



Chemistry and Structure of Sony's Nexelion Li-ion Electrode Materials

**by J. Wolfenstine, J. L. Allen,
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14. ABSTRACT The composition and structure of Sony Corporation's new 14430 lithium-ion battery electrodes was investigated. It was observed that the anode is a composite consisting of an equal amount on a weight basis of graphite and an amorphous alloy phase. The alloy phase consists mainly of tin and cobalt, with a tin:cobalt ratio of about 1:1. The particle size of the alloy phase is less than 1 µm. For the cathode it was observed that it is a composite consisting of a majority LiCoO₂ phase and a second phase (15 to 20 volume %) whose formula is of the form Li(Co_yNi_{1.7x}Mn_x)O₂. The particle size of both phases is in the micron range with many particles for the Li(Co_yNi_{1.7x}Mn_x)O₂ phase in the range between 10 and 20 µm.					
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1. Introduction

Recently, Sony Corporation of Japan has started producing a new 14430-size lithium (Li)-ion cell (14 mm in diameter by 43 mm tall) known as “Nexelion¹” for use as a four-cell battery pack in Handycam camcorder products (1-3). The 14430 Nexelion cell has several advantages over the existing (conventional) 14430 Li-ion cells. According to Sony, these include (1-3): (a) 30% increase in capacity (910 milliAh versus 700 milliAh), (b) 20% increase in power (3.15 Watthour versus 2.6 Wh at rates of 0.2C), (c) 20% increase in volumetric energy density (478 Wh/l versus 395 Wh/l), (d) 10% increase in weight energy density (158 Wh/kg versus 144 Wh/kg), (e) quicker charging times at room temperature (20% increase in charge efficiency), and (f) improved charge and discharge performance at low temperatures (40% increase in discharge capacity at -20 °C). Sony states that most of the advantages result from the change in electrode chemistry in the Nexelion cell compared to the conventional cell (1-3). The anode in the conventional 14430 cell is graphite while the cathode is lithium cobalt oxide. Sony has stated that the anode in the Nexelion cell, also called a hybrid Li-ion cell, is a tin-based amorphous anode consisting of multiple elements such as tin, cobalt, and carbon, whose elements are mixed on the nanometer level. The cathode in the Nexelion cell is a multi-stage composite cathode consisting of a mixture of cobalt, manganese, nickel oxides, and lithium cobalt oxide. From the press releases, it can be observed that very little detailed information about the chemistry and structure of the electrode materials in the 14430 Nexelion cell is available. In order to gain a detailed understanding of the enhanced performance of the 14430 Nexelion cell, such information is needed. Thus, it is the purpose of this technical note to present information about the chemistry and structure of the anode and cathode materials in the 14430 Nexelion cell.

2. Results and Discussion

2.1 Overview

A Handycam camcorder pack was obtained from PC Nation (4). The pack was cut open and the four 14430 Nexelion cells were removed. The dimensions of a typical 14430 Nexelion cell are given in table 1. A 14430 Nexelion cell was cut open for analysis. For chemical and structural analysis, anode powders were removed from the copper current collector while cathode powders were removed from the aluminum current collector.

¹ Nexelion is a trademark of Sony Corporation.

Table 1. Typical dimensions of a 14430 Nexelion cell.

Height (mm)	Diameter (mm)	Weight (g)
14	43	20

2.2 Anode

2.2.1 Composition

To get a first approximation of the elemental composition of the Nexelion anode, energy dispersive x-ray spectroscopy (EDS) was undertaken. Figure 1 shows a typical EDS spectrum for the Nexelion anode powders.

