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Structural Stability of $LiCoO_2$ at 400°C[1]

Y. Shao-Horn,*[,2] S. A. Hackney,* A. J. Kahaian,† and M. M. Thackeray†

**Department of Materials Science and Engineering, Michigan Technological University, Houghton, Michigan 49931; and †Electrochemical Technology Program, Chemical Technology Division, Argonne National Laboratory, Argonne, Illinois 60439*

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The relative stability of the lithiated-spinel structure, $Li_2[Co_2]O_4$, at 400°C to the layered $LiCoO_2$ structure has been investigated. "Low-temperature" LT-$LiCoO_2$ samples were synthesized at 400°C by the solid-state reaction of Li_2CO_3 with $CoCO_3$ (or Co_3O_4) for various times between 10 min and 232 days. Least-squares refinements of X-ray powder diffraction patterns were used to determine the fractions of lithiated-spinel $Li_2[Co_2]O_4$ and layered $LiCoO_2$ in the samples. X-ray powder diffraction and transmission electron microscope data show that $Li_2[Co_2]O_4$ nucleates from an intermediate $Li_xCo_{1-x}[Co_2]O_4$ spinel product before transforming very slowly to layered $LiCoO_2$. The experimental data confirm the theoretical prediction that layered $LiCoO_2$ is thermodynamically more stable than the lithiated-spinel structure at 400°C and support the arguments that a non-ideal cation distribution in $Li_2[Co_2]O_4$, non-stoichiometry and kinetic factors restrict the transformation of the lithiated-spinel structure to layered $LiCoO_2$ at this temperature. © 2002 Elsevier Science (USA)

Key Words: **lithium–cobalt–oxide; spinel; structure, phase transition; X-ray diffraction; transmission electron microscopy; electron diffraction; lithium batteries.**

INTRODUCTION

A "low-temperature" form of $LiCoO_2$ (LT-$LiCoO_2$), synthesized at 400°C, has been studied extensively as a positive electrode material for lithium batteries (1–10). X-ray and neutron powder diffraction data and vibration spectroscopy studies have determined that LT-$LiCoO_2$ has the lithiated-spinel $Li_2[Co_2]O_4$ structure (space group $Fd3m$) (10). LT-$LiCoO_2$ electrodes do not perform well in lithium cells, and there is considerable hysteresis between the lithium de-intercalation and intercalation processes (1–7). This behavior contrasts with the superior electrochemical performance of electrodes with the layered "high-temperature" HT-$LiCoO_2$ structure (space group $R\bar{3}m$) that can be synthesized at 800°C (1, 11). We have shown previously with electron diffraction data that the cobalt distribution in LT-$LiCoO_2$ samples is not ideal, and that it can be considered to be intermediate between an ideal layered $(Li)_{3a}\{Co\}_{3b}O_2$ configuration and an ideal lithiated-spinel $(Li_2)_{16c}[Co_2]_{16d}O_4$ configuration, in which cation layers with 75% Co and 25% Li alternate with layers containing 25% Co and 75% Li. Therefore, it has been proposed that in LT-$LiCoO_2$ structures, the presence of some cobalt ions on the octahedral 16*c* sites would hinder lithium diffusion in the interstitial space of the $[Co_2]O_4$ spinel framework and deleteriously affect the electrochemical performance of Li/LT-$LiCoO_2$ cells (5, 10). Such a structural phenomenon raises questions about the relative thermodynamic stability of the lithiated-spinel versus the layered $LiCoO_2$ structure at 400°C. We have, therefore, investigated the relative stability of these two structure types at this temperature.

Three experimental observations of the phase stability of $LiCoO_2$ samples heated between 400°C and 900°C have previously shown that (1) at 400°C, the lithiated-spinel structure is the dominant phase (1–11); (2) the fraction of layered $LiCoO_2$ increases as the samples are heated at intermediate temperatures, e.g., 500°C (9); and (3) a single-phase, layered $LiCoO_2$ structure is obtained between 800°C and 900°C (1, 11). These experimental results imply that at 400°C the lithiated-spinel is the thermodynamically preferred phase. However, quantum mechanical calculations have predicted that at all temperatures the lithiated-spinel structure is thermodynamically unstable relative to the layered structure (12), i.e. layered $LiCoO_2$ is the ground state structure. Moreover, the lithiated-spinel structure

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[2] To whom correspondence should be addressed. Present address: Department of Mechanical Engineering, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA 02139. E-mail: shaohorn@mit.edu.

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(cubic, *Fd*3*m*) has higher symmetry than the layered structure (trigonal, $R\bar{3}m$). This observation contradicts the general rule of thumb for phase transitions that low-temperature, thermodynamically stable phases tend to have lower symmetry than high-temperature, stable phases (13).

We have, therefore, undertaken an investigation of the relative thermodynamic stability of the lithiated-spinel $Li_2[Co_2]O_4$ structure versus the layered $LiCoO_2$ structure at 400°C. In this paper, we report data concerning the reactions of Li_2CO_3 with $CoCO_3$ (or Co_3O_4) that occur between 10 min and 232 days of heat treatment at 400°C. In particular, we have determined the relative volume fractions of the lithiated-spinel and layered structures as a function of heat-treatment time. Structural analyses of the products by powder X-ray diffraction and transmission electron microscopy have allowed us to propose a reaction pathway for the formation of $Li_2[Co_2]O_4$ at 400°C and an explanation for the slow and sluggish transformation of the lithiated-spinel structure to the layered structure. Our interpretation is consistent with the poor electrochemical behavior of LT-$LiCoO_2$ electrodes in lithium cells (5, 10).

EXPERIMENTAL

LT-$LiCoO_2$ samples were prepared by the solid-state reaction of stoichiometric amounts of Li_2CO_3 (Aldrich) and $CoCO_3$ (Aldrich) at 400°C in air for various times that ranged from 10 min to 232 days. These samples are referred to as LT-$LiCoO_2$-400-*X*, where *X* is the reaction time (days). A $CoCO_3$ reference was heated at 400°C in air for 10 min in the absence of Li_2CO_3 to demonstrate its rapid decomposition at this temperature. An LT-$LiCoO_2$ sample was also prepared at 500°C over 4 days (LT-$LiCoO_2$-500-4). The evolution of lithiated-spinel $Li_2[Co_2]O_4$ and layered $LiCoO_2$ structures was also investigated by reacting Li_2CO_3 with submicron-size Co_3O_4 powder (Aldrich) at 400°C for 1 and 4 days; these samples are referred to as LT-$LiCoO_2$–Co_3O_4-400-1 and LT-$LiCoO_2$–Co_3O_4-400-4, respectively.

