

Particle size control of LiCoO₂ powders by powder engineering methods

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Abstract

The directed influence on the micromorphology of precursors during preparation of lithium cobaltate powders by chemical synthesis methods allows to control the size of LiCoO₂ crystallites from 4–6 μm to 60–100 nm. Localization of melting during thermolysis by mixing acetate precursors with foaming agents promotes the reduction of grain size from 4–6 down to 1–1.5 μm. More efficient prevention of grain coalescence can be performed by introducing a thermally stable inert encapsulation agent (K₂SO₄) removed by dissolution after thermal processing. The combination of this method with intense deagglomeration of precursor mixtures by planetary milling results in keeping the grain size at the level of primary LiCoO₂ particles (60–80 nm) even at $T=800$ °C. Intense mechanical processing of as-formed LiCoO₂ powders is undesirable due to negative influence on the crystallographic ordering processes.

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1. Introduction

LiCoO₂ is one of the principal 4 V cathode materials for the modern lithium rechargeable batteries, though a large number of factors affecting its electrochemical performance has not been studied until now. The crystallographic ordering, usually considered as a phase transition to high temperature (HT) modification of LiCoO₂, results in higher electrochemical capacity and lower fade rate during battery functioning. Dynamic electrochemical parameters of Li-ion batteries like rate capability attracted the growing attention last years. These properties are related not only to the crystallographic features but also to the micromorphology of LiCoO₂ powders: smaller cobaltate particles promote shorter pathways for solid state diffusion of Li ions. At the same time the information about dependence of electrochemical cyclability of LiCoO₂ cathodes on the particle size of cathode material is very limited. Most of

the papers contain no information about particle size of powders under investigation, or deal with powders with fixed grain size (usually 0.5–2 μm).^{1–4} The influence of powder annealing at 900 °C, accompanied by grain growth from 0.8–1 to 3–5 μm, is discussed in Ref. 5.

Main obstacle to establishing correlation between LiCoO₂ particle size and its functional parameters is lack of methods of the preparation of oxide powders with variable grain size. Usual way of obtaining a powder with various grain size is changing the synthesis technique. Meanwhile, the comparison of powders obtained by different synthesis methods is not fairly correct due to simultaneous influence of chemical pre-history on the crystallographic ordering, dominating type of defects, etc. This problem can be solved using powder engineering approach. Systematic study of the formation and evolution of powder micromorphology during thermolysis and further thermal processing resulted in developing the system of particle size control methods.^{6–9} Directed modification of the aggregate structure of powders at the intermediate stages of their synthesis allows to control the grain growth during further thermal processing and to obtain final oxide powders with various size of crystallites.

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Efficient method of particle size control has been recently proposed for the oxide nanopowders obtained by mechanochemical synthesis. Planetary milling of reaction products with excess of NaCl powder leads to the encapsulation of nanoparticles and prevention of their recrystallization during the following thermal processing.^{10–12} Combination of this technique with powder engineering methods might be a useful tool for controlling the size of crystallites in the submicron range.

2. Experimental

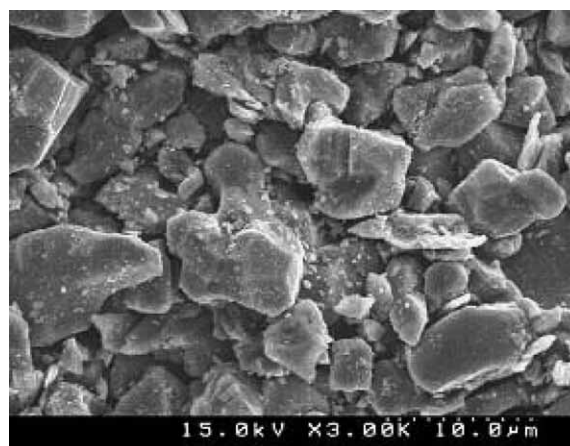
Preparation of precursors for LiCoO₂ synthesis was performed by freeze drying method. Aqueous solution of Li and Co acetates with Li/Co ratio 1.2/1 has been sprayed into liquid nitrogen and freeze dried at $P=0.2\text{--}0.3$ mBar. Mixing of precursor powders with various modifiers was realized by hand mixing in agate mortar, by wet milling in hexane in the ball mill with ZrO₂ balls at 130 rpm for 24 h or in planetary mill Pulverisette 5 (Fritsch) in ZrO₂ bowls at 600 rpm. Thermal decomposition of precursors was carried out by heating in air to 400 °C at 1–3 K/min followed by 6 h dwelling. In order to ensure identical conditions for the crystallographic ordering of various powders, all the samples were processed at 800 °C for 12 h in air. In order to remove inert soluble modifiers after thermal processing, powder samples were stirred twice in the excess of water (3 g of K₂SO₄/LiCoO₂ mixture per 100 ml H₂O) and centrifuged for LiCoO₂ separation.