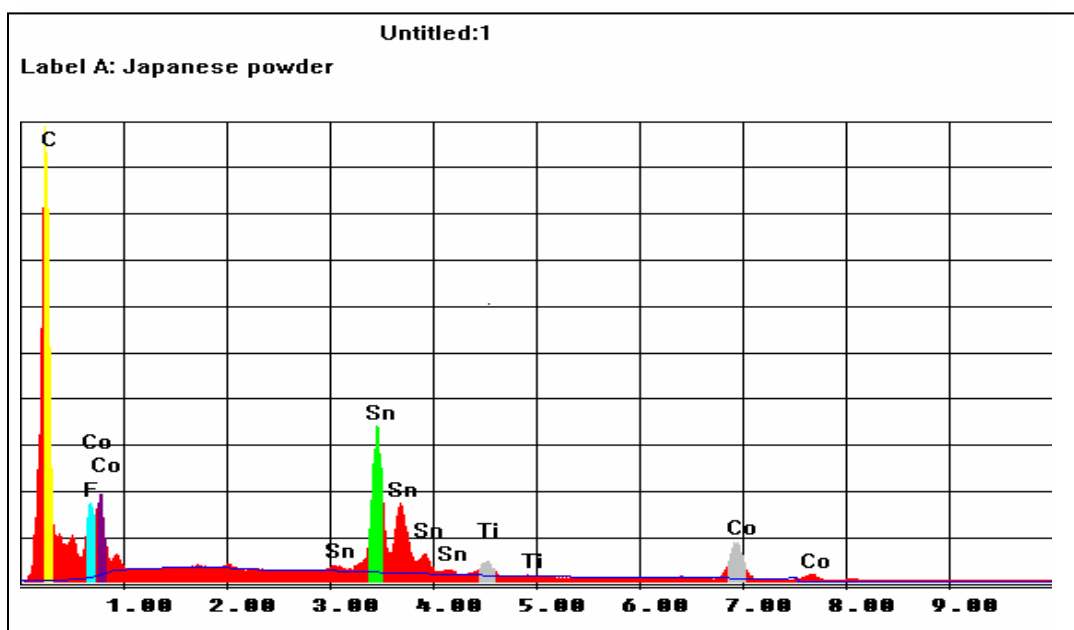


Figure 1. EDS spectrum of the Nexelion anode powders.

From figure 1 it can be seen that the powder contains cobalt, tin, titanium, fluorine, and carbon. EDS suggested that the major elements were cobalt, tin, and carbon. The presence of tin, cobalt, and carbon is in agreement with Sony press release information (1-3). Fluorine most likely comes from the binder. Titanium was not mentioned in the Sony press releases or a Sony Corporation patent (5) on tin-cobalt alloy anodes.

Based on the EDS results, the anode powders were sent to Galbraith Laboratories, Inc. (Knoxville, TN) to quantitatively determine the amount of cobalt, tin, carbon, and titanium. The amount of cobalt, tin, and titanium was determined by inductively coupled plasma (ICP). The amount of carbon was determined by a combustion method. The weight % for these elements is listed in table 2.

Table 2. Weight % of elements in the Nexelion anode.

Element	Weight %
Carbon	35.86
Tin	27.3
Cobalt	16
Titanium	2.42

From table 2 it can be seen on a weight % basis that the ratio of carbon to alloy (tin, cobalt, and titanium) is about 36 wt. % : 46 wt. % ~ 0.8 . This ratio is in agreement with the ratio of 45 wt. % graphite : 45 wt. % alloy ~ 1.0 given in the Sony Corporation patent (5).

With the data in table 2, several Nexelion anode compositions were determined and are listed in table 3.

Table 3. Nexelion anode composition(s).

Elements	Composition
Sn and Co	$\text{Sn}_{0.47}\text{Co}_{0.53}$
Sn, Co and Ti	$\text{Sn}_{0.42}\text{Co}_{0.49}\text{Ti}_{0.09}$
Sn, Co and C	$\text{Sn}_{0.07}\text{Co}_{0.08}\text{C}_{0.85}$
Sn, Co, C and Ti	$\text{Sn}_{0.065}\text{Co}_{0.076}\text{Ti}_{0.014}\text{C}_{0.85}$

The data in table 3 reveal several important points. First, they suggest that the major constituents in the alloy are tin and cobalt, with a tin:cobalt ratio of about 1:1. EDS analysis also suggested that the tin:cobalt ratio is about 1:1. This ratio is within the tin:cobalt ratio investigated in the Sony Corporation patent (5). Second, the major constituent on an atomic % is carbon, with an amount $> 80\%$.

2.2.2 Phases

In order to determine the phases present in the Nexelion anode powders, x-ray diffraction was undertaken. X-ray diffraction was conducted using Cu K alpha radiation. An x-ray diffraction pattern of the Nexelion anode powders is shown in figure 2.

