A TEM study of cycled nano-crystalline HT-LiCoO₂ cathodes for rechargeable lithium batteries

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Abstract

LiCoO₂ has a NaFeO₂ structure type and it has been reported that layered cation ordering is preserved during repeated insertion and removal of Li⁺. We have observed, at a nano-particle scale, cation disorder induced in LiCoO₂ after prolonged cycling. LiCoO₂ cathode powders with nano-grain sized of 70–300 nm were synthesized by a mechano-chemical method. Transmission electron microscopy study of LiCoO₂ showed that the initial O₃ crystal structure partially transformed to a cubic spinel phase. This spinel phase formation may be responsible for capacity degradation after prolonged cycling of LiCoO₂-based rechargeable lithium batteries. Cycle life of small size (70 nm) LiCoO₂ powder until 200 cycles is better than that of large size (300 nm) LiCoO₂ powder due to shorter diffusion distance.

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1. Introduction

LiCoO₂ heat-treated above 700 °C (HT-LiCoO₂) has a high cycle life compared to other cathode materials, such as LiNiO₂ and LiMn₂O₄. The structure of LiCoO₂ is rhombohedral (R₃m space group) with lattice parameters $a = 2.816$ Å and $c = 14.051$ Å in a hexagonal setting. 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 [1–4]. Recently, an useful method for the preparation of nano-crystalline individual oxides has been found during studies of mechano-chemical solid state exchange reactions [5,6]. Mixing the reaction products with inert thermostable salt prevents particle coarsening during further heat treatment of the reaction mixture. Combination of salt encapsulation with an earlier proposed powder engineering technique [7,8] ensures fine particle size control of LiCoO₂ powders obtained by wet chemical methods [9].

During delithiation, Li₁ₓCoO₂ experiences a sequence of phase transformations involving Li ordering within its octahedral layers, accompanied by changes in crystal symmetry, first to the monoclinic and then to the hexagonal phase. There have been many studies on how the crystal structure changes over one charge–discharge cycle [10–12]. The typical reversible limit of delithiation for Li₁ₓCoO₂ in commercial batteries is $x \sim 0.5$ [2], corresponding to a charge capacity of ~140 mA h/g. This has been mostly attributed to mechanical failure associated with the large change in the c-axis dimension, rather than any changes in cation ordering. There have been few studies, however, on how the crystal structure changes after prolonged cycling [13]. In the present work, we have used transmission electron microscopy (TEM) to study microstructural changes of nano-crystalline LiCoO₂ after prolonged cycling.

2. Details of experiment

An aqueous solution of Li and Co acetates (Li/Co = 1:1) was frozen by spraying on liquid nitrogen followed by freeze drying for 2 days at $P = 5 \times 10^{-6}$ mbar (Alpha 2–4, Christ). A part of the freeze-dried product was mixed with K₂SO₄ (1:10) and subjected to planetary milling (Pulverisette-5, Fritsch) in ZrO₂ media at 600 rpm for 24 h (ball to powder...
mass ratio of 10:1). Thermal decomposition of a precursor and a precursor mixture with K$_2$SO$_4$ was performed in air first at 400 °C for 10 h, then at 800 °C for 12 h. The thermally processed mixture was washed by distilled water several times for elimination of SO$_4^{2-}$ ions; LiCoO$_2$ residue was separated by centrifuging.

Obtained LiCoO$_2$ powders have been studied by XRD (Geigerflex, Rigaku, 2°/min, Cu Kα), scanning electron microscopy (SEM, Philips ESEM) and TEM (Philips CM-30, $U = 200$ kV). Commercial LiCoO$_2$ powder, supplied by Seimi Co. was used for comparison.

Electrochemical characterizations were performed using a CR2032 coin-type cell with the following parameters: cut-off voltage 3.2–4.2 V and $I = 0.5$ mA at room temperature. The cathode was fabricated with 20 mg of accurately weighed active material and 12 mg of conductive binder (8 mg of teflonized acetylene black (TAB) and 4 mg graphite). The cathode was pressed on 200 mm$^2$ stainless steel.
steel mesh, which was used as the current collector, under a pressure of 300 kg/cm² and subsequently dried at 180°C for 24 h in a vacuum oven. The test cell was made of cathode and a lithium metal as an anode separated by a porous polypropylene film (Celgard 3401). A mixture of 1 M LiPF₆-ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:2 by vol., Merck) was used as the electrolyte.

We focused on a cell that was electrochemically cycled 10 times and the cycled material left in the discharged (lithiated) state. The cell was disassembled and cycled LiCoO₂ powders were obtained by washing in n-methyl-pyrrolidinone (NMP) to dissolve the binder. Specimens for TEM analysis were prepared from a suspension of LiCoO₂ powder in methanol. A droplet was placed on a carbon film supported by a copper grid.