All of the X-ray diffraction data were collected on a Siemens D5000 powder diffractometer with CuK_α radiation at room temperature (22°C). The LT-$LiCoO_2$ patterns used for structural refinements were recorded between 10° and 110° 2θ using a step size of 0.03° 2θ and a step time of 15 s. The powder X-ray diffraction profiles were refined with the GSAS program (14) using a Pseudovoigt function (15) in which the peak-shape parameters *W* (peak width) and *X* (peak tail) were varied. With these refinements, the "goodness of fit" between the observed and calculated data is given by the weighted residual factor, wR_p (15). The lattice parameters and oxygen positional parameters of the lithiated-spinel and layered structures were held constant during the two-phase refinements and quantitative analysis of the LT-$LiCoO_2$ patterns.

The phase transformation from the lithiated-spinel structure to the layered structure in LT-$LiCoO_2$ samples was investigated by imaging and convergent-beam electron diffraction with a transmission electron microscope (JEOL-JEM 4000FX-1) under an accelerating voltage of 200 keV. Sample preparation for these microscopy studies has been described elsewhere (16).

RESULTS AND DISCUSSION

X-Ray Diffraction

The X-ray diffraction patterns obtained after heating $CoCO_3$ in air in the absence of Li_2CO_3, and together with Li_2CO_3, for 10 min are shown in Figs. 1(a) and (b), respectively. The patterns for LT-$LiCoO_2$ samples heated at 400°C for 0.5, 1 and 2 days are shown in Figs. 1(c–e), and in Figs. 2(a–e) for 10, 39, 67, 131 and 232 days. In the absence of Li_2CO_3, $CoCO_3$ decomposes very rapidly to CO_3O_4 with a spinel structure at 400°C (Fig. 1(a)). When Li_2Co_3 is present, the X-ray diffraction patterns show that the decomposition of $CoCO_3$ proceeds at a much faster rate than that of Li_2CO_3. In addition, the subsequent growth of a lithiated-spinel phase, $Li_2[Co_2]O_4$ (LS), is derived predominantly from a Co_3O_4 intermediate product (Figs. 1(b–e)) that may contain a small amount of substituted lithium on the tetrahedral sites, namely $Li_xCo_{1-x}[Co_2]O_4$ ($x \leq 0.4$) (17). The growth of the

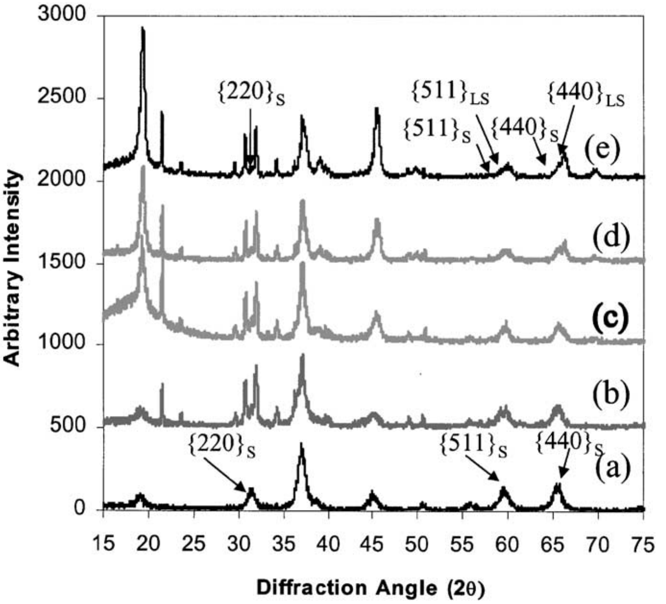

FIG. 1. X-ray diffraction patterns: (a) $CoCO_3$ heated at 400°C for 10 min; (b)–(e) LT-$LiCoO_2$ samples heat treated at 400°C for 10 min, 12, 24 and 48 h, respectively. The {220}, {511} and {440} peaks of the spinel phase (S) and the {511} and {440} peaks of the lithiated-spinel phase (LS) are indicated in (a) and (e), respectively.

$Li_2[Co_2]O_4$ phase is evident (particularly when the X-ray patterns are enlarged) from (1) a decrease in the magnitude of the {220} spinel peak (S) at ~31.5° 2θ, and (2) the evolution of independent {511} and {440} peaks at slightly higher 2θ values (near 59° and 66° 2θ, respectively) which grow at the expense of the {511} and {440} $Li_xCo_{1-x}[Co_2]O_4$ spinel peaks. As shown in Fig. 1(e), after 2 days, the reaction is still far from complete.

For prolonged heating (≥10 days), the dominant peaks in the patterns of the LT-$LiCoO_2$ samples could be indexed to the lithiated-spinel $Li_2[Co_2]O_4$ structure (Figs. 2(a–e)). Note that there is no evidence of the {220} $Li_xCo_{1-x}[Co_2]O_4$ spinel peak in Figs. 2(b–e). The most noticeable changes in the X-ray diffraction patterns of LT-$LiCoO_2$ samples are observed between 58° and 71° 2θ, as shown in Fig. 3, in which the X-ray diffraction pattern of the LT-$LiCoO_2$-500-4 sample is also given for comparison (Fig. 3(f)). In Figs. 3(a–e), it is clear that the {440} peak of the lithiated-spinel phase ($Fd3m$) gradually splits on prolonged heating into the (108) and (110) peaks of the layered $LiCoO_2$ structure ($R\bar{3}m$); the {511} peak of the lithiated-spinel structure shifts to the left to generate the overlapping (107) and (009) peaks of layered $LiCoO_2$. These effects are more pronounced in the LT-$LiCoO_2$-500-4 sample (Fig. 3(f)). The data clearly indicate that the transformation of the lithiated-spinel LT-$LiCoO_2$ structure to layered $LiCoO_2$ at 400°C is sluggish, and that it can be achieved more rapidly, but not completely, after reaction for 5 days at 500°C.