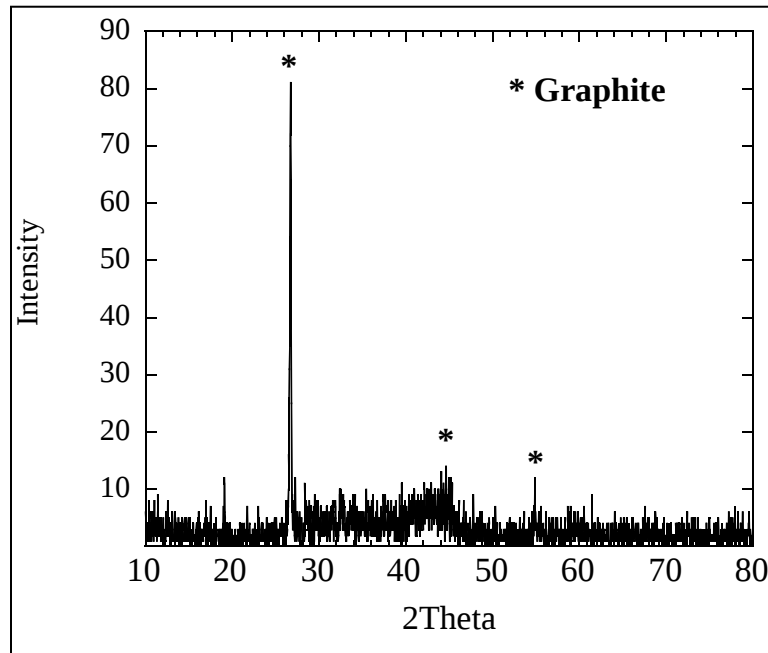


Figure 2. X-ray diffraction pattern of the Nexelion anode powders.

From figure 2 two important points are noted. First, the only crystalline peaks exhibited in the powders are for graphite. Second, no crystalline peaks could be observed for any tin-cobalt alloys or tin and cobalt. The lack of any crystalline peaks for the tin:cobalt alloy suggests that the alloy is amorphous. This observation is in agreement with the Sony press releases (1-3). In addition, there is an unidentified peak around $2\theta \sim 19^\circ$.

2.2.3 Microstructure

A typical scanning electron micrograph of the Nexelion anode powders is shown in figure 3. From scanning electron micrographs it was observed that most of the tin:cobalt alloy particles were equiaxed with particle sizes less than $1\ \mu\text{m}$. However, many of these particles were agglomerated into larger particles.