3. Results and discussion

SEM analysis of the LiCoO₂ powders, obtained by matrix isolation of precursor particles by K₂SO₄, confirmed the efficiency of this method in terms of grain coarsening prevention. Commercial Seimi Co. powder (powder A) formed micron-sized crystallites (Fig. 1A), while K₂SO₄-processed powder (powder B) was characterized by a grain size distribution in a range of 30–70 nm (Fig. 1B).

XRD analysis of micron-sized (powder A) and nano-crystalline powders (powder B) revealed the formation of single phase hexagonal HT-LiCoO₂ in both cases (Fig. 2A and B). Processing of LiCoO₂ powders at 800°C in contact with K₂SO₄ was not accompanied by formation of secondary phases or by significant displacement of the main reflections displayed in the formation of solid solutions. Sharp and well-resolved reflections of both patterns were observed at perfect crystallographic ordering. The uncharacteristic (0 0 3)/(1 0 4) peak ratio for the nano-crystalline powder can be related to anomalies of element distribution within the Co sublattice [14]. Comparing the XRD of uncycled (Fig. 2A and B) and cycled cathodes (Fig. 2C and D), we confirmed that the characteristic peak positions of the LiCoO₂ phase remained unchanged. Extraneous peaks in the cycled cathodes arose from the binder. The relative intensities of the peaks changed; however, this may be due to varying levels of preferential orientation introduced during preparation of the XRD samples.

The electron diffraction pattern of powder A, recorded along the [0001] zone axis, was also typical for well-ordered LiCoO₂ with hexagonal structure (Fig. 3A). The major spots corresponded to the {1 1 2 0} reflections. On the other hand, SAED pattern of the small particles in powder B (Fig. 3B) partially contained cubic spinel phase. These patterns were attributed to the formation of a spinel structure due to cation disorder in the hexagonal lattice of LiCoO₂. In the case of powder B, partial cubic spinel phase affected the electrochemical characteristics of the LiCoO₂ cathode. This result is discussed hereafter.

After electrochemical cycling some particles displayed a variety of contrast features including strain contours and other extended defects as compared to uncycled powders. Stresses can arise from lattice expansion and contraction, because upon delithiation LiₓCoO₂ exhibits a c-axis expansion of up to 1.8% at x = 0.5, followed by a c-axis contraction of up to −1.8% at x = 0.2 [11]. Microstructural changes in LiCoO₂ were observed after 10 cycles. The diffraction pattern of Fig. 4, recorded along the [1 1 1] zone axis, shows weak new diffraction spots that lie halfway between the fundamental {1 2 0} diffraction spots (⟨1 1 2 0⟩ reflections at [0001] zone axis) observed in the uncycled material. This indicates a change in the crystal structure. These diffractions were {2 2 0} superlattice diffractions, characteristic of the cubic spinel phase. Cubic spinel LiCoO₂ with both Li and Co sitting on octahedral 16c and 16d sites displayed a {2 2 0} peak. We confirmed from diffraction patterns that the initial O₃ crystal structure partially transformed to a cubic spinel phase after electrochemical cycling.

In addition, other new reflections appeared in the cycled powders of both powder A and B. These reflections, in-
dexed as \{110\} (\{100\}) reflections at [0001] zone axis), are forbidden reflections for HT-LiCoO2. We occasionally observed these reflections in uncycled powders calcined at lower temperatures as well. The \{110\} reflections remain extinct as long as the cation site symmetry is unchanged and all cations within each layer have identical properties. Instead, when Li/Co substitutional disorder occurs, the cation sites are chemically inhomogeneous and the cation site symmetry is reduced. Therefore, these crystallographic defects can cause \{110\} reflections (Fig. 4).

Fig. 5 shows the cycle performance of coarse-grained (powder A) and nano-crystalline (powder B) LiCoO2 cathode. The initial discharge capacity of powder B is smaller than that of powder A. The smaller discharge capacity is due to the partial cubic spinel phase in powder B (Fig. 3B). Since the cubic spinel phase is less electrochemically active, its formation could be a source of the capacity loss. However, the cycle life of powder B until 200 cycles is better than that of powder A, due to smaller particle size.

4. Conclusions

We have observed, at a particle scale, cation disorder induced in LiCoO2 after prolonged cycling. Transmission electron microscopy study of LiCoO2 showed that the initial O3 crystal structure partially transformed to a cubic spinel phase. This spinel phase formation may be responsible for capacity degradation after prolonged cycling of LiCoO2-based rechargeable lithium batteries.

The initial discharge capacity of nano-crystalline LiCoO2 (powder B) is smaller than that of a coarse-grained LiCoO2 (powder A) cathode due to the partial cubic spinel phase in nano-crystalline LiCoO2. However, the cycle life of powder B until 200 cycles is better than that of powder A, due to smaller particle size.

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