

# A transmission electron microscopy study of cycled $\text{LiCoO}_2$

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## Abstract

A sample of  $\text{LiCoO}_2$  was prepared as a cathode for a lithium battery, and subjected to a large number of charge/discharge cycles that induced an irreversible loss in capacity. A transmission electron microscopy study of this material showed that the initial O3 crystal structure transformed partially to a cubic spinel phase, especially on the surfaces of the particles. We suggest that this spinel phase formation could be responsible in part for the irreversible capacity fade.

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## 1. Introduction

$\text{LiCoO}_2$  heat-treated above 700 °C (HT- $\text{LiCoO}_2$ ) is used in positive electrodes (cathodes) of rechargeable Li-ion batteries. Compared to other cathode materials it has a high energy density, high cycle life and good capacity retention. The structure of HT- $\text{LiCoO}_2$  is trigonal (also referred to as hexagonal) of  $R\bar{3}m$  symmetry. The lattice is formed by oxygen atoms in ABC stacking with alternating layers of Li and Co ions in octahedral interstitial sites between the oxygen planes. Lithium is removed from the structure (and moved to the anode) when the battery is charged. During charge–discharge cycling the Li-content in  $\text{Li}_x\text{CoO}_2$  is cycled between  $x = 0.5$  (charged) and  $x = 1$  (discharged).

During delithiation of  $\text{Li}_x\text{CoO}_2$  (charging), the following changes occur in the crystal structure of  $\text{Li}_x\text{CoO}_2$ . Between  $x = 1$  and 0.75, two hexagonal lattices co-exist, followed by a regime of one phase (hexagonal) for  $x = 0.75$ –0.25. Around  $x = 0.5$ , a monoclinic unit cell is observed, but it is stable only in the very narrow concentration range of  $x = 0.44$ –0.49 [1,2]. There have been many studies on how the crystal structure evolves over one charge–discharge cycle. On the other hand, there have been few studies on how the crystal structure evolves after extensive electrochemical cycling [3,4]. Nevertheless, irreversible capacity fade after cycling is an important phenomenon that is not well understood, and likely involves some change in the crystal structure of the  $\text{LiCoO}_2$ .

Here, we report the results of a transmission electron microscopy (TEM) investigation on the microstructural evolution of

$\text{LiCoO}_2$  after extensive electrochemical cycling, where the cathode has undergone a capacity loss. Although the starting material was entirely the O3 structure, we found cubic spinel phase in the cycled  $\text{LiCoO}_2$ . Since the cubic spinel phase is less active electrochemically, its formation could be a source of the capacity fade. Furthermore, we observed degradation of crystal quality at the surface of  $\text{LiCoO}_2$  particles after cycling, and this deterioration may affect electrical contact between the  $\text{LiCoO}_2$  particles in the electrode.

## 2. Experimental

Virgin  $\text{LiCoO}_2$  powder and  $\text{LiCoO}_2$  that was electrochemically cycled in a battery between 3.0 and 4.2 V at room temperature, were provided by the courtesy of ENAX, Inc., Japan. The electrochemically cycled material was subjected to 334 charge–discharge cycles, and left in the discharged (lithiated) state. The cycled  $\text{LiCoO}_2$  powder was retrieved by scraping the carbon/binder (PVDF: polyvinylidene difluoride)/ $\text{LiCoO}_2$  mix from the cathode and washing it in *n*-methyl-pyrrolidinone (NMP) to dissolve the binder.

Specimens for TEM examination were prepared from a suspension of  $\text{LiCoO}_2$  powder in methanol. A droplet was placed on a holey carbon film supported by a copper grid. The TEM observations were performed with a Philips EM420 instrument operated at 120 kV. Several particles of the uncycled and cycled material were viewed in low-index zone axes. Images were taken along with their corresponding diffraction pattern. The experimental studies were accompanied by simulations of diffraction patterns for various crystal structures using the software package “Desktop Microscopist”. For these simulations we used Co  $K\alpha$  rays with  $\lambda = 0.17904$  nm.