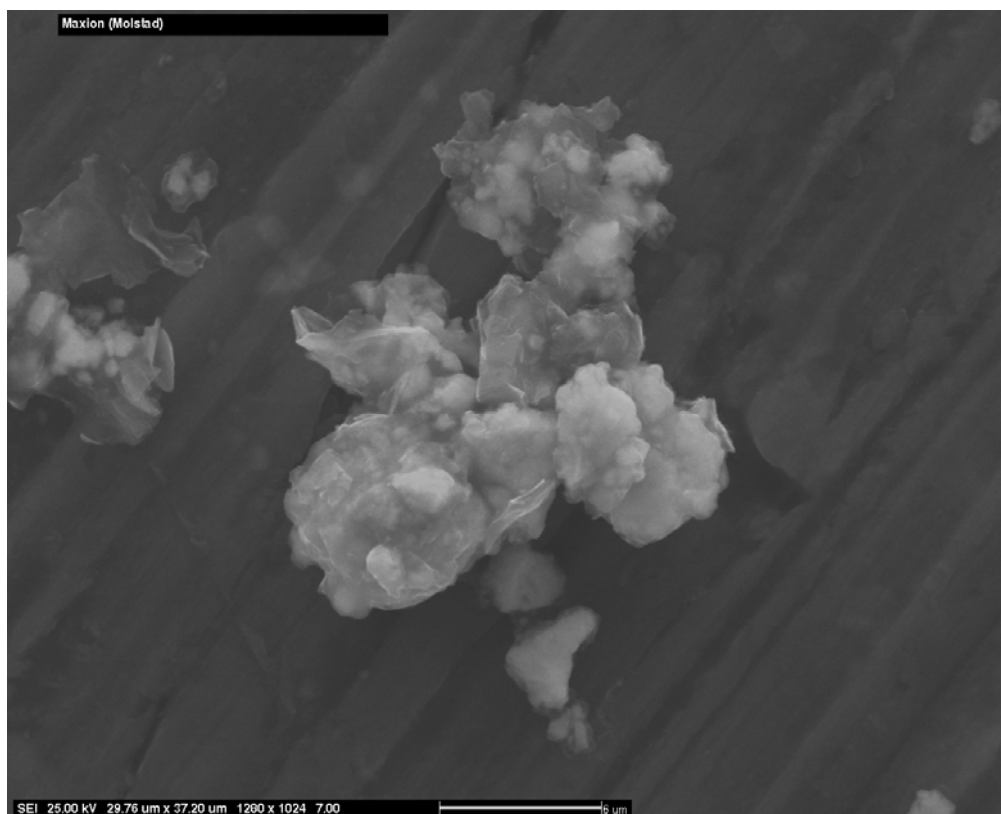


Figure 3. Scanning electron micrograph of Nexelion anode powders.

The chemistry and structural results suggest that the Nexelion anode is a composite consisting of a graphite phase and an amorphous alloy phase, consisting of tin and cobalt, with a tin:cobalt ratio of about 1:1, where the particle size of the alloy phase is less than 1 μm.

2.3 Cathode

2.3.1 Composition

The EDS spectrum of the elements present in the Nexelion cathode powders is shown in figure 4.

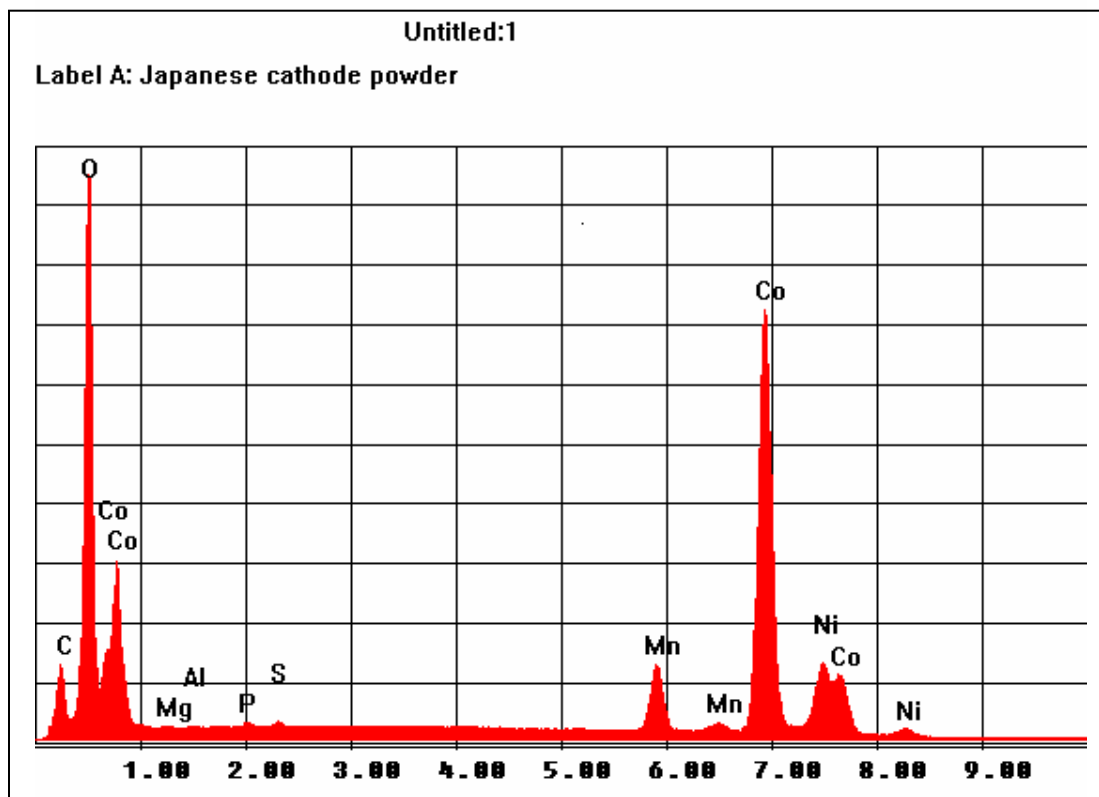


Figure 4. EDS spectrum of the Nexelion cathode powders.