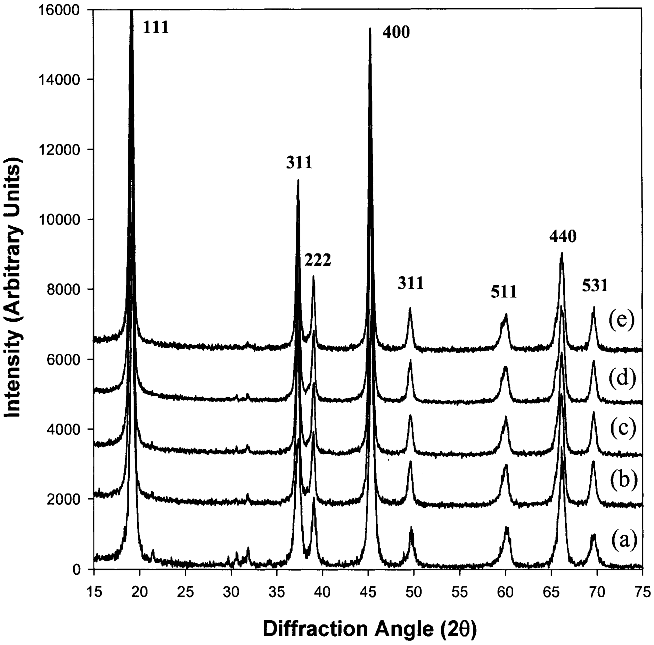

FIG. 2. X-ray diffraction patterns of LT-$LiCoO_2$ samples heated at 400°C for (a) 10 d, (B) 39 d, (c) 67 d, (d) 131 d and (e) 232 d. The major peaks in (e) are indexed to the lithiated-spinel $Li_2[Co_2]O_4$ structure. Peaks from unreacted Li_2CO_3 are indicated by asterisks.

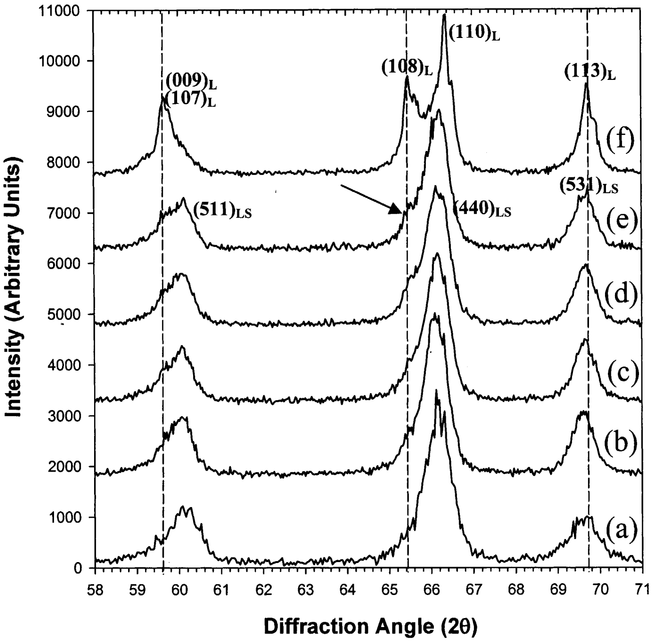

FIG. 3. X-ray diffraction patterns between 58° and 71° 2θ; (a)–(e) LT-$LiCoO_2$-400 samples shown in Figs. 2(a–e); (f) LT-$LiCoO_2$-500-4, showing the growth of layered $LiCoO_2$ over long reaction times and at higher temperature.

The lattice parameters and the oxygen positional parameter of the lithiated-spinel $Li_2[Co_2]O_4$ and the layered $LiCoO_2$ structures were initially obtained from refinements of the LT-$LiCoO_2$-400-10 and LT-$LiCoO_2$-500-4 patterns, respectively (Table 1); they are consistent with those reported previously (1–7, 11). These parameter values were held invariant in the subsequent quantitative analyses of these phases in the LT-$LiCoO_2$ X-ray diffraction patterns, the results of which are shown in Table 2. Although the quality of the X-ray patterns does not allow an accurate determination of the volume fraction of the lithiated-spinel and layered $LiCoO_2$ components, the results show a clear trend. As expected, the lithiated-spinel structure is the major component in the LT-$LiCoO_2$-400-10

TABLE 1

Structural Parameters of the Lithiated-Spinel $Li_2[Co_2]O_4$ and Layered $LiCoO_2$ Structures Determined from the Refinement of the X-Ray Diffraction Patterns

Phases	Space group	Lattice parameters (nm)	Oxygen position parameter
Lithiated-spinel $Li_2[Co_2]O_4$	$Fd\bar{3}m$	$a = 0.7995$	0.259
Layered $LiCoO_2$	$R\bar{3}m$	$a = 0.2816$ $c = 1.4044$	0.240

TABLE 2
Volume Fractions of the Lithiated-Spinel and Layered Components in LT-$LiCoO_2$ Samples, Obtained from Two-Phase Refinements of the X-Ray Diffraction Patterns

$LiCoO_2$ samples	Volume fraction of $Li_2[Co_2]O_4$	Volume fraction of $LiCoO_2$	Sigma	wR_p
400°C—10 days	0.93	0.07	0.0683	0.2183
400°C—39 days	0.67	0.33	0.0047	0.1097
400°C—67 days	0.61	0.39	0.0038	0.1038
400°C—131 days	0.57	0.43	0.0034	0.0976
400°C—232 days	0.56	0.44	0.0052	0.1254
500°C—4 days	0.24	0.76	0.0018	0.1036

sample, whereas in the LT-$LiCoO_2$-500-4 sample, the layered structure predominates. It is also clear from Table 2 that on prolonged heating of LT-$LiCoO_2$ samples at 400°C, the volume fraction of the lithiated-spinel phase in the sample decreases gradually with respect to the amount of layered $LiCoO_2$. Although incomplete, the slow transformation of the $[Co_2]O_4$ spinel framework to a layered configuration implies that layered $LiCoO_2$ is thermodynamically more stable than the lithiated-spinel $Li_2[Co_2]O_4$ structure at 400°C. This finding provides experimental evidence to support the theoretical prediction of the relative stability of these two structure types (12).

In the structural analyses of LT-$LiCoO_2$ samples (Table 3), the peak profile parameters revealed that (1) after heating for 232 days at 400°C, the peak width parameter (W) of the lithiated-spinel phase (108.6) is significantly larger than that of the layered $LiCoO_2$ phase (21.1); (2) the value of W for the layered $LiCoO_2$ component at 400°C (21.1) is significantly larger than it is at 500°C (0.1); and (3) at 500°C, the layered component (21.1) is substantially more crystalline than the lithiated-spinel component (86.2). These points are consistent with the expectation that low synthesis temperatures should provide small crystals that increase in size and crystallinity on further heating; they also emphasize the difficulty in synthesizing a highly ordered, lithiated-spinel structure $Li_2[Co_2]O_4$ by solid-state reactions, even at moderate temperatures.

