT-$LiCoO_2$ compounds that have *quasi-spinel* character show limited use as electrodes for rechargeable lithium cells; they lose capacity steadily on cycling. By modifying the processing techniques, it should be possible to synthesize LT-$LiCoO_2$ with the ideal lithiated spinel arrangement, $Li_2[Co_2]O_4$. This challenge is currently being taken up in the hope of improving the performance of rechargeable Li/LT-$LiCoO_2$ cells.

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