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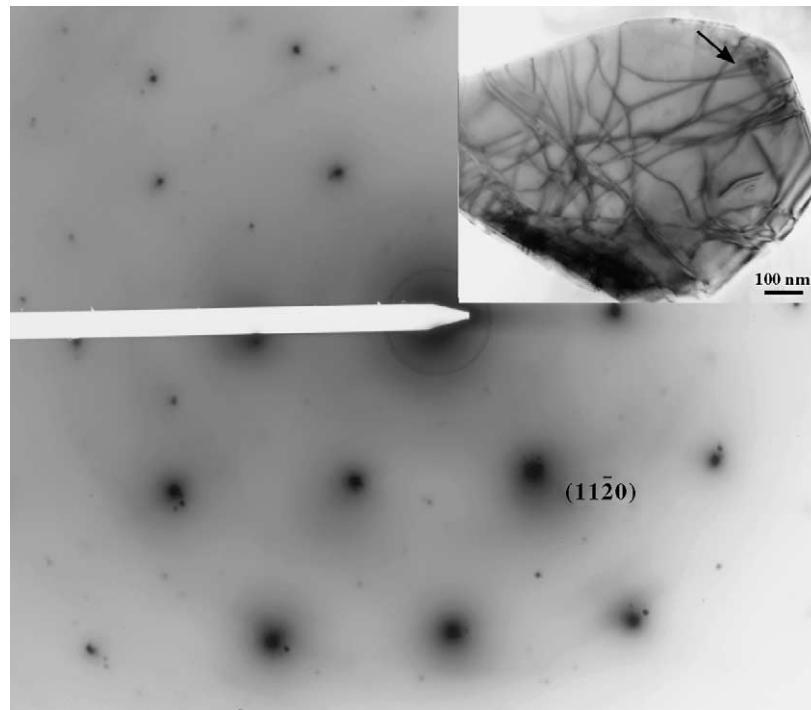


Fig. 1. Electron diffraction pattern of  $\text{LiCoO}_2$  ( $R\bar{3}m$  structure) in  $[0\ 0\ 0\ 1]$  zone axis.

### 3. Results

#### 3.1. Uncycled $\text{LiCoO}_2$

Fig. 1 shows a typical selected area diffraction pattern of virgin  $\text{LiCoO}_2$  from a  $[0\ 0\ 0\ 1]$  zone axis of the particle shown in the inset. The  $a/3 \langle 1\ 1\ \bar{2}\ 0 \rangle$  type diffractions of this zone axis correspond to a lattice spacing of approximately 0.141 nm

between  $\{1\ 1\ \bar{2}\ 0\}$  planes. In the image, a dislocation network in the particle can be seen. The majority of dislocations are of  $a/3 \langle 1\ 1\ \bar{2}\ 0 \rangle$  type Burgers vectors. In some places these perfect dislocations dissociate into Shockley partial dislocations according to the reaction  $a/3 [1\ 1\ \bar{2}\ 0] \Rightarrow a/3 [1\ 0\ \bar{1}\ 0] + a/3 [0\ 1\ \bar{1}\ 0]$  (indicated by an arrow in Fig. 1) [5].

Other features often observed in these powders of virgin  $\text{LiCoO}_2$  are moiré fringes formed by double diffraction of