The transformation from the lithiated-spinel to the layered structure is kinetically sluggish because, after 131 days at 400°C, there is still 57% of the lithiated-spinel phase in the sample and further heating appears to have little effect. It is therefore believed that the following structural factors limit this phase transition at 400°C: (1) the ideal $Li_2[Co_2]O_4$ and $LiCoO_2$ structures have ordered rocksalt-type configurations in which all the octahedral sites are filled, (2) the transformation of $Li_2[Co_2]O_4$ to layered $LiCoO_2$ requires that there must be an exchange of one quarter of the cobalt and lithium ions within the cubic-close packed oxygen array, and (3) there is no readily available and energetically favorable interstitial space in the rocksalt structures for Li and Co diffusion.

Transmission Electron Microscopy Studies

A transmission electron microscope image of the LT-$LiCoO_2$-400-39 sample, shown in Fig. 4, reveals equiaxed and rod-like crystal shapes. Most of the smaller crystals, which range in size from 20 to 80 nm, are equiaxed, whereas the larger crystals, typically 100–300 nm in length, are rod shaped. Single-crystal electron diffraction revealed that the equiaxed crystals have the lithiated-spinel $Li_2[Co_2]O_4$ structure, whereas the rod-shaped crystals have the layered $LiCoO_2$ structure, with the rod axis being contained within the closed-packed (003) planes. These observations are consistent with the smaller peak-width parameter (W) of the layered $LiCoO_2$ component obtained from the refinement of the X-ray diffraction data (Table 3). The development of these large, rod-shaped crystals is referred to as "abnormal" growth. This contrasts with the "normal" growth of the small $Li_2[Co_2]O_4$ crystals on heating at 400°C from 10 days to 39 days (Figs. 5(a) and (b)) during which they remain equiaxed. Note, however, that some small crystals show the onset of rod-like character. The abnormal growth of the $LiCoO_2$ crystals implies that the Gibbs volume free energy of layered $LiCoO_2$ is lower than that of the lithiated-spinel $Li_2[Co_2]O_4$; this provides the driving force to reduce the surface free energy and to promote the growth of the layered $LiCoO_2$ crystals. The transmission electron micro-

TABLE 3
Peak Profile Parameters Determined from the Refinements of the X-Ray Diffraction Patterns

$LiCoO_2$ samples	Lithiated-spinel W	Lithiated-spinel X	Layered W	Layered X
400°C—10 days	204.2	31.7	21.1 (not refined)	28.2 (not refined)
400°C—39 days	104.2	19.9	21.1 (not refined)	28.2 (not refined)
400°C—67 days	97.1	18.2	21.1 (not refined)	28.2 (not refined)
400°C—131 days	106.3	17.3	21.1 (not refined)	28.2 (not refined)
400°C—232 days	108.6	15.7	21.1	28.2
500°C—4 days	86.2	18.4	0.1	17.8

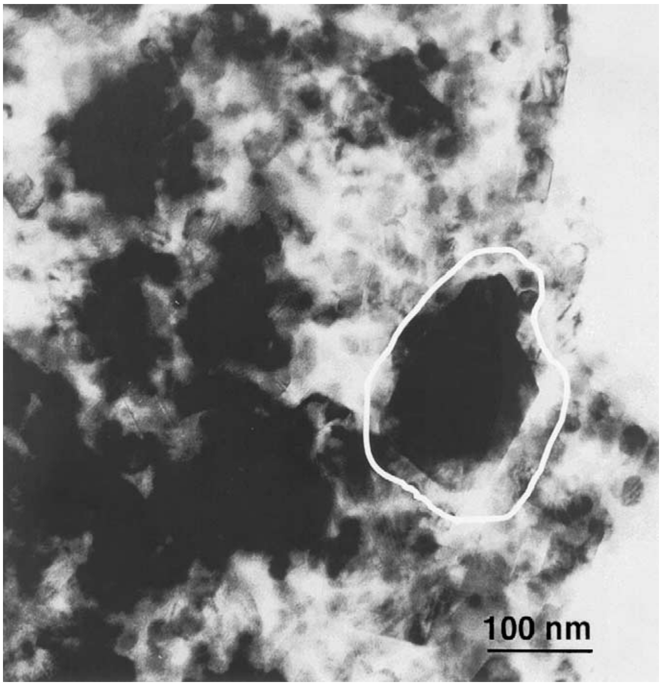

FIG. 4. A transmission electron microscope image of an LT-$LiCoO_2$-400-39 sample showing two crystal shapes: equiaxed and rod like (circled).

scope studies are consistent with the X-ray diffraction refinements and theoretical calculations; they provide further evidence for a gradual transition of the lithiated-spinel structure to the layered structure at 400°C and for layered $LiCoO_2$ being thermodynamically more stable than $Li_2[Co_2]O_4$ at 400°C.

Proposed Reaction for $Li_2[Co_2]O_4$ Formation

If the layered $LiCoO_2$ structure is the thermodynamically preferred structure at 400°C, then the presence of a lithiated-spinel structure after prolonged heating of $CoCO_3$ and Li_2CO_3 at this temperature implies that the formation of a spinel configuration is kinetically preferred. Therefore, we propose the following reaction route for the formation of a lithiated-spinel structure, $Li_2[Co_2]O_4$, from Li_2CO_3 and $CoCO_3$ precursors:

Reaction I—lithiation and oxidation of $CoCO_3$:

$$\begin{aligned}&(6-2x)\mathrm{CoCO_3} + x\mathrm{Li_2CO_3} + (1 + x/2)\mathrm{O_2}\\ &\Leftrightarrow 2\mathrm{Li}_x\mathrm{Co}_{1-x}[\mathrm{Co_2}]\mathrm{O_4} + (6-x)\mathrm{CO_2} \quad (0 \le x \le 0.4).\end{aligned}$$

Reaction II — subsequent formation of $Li_2[Co_2]O_4$:

$$\begin{aligned}&\mathrm{Li}_x\mathrm{Co}_{1-x}[\mathrm{Co_2}]\mathrm{O_4} + (\tfrac{3}{2}-x)\mathrm{Li_2CO_3} + (\tfrac{1}{4}-x/2)\mathrm{O_2}\\ &\Leftrightarrow (\tfrac{3}{2}-x/2)\mathrm{Li_2[Co_2]O_4} + (\tfrac{3}{2}-x)\mathrm{CO_2}.\end{aligned}$$