3. Results and discussion

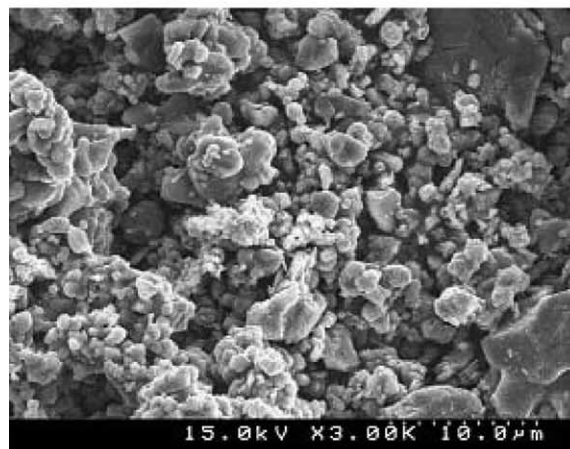
Usual particle size during synthesis of LiCoO₂ varies from 0.4 to 0.7 μm for chemical methods to several microns for solid state synthesis from oxides and Li₂CO₃. One of the main complications for the preparation of finely grained LiCoO₂ is a need to convert a low temperature modification, having a large number of defects and, hence, much poorer electrochemical properties, into ordered HT-polymorph. It is usually achieved by annealing of obtained LiCoO₂ at 750–850 °C. The process is usually accompanied by intensive grain growth. Due to these features, even the application of freeze drying method, usually producing rather small particles, without special precautions resulted in forming cobaltate particles of 4–6 μm in size (Fig. 1A).

Development of particle size reduction methods should be based on the features of formation and evolution of oxide particles during thermal decomposition. It is known that a large difference of specific molar volumes of precursor/intermediate phase and final phase leads to the destruction of precursor crystallites

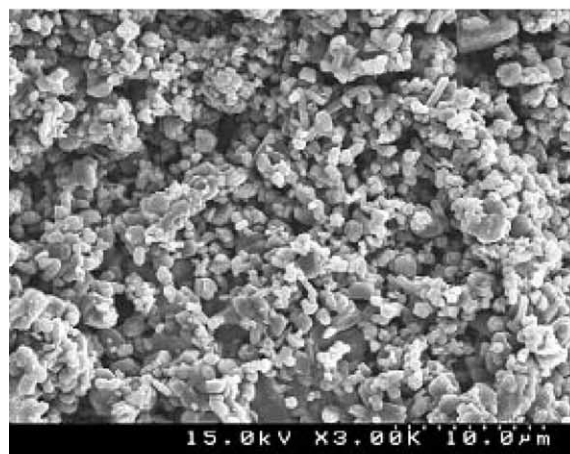
(Fig. 2A) to smaller (30–70 nm) particles of the oxide product of thermolysis. These new particles (Fig. 2B) are usually interconnected to primary aggregates, posed by precursor crystallites and similar with them in shape



(A)



(B)



(C)

Fig. 1. SEM micrographs of LiCoO₂ powders, obtained by thermal decomposition at 400 °C followed by annealing at 800 °C: (A) acetate precursor, $c=1$ M/l; (B) acetate precursor ($c=1$ M/l) + (NH₄)₂CO₃; (C) acetate precursor ($c=0.1$ M/l) + (NH₄)₂CO₃.