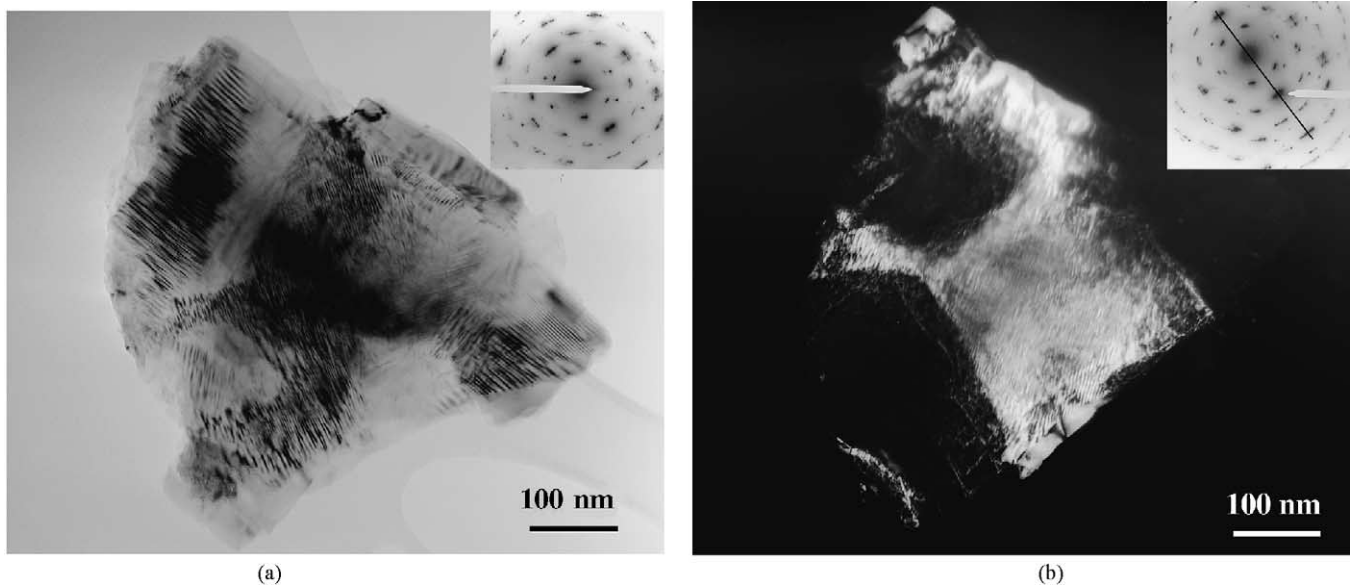


Fig. 2. (a) Uncycled  $\text{LiCoO}_2$  particle covered with moiré fringes. (b) Dark field image illustrating the orientation relationship between moiré fringes and excited lattice reflection. The direction of the moiré fringes is indicated by the line drawn into the diffraction pattern.

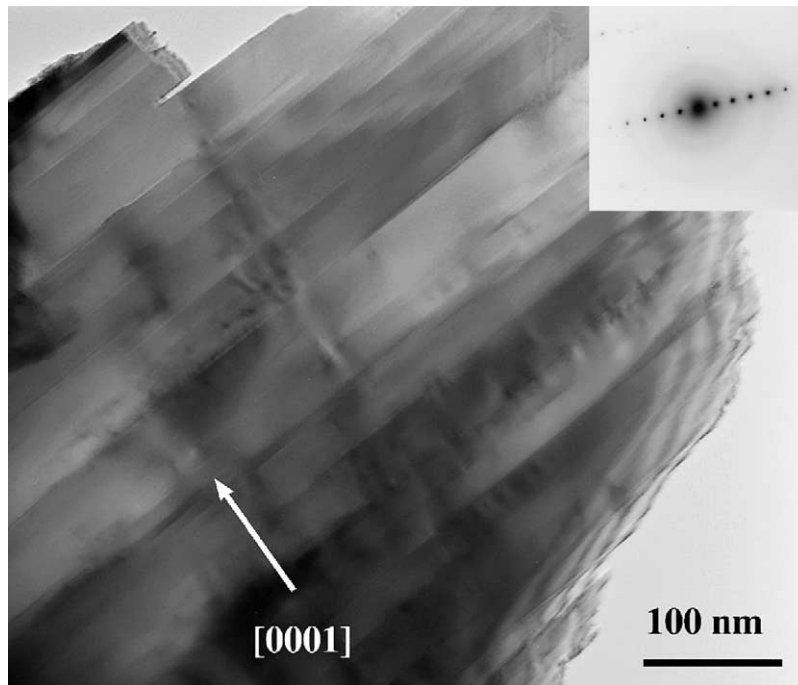
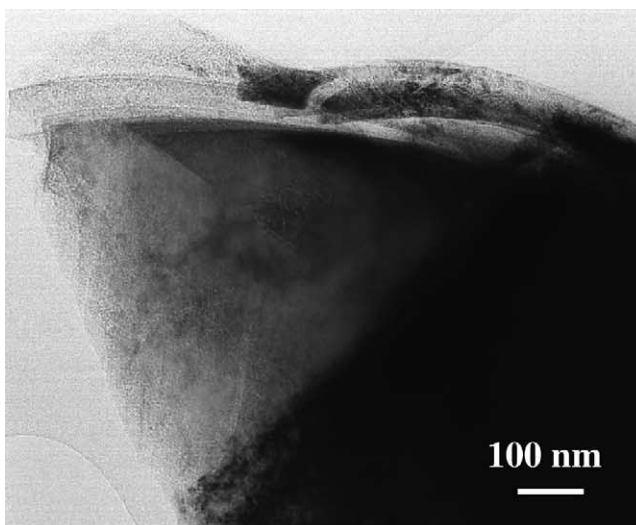


Fig. 3. Cross-section illustrating the stacking of crystallites that form a  $\text{LiCoO}_2$  particle.