Reaction I is consistent with the experimental X-ray data in Figs. 1 and 2 that show convincing evidence that an intermediate $Li_xCo_{1-x}[Co_2]O_4$ spinel phase ($0 \le x \le 0.4$) is nucleated prior to the formation of the lithiated-spinel (rocksalt) $Li_2[Co_2]O_4$ structure. Because layered $LiCoO_2$ appears to be the thermodynamically favored structure at 400°C, we conclude that the presence of an intermediate

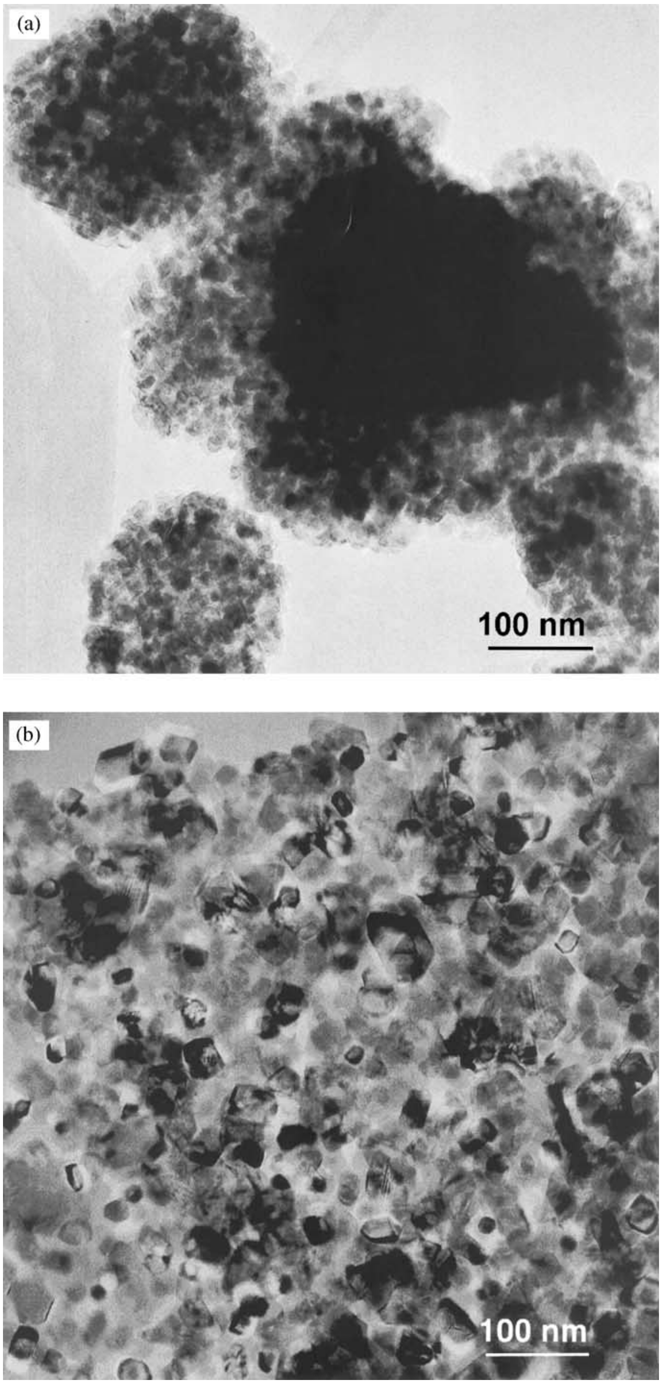

FIG. 5. Transmission microscope images showing the crystal growth and change in morphology on heating LT-$LiCoO_2$-400 samples from (a) 10 d to (b) 39 d.

$Li_xCo_{1-x}[Co_2]O_4$ spinel structure is essential for the formation of a metastable lithiated-spinel $Li_2[Co_2]O_4$ product; in this respect, the possibility that a spinel intermediate structure is formed has already been proposed, but not demonstrated, by Garcia *et al.* (9).

Reaction of Co_3O_4 with Li_2CO_3

The reaction of submicron-size Co_3O_4 particles with Li_2CO_3 was studied in an attempt to gather more information about the reaction route by which LT-$LiCoO_2$ structures are formed from a spinel precursor and, in particular, about the crystallographic orientation relationships that develop between the structures of the precursor and the $LiCoO_2$ products. No change in the X-ray powder diffraction pattern was found in the LT-$LiCoO_2$–Co_3O_4-400-1 sample, i.e., after heating Co_3O_4 and Li_2CO_3 for 1 day at 400°C, whereas substantial changes were observed after heating for 4 days as shown in Fig. 6. In the latter case, in addition to unreacted Li_2CO_3, the X-ray diffraction pattern showed two cubic phases that are clearly evident from the doublet peaks at approximately 45° and 66° 2θ, and could be attributed to $Li_2[Co_2]O_4$ ($a = 0.7995$ nm) and a spinel component $Li_xCo_{1-x}[Co_2]O_4$ ($0 \leq x \leq 0.4$), $a = 0.8080-0.8089$ nm). The strong singlet spinel peak at approximately 31.5° 2θ, which corresponds to the {220} reflections, provides unequivocal evidence for tetrahedral-site cobalt in the $Li_xCo_{1-x}[Co_2]O_4$ phase; this peak is forbidden by the $Li_2[Co_2]O_4$ rocksalt structure. The presence of $Li_2[Co_2]O_4$ in LT-$LiCoO_2$–Co_3O_4-400-4 was confirmed by comparing the X-ray diffraction data near 19° and 66° 2θ with LT-$LiCoO_2$-400-232 and LT-$LiCoO_2$-500-4 samples (Figs. 7 and 8, respectively). It is evident that LT-$LiCoO_2$–Co_3O_4-400-4 contains an $Li_xCo_{1-x}[Co_2]O_4$