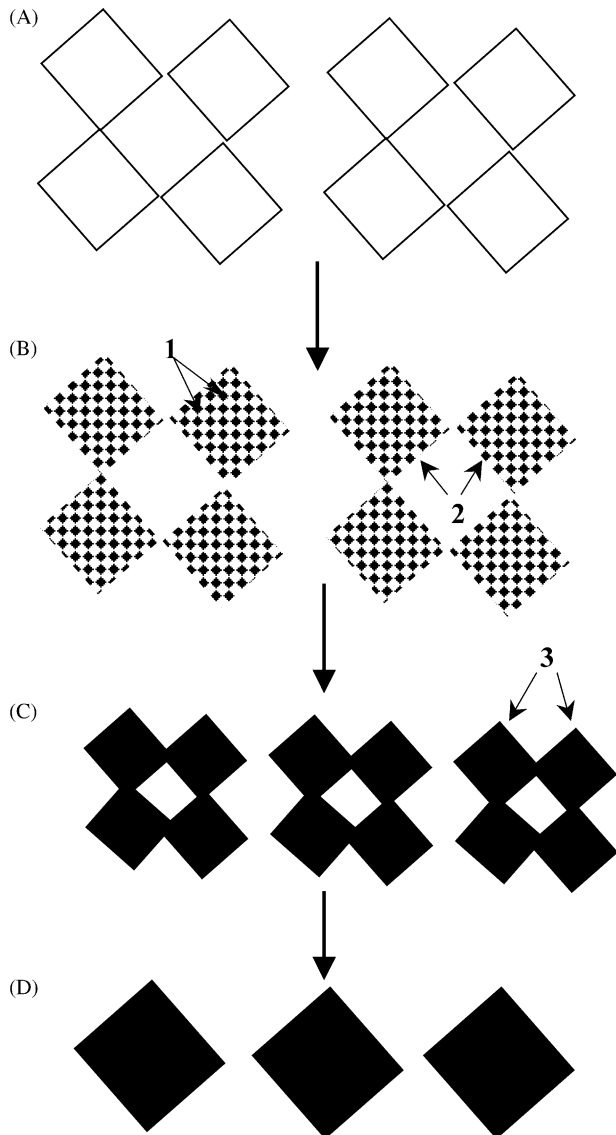


Fig. 2. Three stages of the morphological evolution of oxide powders during thermal decomposition and following thermal processing: (A) initial state (salt precursor or the last intermediate product of multistep process); (B) formation of the primary oxide particles network; (C) primary crystallization of the oxide product; (D) particle coarsening.

and size (/2/, Fig. 2B). Large excess of surface energy of crystallites /1/ causes their coalescence with the nearest neighbors in primary aggregates /2/ during thermolysis or further thermal processing and the formation of relatively stable crystallites of thermolysis products of 200–500 nm in size (/3/, Fig. 2C), typical for a large number of chemical synthesis methods of complex oxides. Further coarsening of particles /3/ (Fig. 2D) may occur during further higher temperature processing of powders or when their coalescence is promoted by liquid phases (eutectic melts, etc.).

Our investigation of thermal decomposition of freeze dried acetate precursor in air (see [13] for details of thermolysis mechanism) demonstrated that the process

is accompanied by the appearance of liquid phases at the intermediate stages of the process. In this case stages A–D (Fig. 2) may occur almost simultaneously, leading to the grain growth up to several microns. Full prevention of liquid phase formation for Li and Co acetates is rather complicated, but there are many ways to localize this process within small particles of precursor. One of them is foaming- mixing of precursor with inert agent forming large amount of gaseous products during thermolysis. Ammonium salts are very attractive from this point of view due to their ability to be completely decomposed without the formation of solid reaction products. Thermal decomposition of the mechanical mixture of Li–Co acetate precursor and $(\text{NH}_4)_2\text{CO}_3$ (1:6 by weight) is accompanied by substantial decrease of LiCoO_2 grain size (Fig. 1B).

Numerous authors discussed the correlations between micromorphology of salt precursors and their decomposition products. In spite of substantial contribution of the melting processes, similar relationship was also observed in our decomposition experiments. The decrease in concentration of the acetate stock solution for freeze drying synthesis, usually followed by the formation of more uniform aggregate structure of the salt precursor,⁶ resulted in complete disappearance of unusually large particles and in decreasing the mean size of crystallites to the submicron level (Fig. 1C).