From figure 4 it is observed that the Nexelion cathode powders contain cobalt, manganese, nickel, and oxygen as the major elements. This is in agreement with Sony information (1-3). In addition, EDS revealed the presence of carbon, magnesium, phosphorous, aluminum, and sulfur. It is highly likely that the source of the aluminum and magnesium is from the active cathode material. The other trace elements come from the binder, conductive additive, or electrolyte. Lithium is not observed in the EDS spectrum because it has too low of an atomic number to be detected with EDS.

Cathode powders were sent to Galibraith Laboratories, Inc., to quantitatively determine the amount of cobalt, manganese, and nickel. The amount of cobalt, manganese, and nickel was determined by ICP. The weight % for these elements is listed in table 4. The weight % determined by ICP for cobalt, manganese and nickel is in close agreement with the EDS results.

Table 4. Weight % of elements
in the Nexelion cathode.

Element	Weight %
Cobalt	48.1
Nickel	5.73
Manganese	3.12

3.2.3 Phases

An x-ray diffraction pattern of the Nexelion cathode powders is shown in figure 5.

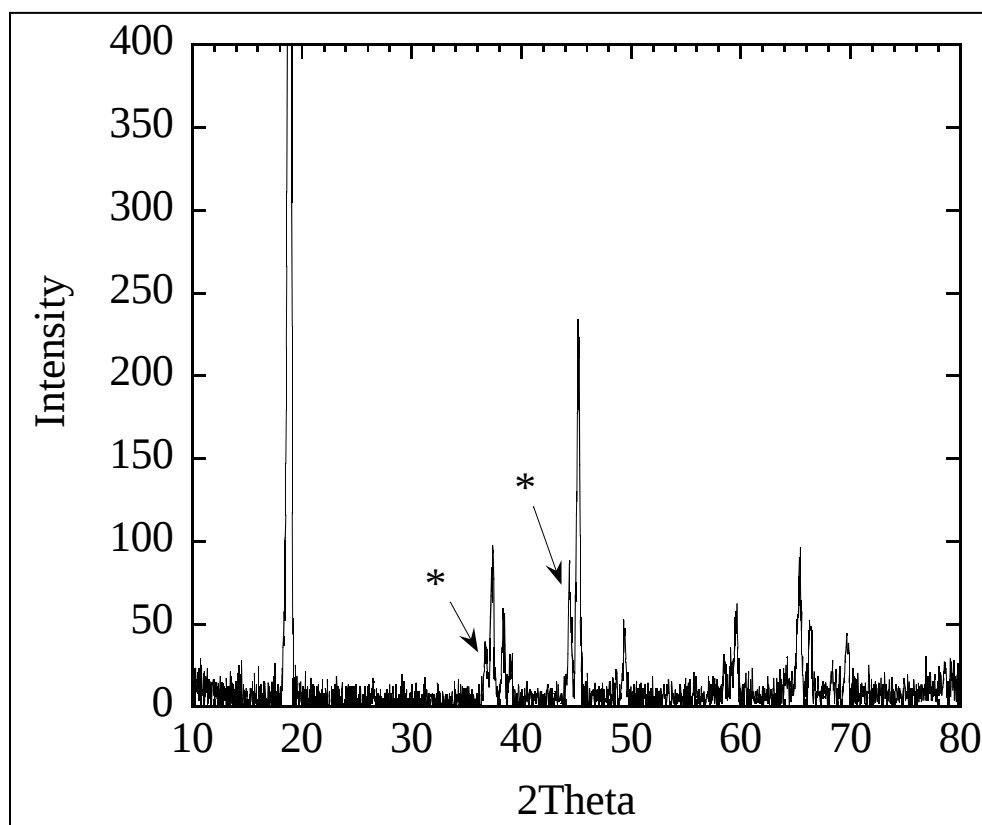


Figure 5. X-ray diffraction pattern of the Nexelion cathode powders.

The x-ray diffraction pattern for the Nexelion cathode powders reveals sharp crystalline peaks. All the peaks except those marked with an * are identified as LiCoO_2 . At present, the second phase marked with an * cannot be identified.

2.3.3 Microstructure:

A scanning electron micrograph of the Nexelion cathode powders is shown in figure 6.