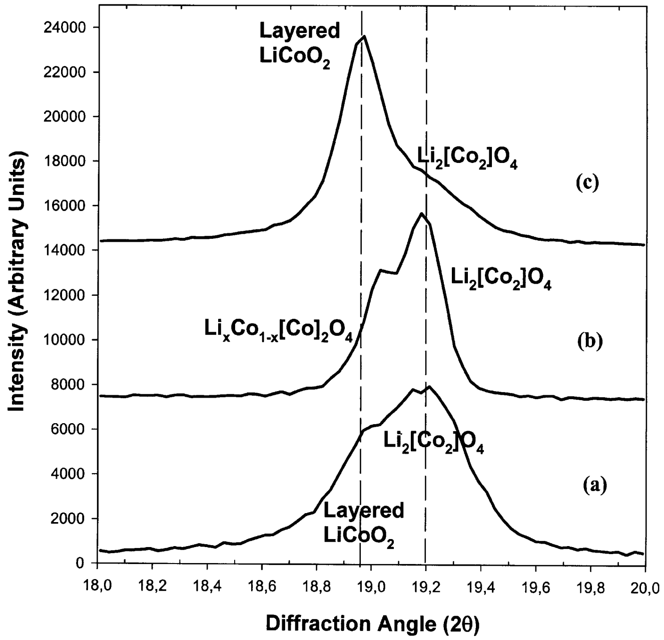

FIG. 7. X-ray diffraction peaks near 19° 2θ for (a) LT-$LiCoO_2$-400-232, (b) LT-$LiCoO_2$–Co_3O_4-400-4, and (c) LT-$LiCoO_2$-500-4.

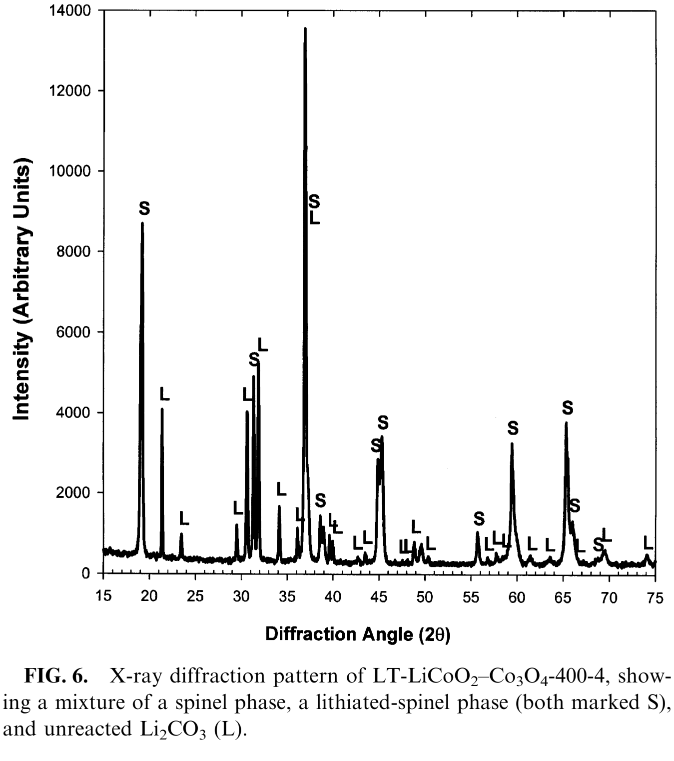

FIG. 6. X-ray diffraction pattern of LT-$LiCoO_2$–Co_3O_4-400-4, showing a mixture of a spinel phase, a lithiated-spinel phase (both marked S), and unreacted Li_2CO_3 (L).

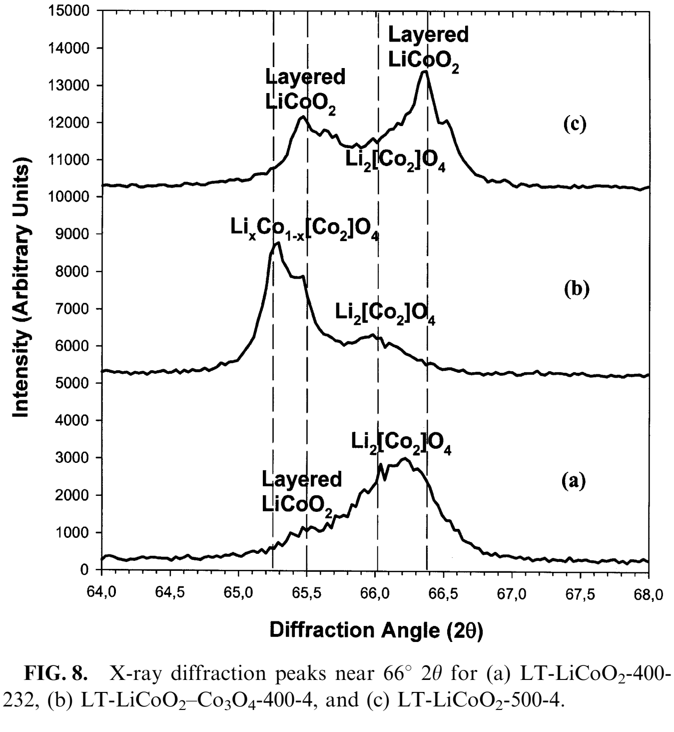

FIG. 8. X-ray diffraction peaks near 66° 2θ for (a) LT-$LiCoO_2$-400-232, (b) LT-$LiCoO_2$–Co_3O_4-400-4, and (c) LT-$LiCoO_2$-500-4.

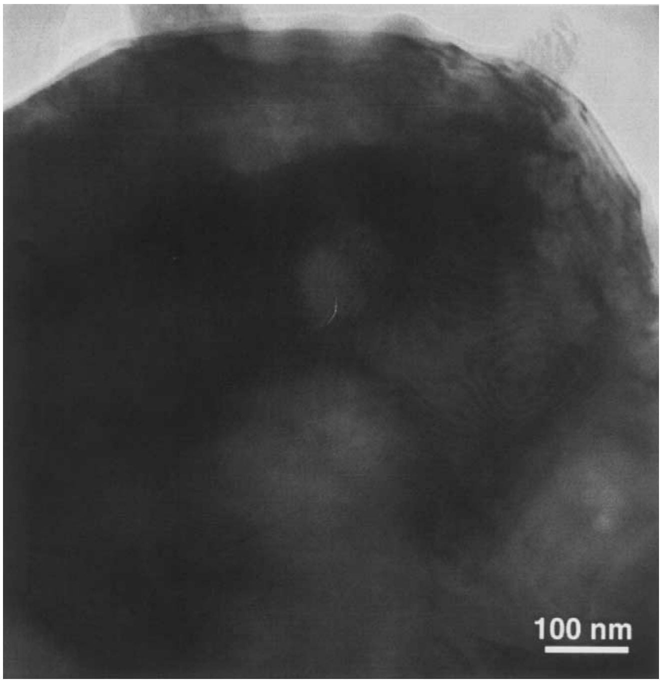

FIG. 9. A transmission electron microscope image of a lithiated Co_3O_4 crystal in an LT-$LiCoO_2$–Co_3O_4-400-4 sample.

spinel component and an $Li_2[Co_2]O_4$ lithiated-spinel component. There is also evidence of a small amount of layered $LiCoO_2$ in LT-$LiCoO_2$–Co_3O_4-400-4 (Fig. 8).