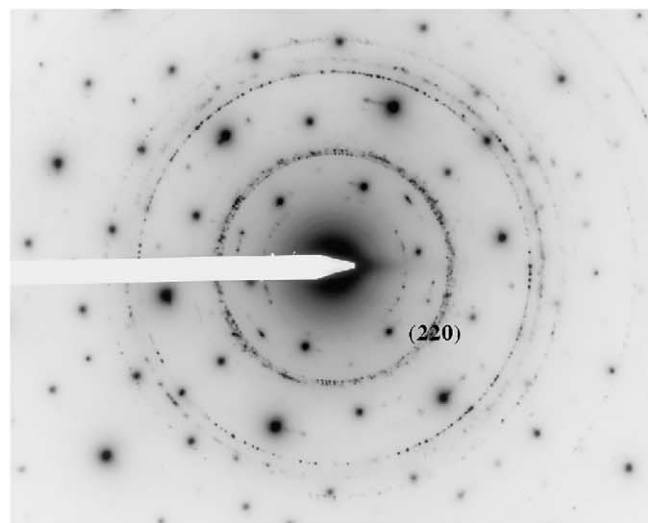
the beam in overlaying crystal sheets (Fig. 2a). We analyzed several orientations of the fringe patterns with respect to the diffraction spots active for image formation. From these analyses, the nature of the double diffractions could be determined. In uncycled  $\text{LiCoO}_2$ , we found that the moiré patterns are caused by double diffraction from overlapping crystallites having the same lattice constants, but rotated with respect to each other about the  $c$ -axis, i.e. they were “rotational moiré fringes” (Fig. 2b). In Fig. 3a, cross-section of a particle is shown which illustrates the stacking of separate crystal sheets.

### 3.2. Cycled $\text{LiCoO}_2$

After 334 cycles, we found microstructural changes in the  $\text{LiCoO}_2$ , especially at the surfaces of the particles. In some places thick surface layers (approximately 100 nm thickness) peel off the particle (see Fig. 4a). The diffraction pattern of Fig. 4b shows new diffraction spots that lie halfway between the fundamental  $\langle 1\ 1\ \bar{2}\ 0 \rangle$  diffraction spots observed in the uncycled material. By comparison to diffraction patterns calculated for different structures, we identified this diffraction pattern as one of the cubic spinel structure.



(a)



(b)

Fig. 4. (a) Surface degradation after 334 cycles. (b) SAD pattern after cycling showing the  $\{2\ 2\ 0\}$  superlattice diffraction of the cubic spinel structure.

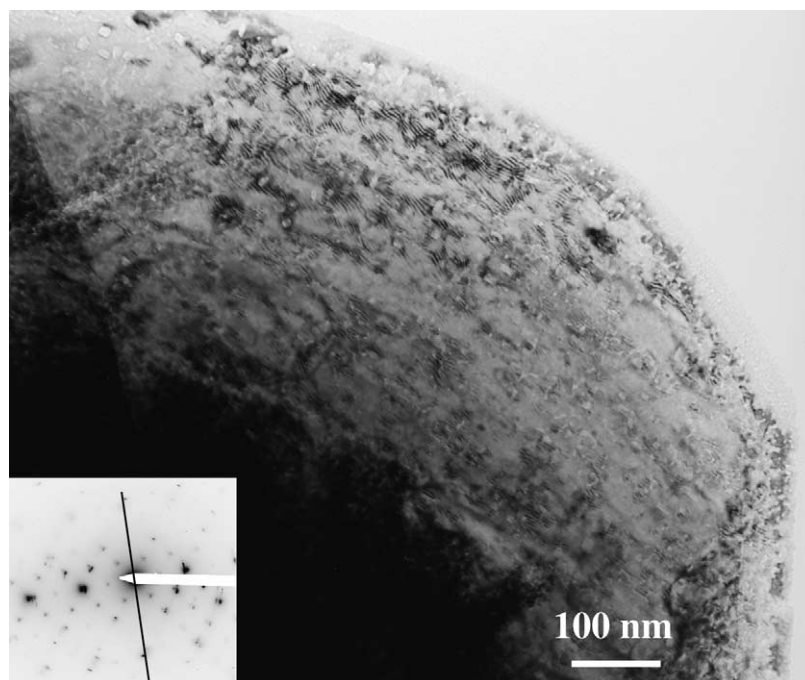


Fig. 5. The superposition of cubic spinel phase and hexagonal layered phase gives rise to formation of parallel moiré fringes. The orientation of the fringes with respect to the exited lattice reflection is indicated by the line drawn into the diffraction pattern.