Further reduction of the crystallite size demands a more efficient prevention of the coalescence of primary oxide particles (/1/, Fig. 2B). Low temperatures of ammonium salts decomposition confine the range of their efficient application within the initial stages of precursor thermolysis. Meanwhile, the grain growth occurs not only during thermal decomposition but also during subsequent thermal conversion of disordered reaction product into regular high temperature LiCoO_2 polymorph at 800 °C; hence, the elimination of particle coalescence is necessary at higher temperatures too. It can be achieved by means of method, proposed in Refs. 10–12 for stabilization of nanoparticles: crystallites and/or agglomerates are insulated by thermostable soluble agent which can be removed by subsequent washing the powder with water. The substance used for particle insulation should fit the following demands:

1. thermal and chemical stability in contact with target material;
2. the melting temperature of the substance and its eutectics with target product are higher than the maximum powder processing temperature;
3. high solubility in water or in other solvent, inert to the target material.

Sodium chloride, successfully used in Refs. 10–12 for various oxides, cannot be used in this case due to insufficient melting temperature ($T_m = 801$ °C). Several test

experiments with various salts have led to the selection of K_2SO_4 ($T_m = 1069\text{ }^\circ\text{C}$) which demonstrated the best compatibility with $LiCoO_2$, its precursors and intermediates.

The size of oxide particles, obtained by using soluble encapsulating agent, depends greatly on the character of its distribution among particles of oxide product. If the mixing of precursor and inert salt is realized at the level of agglomerates, the evolution of powder micromorphology from stage C to D (Fig. 2) will be effectively prevented while the transformation from B to C cannot be influenced. The last task could be solved by filling the agglomerates [2] with inert salt, but this way is rather complicated due to tight bonding of salt crystallites in freeze drying products and high viscosity of filling agent (K_2SO_4) during mechanical processing.

Various kinds of K_2SO_4 distribution among precursor particles have been realized by various mixing techniques. The analysis of the micromorphology of washed thermal decomposition products shows at the allocation of K_2SO_4 mostly at the interagglomerate space during mixing the components in the rotary ball mill (Fig. 3-1). The efficiency of the encapsulation of $LiCoO_2$ particles

in this case is proved to be higher than for $(NH_4)_2CO_3$, as the final size of cobaltite particles, formed during final annealing at $800\text{ }^\circ\text{C}$ (Fig. 3-3), is substantially smaller ($200\text{--}400\text{ nm}$ vs $800\text{--}1000\text{ nm}$ at Fig. 1C).

The application of planetary ball milling for introduction of encapsulating agent results in both mixing the precursor and K_2SO_4 and intense deagglomerating the precursor. The product of thermal decomposition of this mixture is non-agglomerated individual $LiCoO_2$ crystallites of $30\text{--}40\text{ nm}$ in size (Fig. 3-2). Following thermal conversion of decomposition product to HT-polymorph is accompanied by the moderate reagglomeration of these active particles and the formation of larger grains of about 100 nm (Fig. 3-4).

High viscosity of K_2SO_4 during mechanical processing has both positive and negative influence. The main negative factor is substantial milling duration ($10\text{--}20\text{ h}$), necessary for the uniform filling the precursor particles with K_2SO_4 . Nevertheless, it should be noted that this duration is still much smaller than $60\text{--}80\text{ h}$, necessary for the encapsulation of nanoparticles, obtained by mechanochemical processing.^{10–12} Positive effect of the high viscosity of salts during planetary milling is related