The crystallographic relationships between the spinel and lithiated-spinel (rocksalt) components in the LT-$LiCoO_2$–Co_3O_4-400-4 sample were examined by transmission electron microscopy; a typical image of a lithiated Co_3O_4 crystal is shown in Fig. 9. Electron diffraction patterns collected from the surface and the center of the crystal are shown in Figs. 10(a) and (b), respectively. Although both patterns show six-fold symmetry, there are marked differences in the scattering intensities of the {220} reflections from the face-centered-cubic unit cells. The absence of the {220} reflections in Fig. 10(a) is consistent with the formation of the lithiated-spinel $Li_2[Co_2]O_4$ structure on the crystal surface, whereas Fig. 10(b) shows the set of these reflections, which is indicative of an $Li_xCo_{1-x}[Co_2]O_4$ spinel structure within the bulk of the crystal. The absence of distortion of the reciprocal lattice points in Figs. 10(a) and (b) implies that during the crystallographic transformation at the phase boundary, the crystallographic planes of the lithiated-spinel $Li_2[Co_2]O_4$ structure remain parallel to those of $Li_xCo_{1-x}[Co_2]O_4$. This is perhaps not too surprising because the transition takes place between two cubic phases with only a small change ($\sim 1\%$) in the lattice parameter. By contrast, such a strong crystallographic relationship does not exist between cubic $Li_2[Co_2]O_4$ and layered $LiCoO_2$, which has trigonal symmetry ($R\bar{3}m$). In this case, the growth of layered $LiCoO_2$ from the $Li_2[Co_2]O_4$-rich surface of the lithiated Co_3O_4 particle is far more dramatic, as shown in Fig. 11. The large crystallite was confirmed unequivocally by electron diffraction to have trigonal symmetry, as required by layered $LiCoO_2$ (Fig. 12(a)), whereas the symmetry of the bulk structure

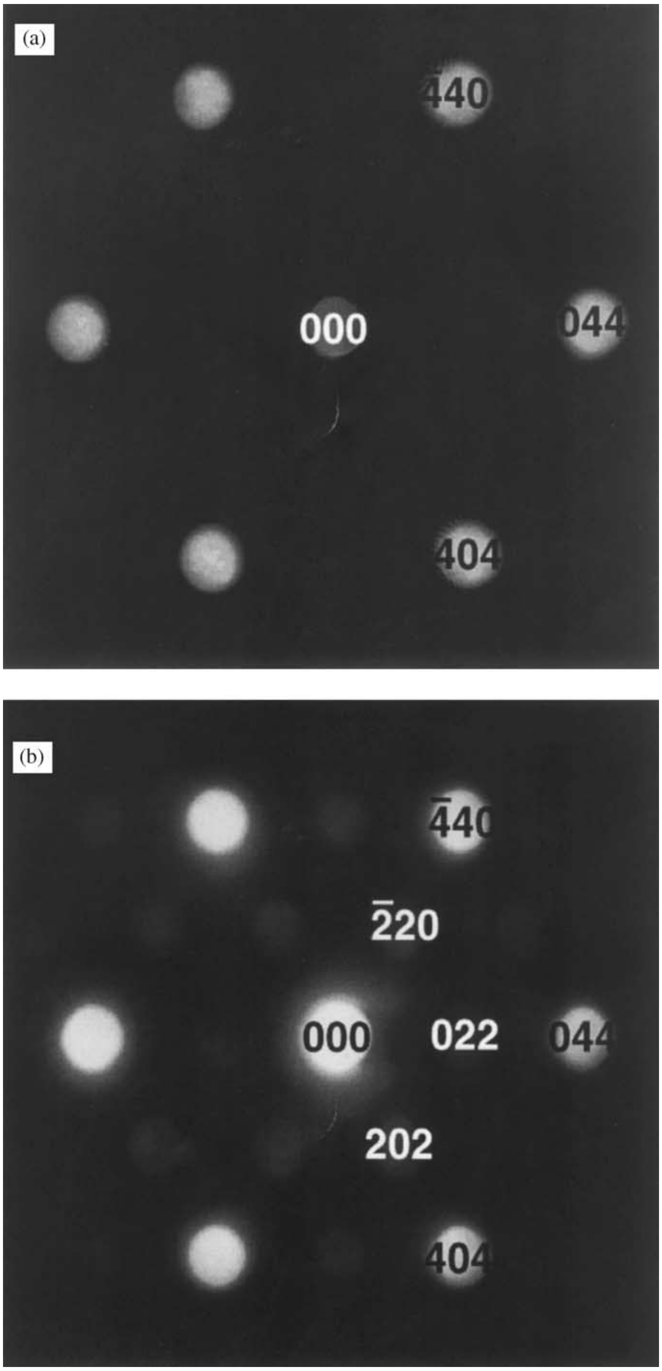

FIG. 10. Single-crystal electron diffraction patterns collected from (a) the surface and (b) the center of the lithiated Co_3O_4 crystal as shown in Fig. 9.

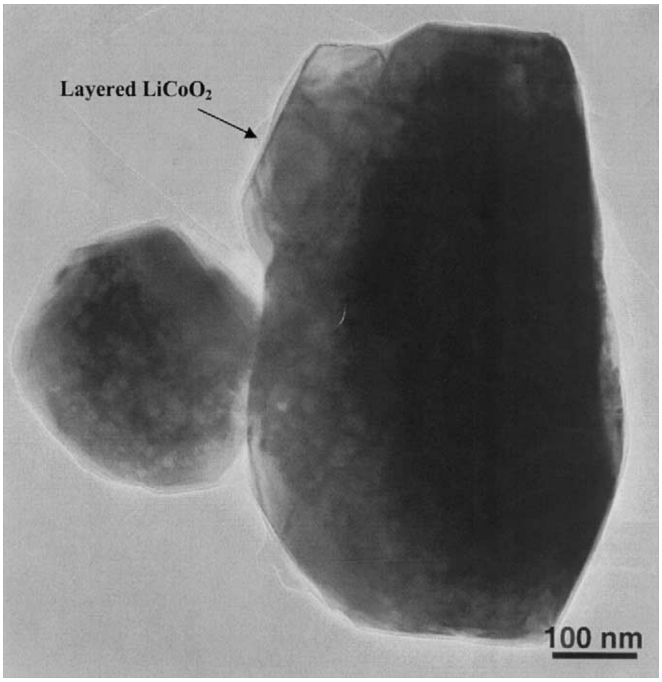

FIG. 11. A transmission electron microscope image of a lithiated Co$_3$O$_4$ crystal in an LT-LiCoO$_2$–Co$_3$O$_4$-400-4 sample, showing the growth of layered LiCoO$_2$ on the crystal surface.