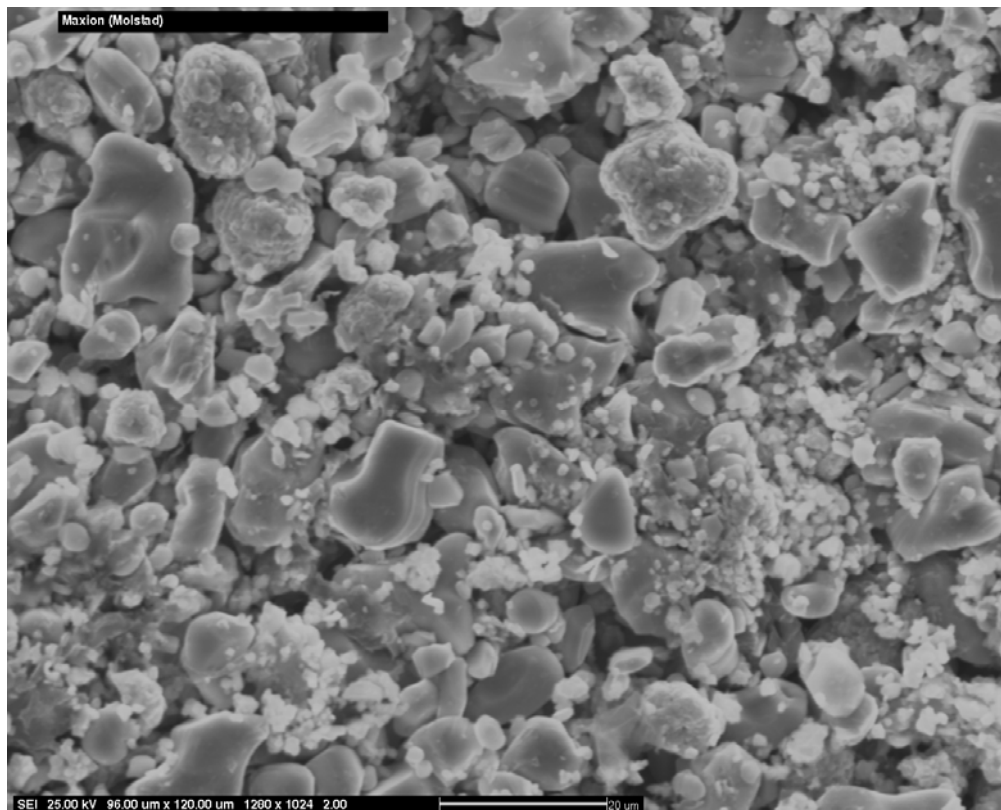


Figure 6. Scanning electron micrograph of the Nexelion cathode powders.

From figure 6 it can be seen that the particles of the cathode are fairly equi-axed with particle sizes in the micron range. Several particles have sizes between 10 and 20 μm . X-ray mapping revealed that most of the larger particles were second phase particles (rich in nickel and manganese and deficient in cobalt). From the x-ray maps it was estimated that the volume % of second phase is ~ 15 to 20 %.

The chemistry and structural results suggest that the Nexelion cathode is a composite consisting of a majority LiCoO_2 phase and a second phase (15 to 20 volume %) whose formula is of the form $\text{Li}(\text{Co}_y\text{Ni}_{1.7x}\text{Mn}_x)\text{O}_2$, with particle sizes in the micron range for both phases. At present, the values for x and y cannot be determined. Based on the nickel: manganese ratio (1.7:1) given in table 1 and using charge balance (assuming Co^{+3} , Ni^{+2} and Mn^{+4} (6)), it is tempting to suggest in a first approximation that the second phase has the following composition; $\text{Li}(\text{Co}_{0.36}\text{Ni}_{0.4}\text{Mn}_{0.24})\text{O}_2$. However, much more information is required to accurately determine the exact composition of the second phase.

3. Conclusions

The chemistry and structural results suggest that the Nexelion anode is a composite consisting of an equal amount on a weight basis of a graphite and an amorphous alloy phase. The alloy phase consists mainly of tin and cobalt, with a tin:cobalt ratio of about 1:1. The particle size of the alloy phase is less than 1 μm .

The chemistry and structural results suggest that the Nexelion cathode is a composite consisting of a majority LiCoO_2 phase and a second phase (15-20 volume %) whose formula is of the form $\text{Li}(\text{Co}_y\text{Ni}_{1.7x}\text{Mn}_x)\text{O}_2$. The particle size of both phases is in the micron range with many particles for the $\text{Li}(\text{Co}_y\text{Ni}_{1.7x}\text{Mn}_x)\text{O}_2$ phase in the range between 10 and 20 μm .

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