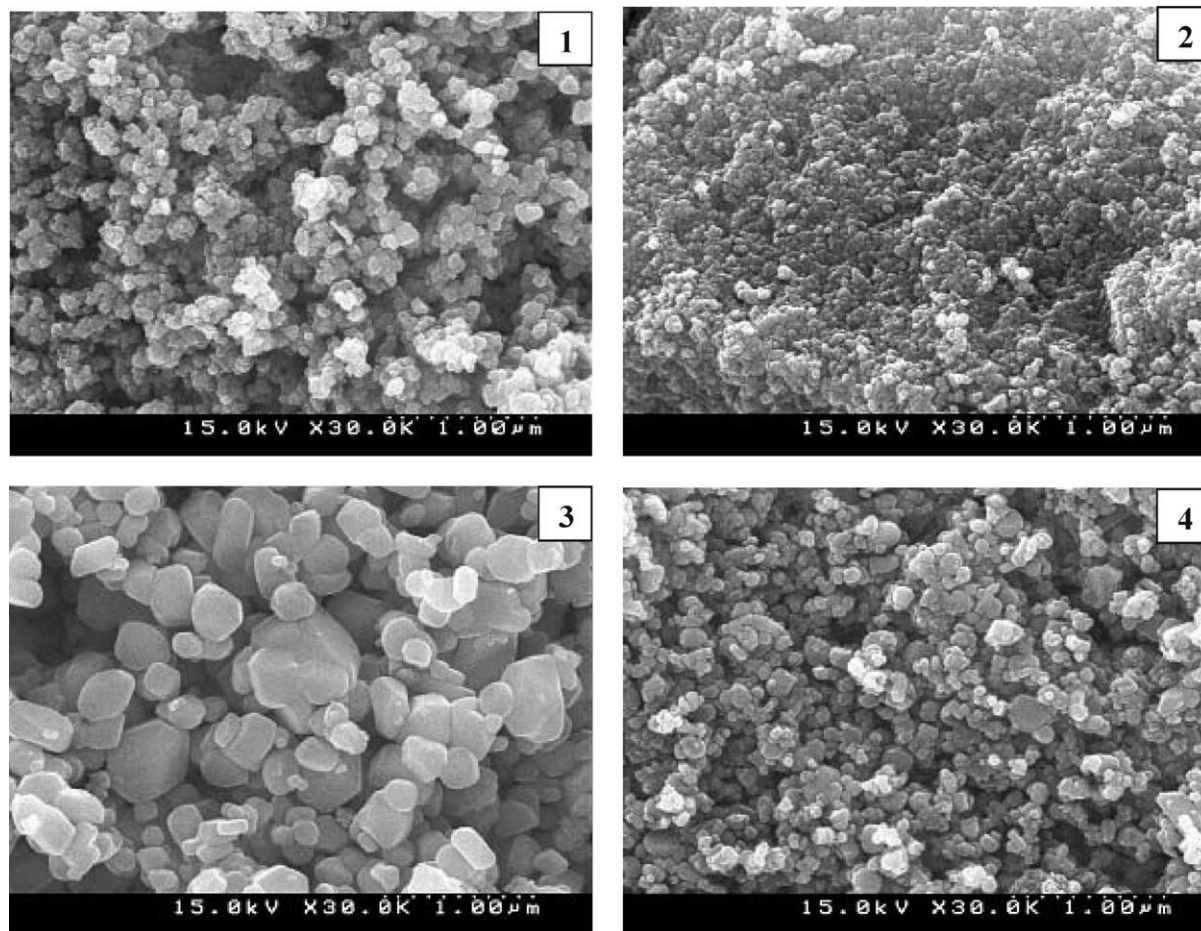
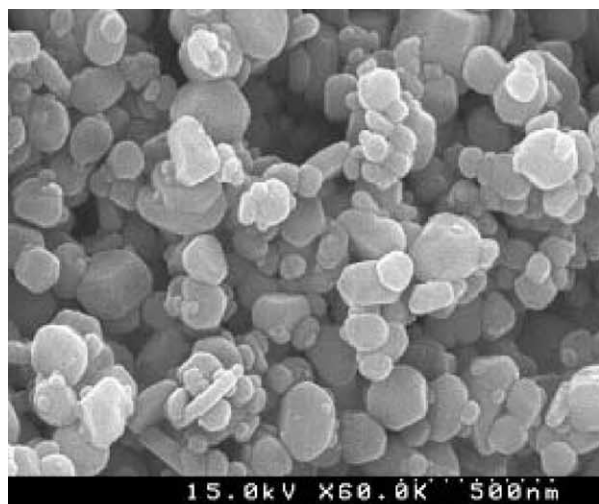