was clearly still cubic (Fig. 12(b)). The dramatic crystal growth and change in crystal morphology suggest that long-range diffusion of cobalt and lithium (requiring a high activation energy) is needed to bring about the significant change in distribution of lithium and cobalt during the rocksalt-to-rocksalt transition of Li$_2$[Co$_2$]O$_4$ to layered LiCoO$_2$, whereas only short-range diffusion of cobalt, lithium and oxygen (with lower activation energy) is required to nucleate the growth of Li$_2$[Co$_2$]O$_4$ on the surface of Li$_x$Co$_{1-x}$[Co$_2$]O$_4$. Therefore, when CoCO$_3$ is reacted with Li$_2$CO$_3$ at 400°C, a kinetically favored pathway to the lithiated-spinel configuration Li$_2$[Co$_2$]O$_4$ from an intermediate Li$_x$Co$_{1-x}$[Co$_2$]O$_4$ spinel configuration can account for the formation of this structure type over the thermodynamically favored layered LiCoO$_2$ structure.

CONCLUSION

Studies of the reaction of CoCO$_3$ with Li$_2$CO$_3$ at 400°C have shown that the lithiated-spinel Li$_2$[Co$_2$]O$_4$ is initially formed from an intermediate Li$_x$Co$_{1-x}$[Co$_2$]O$_4$ spinel product before transforming gradually to layered LiCoO$_2$, thereby confirming theoretical calculations that the layered structure is thermodynamically favored at this temperature. The rocksalt-to-rocksalt transition from Li$_2$[Co$_2$]O$_4$ to layered LiCoO$_2$ at 400°C is kinetically hindered, predominantly by structural factors. The lack of an energetically favorable interstitial space, the difficulty of exchanging 25% of the lithium ions in the 16*c* sites of the spinel structure with cobalt ions (and vice versa), and the non-ideal distribution of lithium and cobalt in Li$_2$[Co$_2$]O$_4$

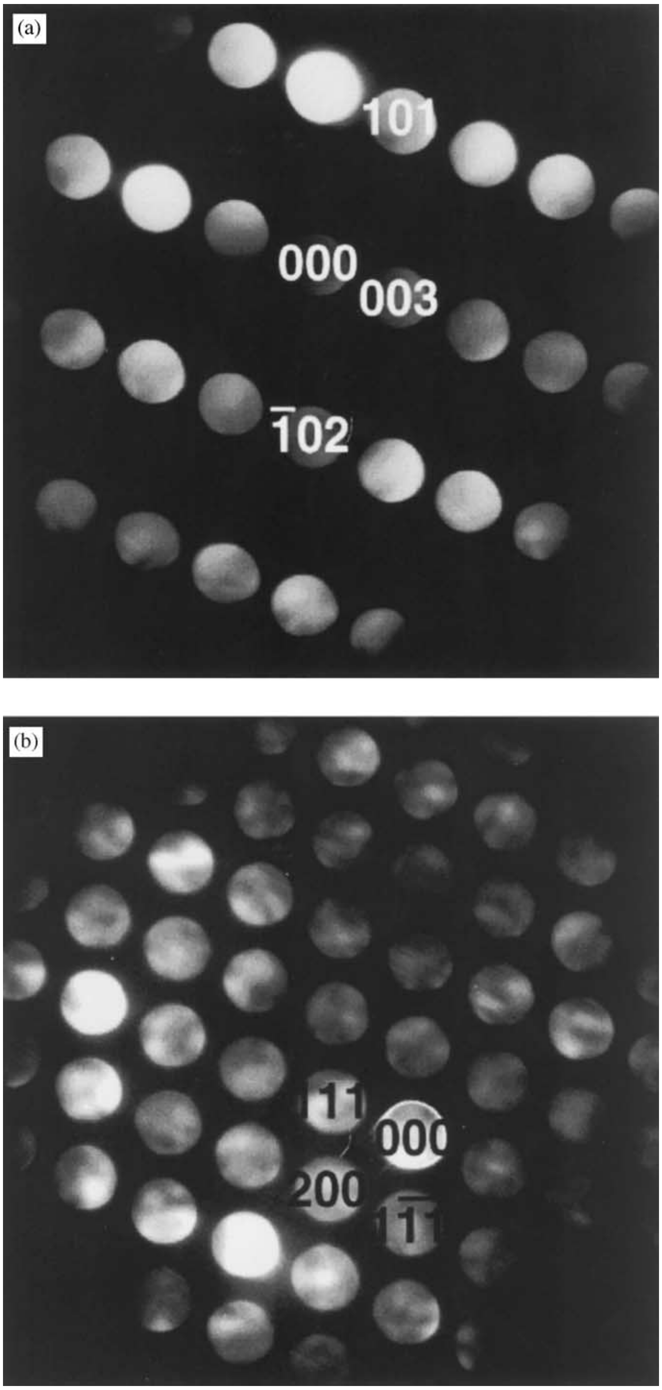

FIG. 12. Single-crystal electron diffraction patterns of (a) the trigonal (layered) LiCoO$_2$ crystal shown at the particle surface in Fig. 11, and (b) a cubic Li$_x$Co$_{1-x}$[Co$_2$]O$_4$ spinel crystal in the bulk.

are believed to contribute to the slow and sluggish transformation, and therefore to the apparent stability of $Li_2[Co_2]O_4$ at 400°C. The difficulty in preparing pure, single-phase $Li_2[Co_2]O_4$ can be attributed to a wide range of solid solution and structural configurations that exist among rocksalt compositions in the $Li_xCo_{1-x}O$ system ($0.4 \leq x \leq 0.5$). These conclusions support previous reports that the structural features of LT-$Li_2[Co_2]O_4$ electrodes are a major reason for the poor electrochemical properties of room-temperature Li/LT-$Li_2[Co_2]O_4$ cells.

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