Fig. 5 shows moiré fringes observed in the cycled material. From the orientation relationship between the direction of the fringe pattern and the active diffraction for image formation, these fringes were identified as parallel moiré fringes. They are caused by double diffraction from two overlapping crystals with parallel lattice planes, but the planes have different  $d$ -spacing. We found the lattice spacing in the spinel phase to be slightly smaller (approximately 0.135 nm) than the corresponding hexagonal lattice spacing (approximately 0.143 nm), accounting for the observed parallel moiré fringes.

#### 4. Discussion

The structure of uncycled  $\text{LiCoO}_2$  is the well-known trigonal or hexagonal phase of  $R\bar{3}m$  symmetry, consisting of oxygen atoms in ABC stacking separated by layers of Li and Co cations in octahedral interstitial sites. A typical diffraction pattern of the  $[0001]$  zone axis was shown in Fig. 1. After extensive electrochemical cycling, a new set of diffraction spots was observed at distances halfway between the diffraction spots of the starting material (Fig. 4b). This indicates a change in the crystal structure. These diffractions were  $\{220\}$  superlattice diffractions, characteristic of the cubic spinel phase. Wang et al., observed these diffractions in cycled  $\text{LiCoO}_2$  [3]. For comparison to their experimental observations, these authors modeled the structure of the cubic spinel phase as having variable occupancies of Li atoms on octahedral 16c and tetrahedral 8a and 8b sites. From the SAD and X-ray patterns simulated for these model

crystals, the authors concluded that the  $\{220\}$  superlattice diffractions in cycled  $\text{LiCoO}_2$  were caused by a cubic spinel with site occupancy (octahedral)  $\text{Co}_{16d}$  and (tetrahedral)  $\text{Li}_{8a}$ . The possibility of Li occupying octahedral 16c positions was ruled out because no superlattice diffractions were observed in the simulation. These structures have been reported before by Gummow et al. [6] and Rossen et al. [7]. It is noteworthy, however, that Wang et al. performed their diffraction simulations for lattices consisting of cations only—there were no contributions from oxygen. This is an acceptable practice in most cases. Unlike these authors, however, we find it is not possible to distinguish between octahedral or tetrahedral site occupancy of the Li atom by SAD using merely the presence of  $\{220\}$  superlattice diffractions. In our model crystals, we included oxygen atoms in 32e positions ( $z = 0.25$ ). We found  $\{220\}$  superlattice diffractions for both tetrahedral and octahedral site occupancies of Li, with differences occurring only in relative intensities. Fig. 6 shows a comparison of X-ray profiles for the cubic spinel  $\text{LiCoO}_2$  with both Li and Co sitting on octahedral 16d and 16c sites, respectively. It is clearly seen that when the oxygen atoms are present (Fig. 6a) a  $\{022\}$  peak occurs. This peak disappears when no oxygen atoms are used in the model crystal (Fig. 6b), indicating incorrectly that no superlattice diffractions could be observed in electron diffraction. The comparison of Fig. 6a and b shows that the contribution of all atoms in this unit cell needs to be considered in order to make correct predictions of diffraction patterns.

The simulation of X-ray diffraction patterns also shows that with the transition from the hexagonal layered phase to the cubic spinel phase, there is a disappearance of the

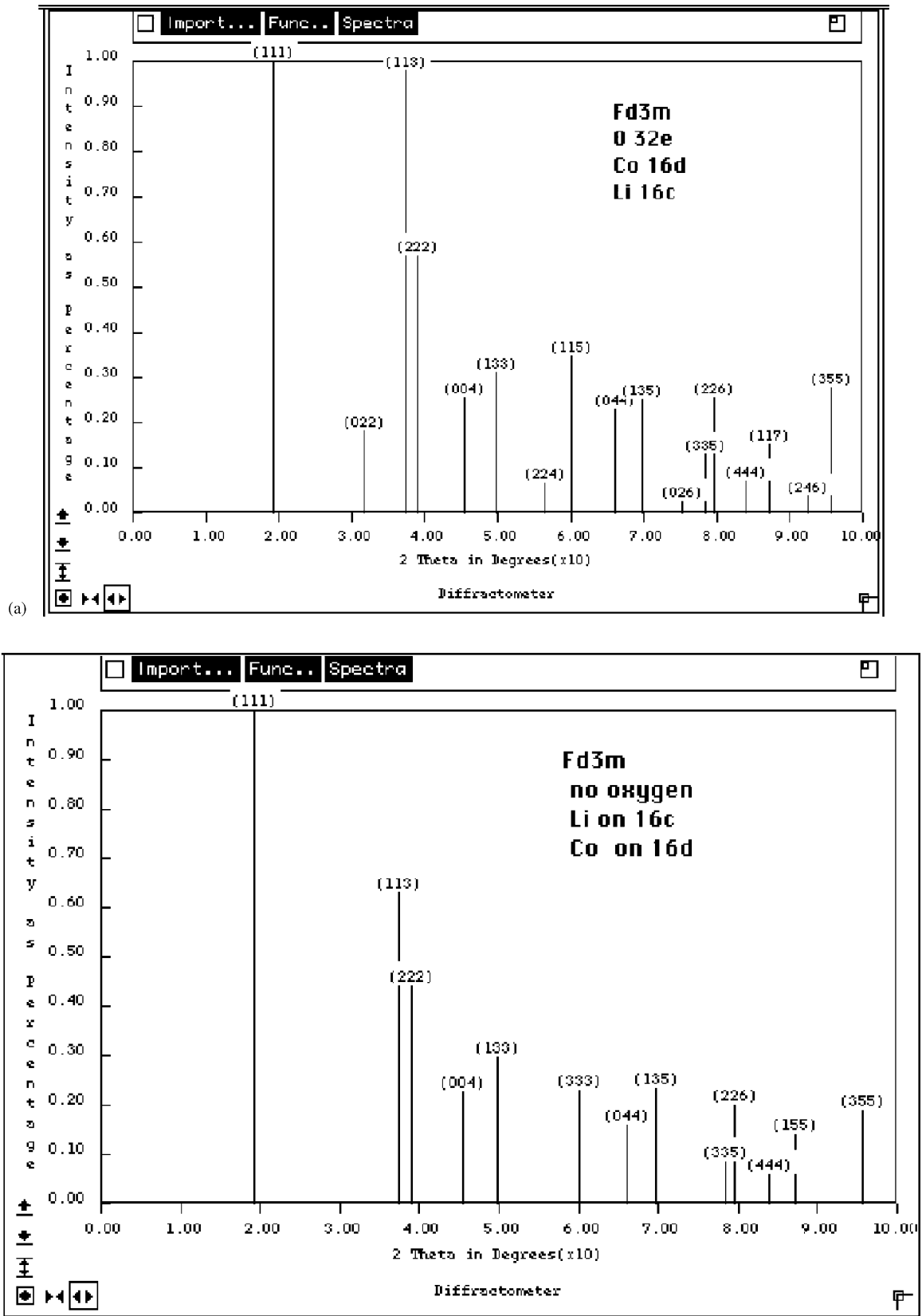


Fig. 6. (a) Simulated X-ray diffraction pattern for cubic spinel with O, Co and Li on 32e, 16d and 16c positions, respectively. Notice the presence of {0 2 2} peak. (b) Simulated X-ray diffraction pattern for cubic spinel with Co and Li on 16d and 16c positions, respectively, no contribution of oxygen. Notice the absence of {0 2 2} peak.

(0 0 0 6) diffraction peak that lies between the  $(\bar{1}101)$  and the (0 1 1 2) peaks (Co K $\alpha$ ). Consequently, only two peaks are observed in the spinel phase near  $2\theta = 40^\circ$  (in Fig. 6), instead of three peaks in the layered phase. An example of this change is seen in Fig. 4 of Murphy et al., for LiCoO<sub>2</sub> cycled 286 times at room temperature [4].

## 5. Conclusions

LiCoO<sub>2</sub> subjected to electrochemical cycling undergoes a phase transition from the trigonal layered phase to the cubic spinel phase. The reduced electrochemical activity of the spinel phase is in part accountable for the observed capacity loss after high cycle numbers. Additionally, degradation of the particle surfaces may decrease the active volume of the cathode by impeding the electrical contact to particles of LiCoO<sub>2</sub>.

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