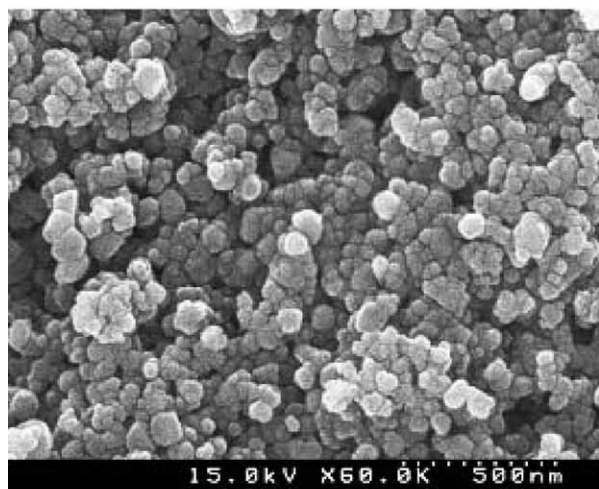
Fig. 3. The influence of milling method on the micromorphology of $LiCoO_2$ powders: (1) rotary ball milling; $T_{proc.} = 400\text{ }^\circ\text{C}$; (2) planetary milling, $T_{proc.} = 400\text{ }^\circ\text{C}$; (3) rotary ball milling, $T_{proc.} = 400\text{ }^\circ\text{C} + 800\text{ }^\circ\text{C}$; (4) planetary milling, $T_{proc.} = 400\text{ }^\circ\text{C} + 800\text{ }^\circ\text{C}$.



(A)



(B)



(C)

Fig. 4. The influence of mechanical processing duration on the particle size of lithium oxide powders ($T_{\text{proc.}} = 400\text{ }^{\circ}\text{C} + 800\text{ }^{\circ}\text{C}$): (1) 2.5 h; (2) 12 h; (3) 24 h.

to the possibility of the fine control of particle size by varying the milling duration (Fig. 4A–C). Along with duration, other factors, affecting the distribution of components like precursor/ K_2SO_4 ratio, milling energy, etc. can be also used for controlling particle size of lithium cobalt oxide.

More efficient deagglomeration and distribution of inert agent could be achieved by additional mechanical processing of the mixture at the intermediate stage of the process, between thermal decomposition and LT–HT conversion annealing. Experimental investigation of such a possibility has demonstrated several obstacles to this way of processing. The conversion of low temperature LiCoO_2 polymorph into HT-form is a kind of crystallographic ordering process. The driving force and the rate of the last one are rather small and strongly influenced by a large number of factors. Increasing the density of stable spatial defects in LiCoO_2 lattice by intense mechanical processing during planetary milling of as-formed LiCoO_2 leads to the significant decrease of LT–HT conversion rate during annealing compared to the samples, mechanically processed at the precursor stage. It has been found also that in many cases planetary milling of the $\text{LiCoO}_2/\text{K}_2\text{SO}_4$ mixtures resulted in appearing reflections of impurities at the diffraction patterns of annealing products (Fig. 5). The appearance of Co_3O_4 and $\text{Li}_{1.5}\text{Co}_3\text{O}_4$ is usually associated with high temperature decomposition of LiCoO_2 and can show at the partial destruction of LiCoO_2 after such processing. Hence, insufficient thermodynamic stability and low driving force of the crystallographic ordering of LiCoO_2 make rather undesirable any kind of intense mechanical processing of this powder after the formation of the final phase.

Main functional parameters of LiCoO_2 -based cathode materials are electrochemical capacity and fade rate during cycling secondary lithium battery. Preliminary evaluation of the electrochemical parameters of various LiCoO_2 powders with crystallite size from 4–6 μm to 60–80 nm, obtained in this work, demonstrated rather small dependence of the electrochemical performance on the grain size. The details of these measurements will be discussed elsewhere.

Summarizing the experimental results, it is reasonable to notice that the application of the various particle size control methods, described in the present paper, allows to modify the size of LiCoO_2 crystallites, leaving the same or similar level of crystallographic disorder, and to obtain from the same precursor the particles of lithium cobalt oxide with the size varying from 60–80 nm to several microns. The selection of modification methods was based on the analysis of the micromorphological evolution of LiCoO_2 powders during their synthesis and was performed by the methodology of powder engineering. Specific features of LiCoO_2 as powder engineering object compared to other single and complex oxide powders, described earlier,^{6–9} can be ascribed to

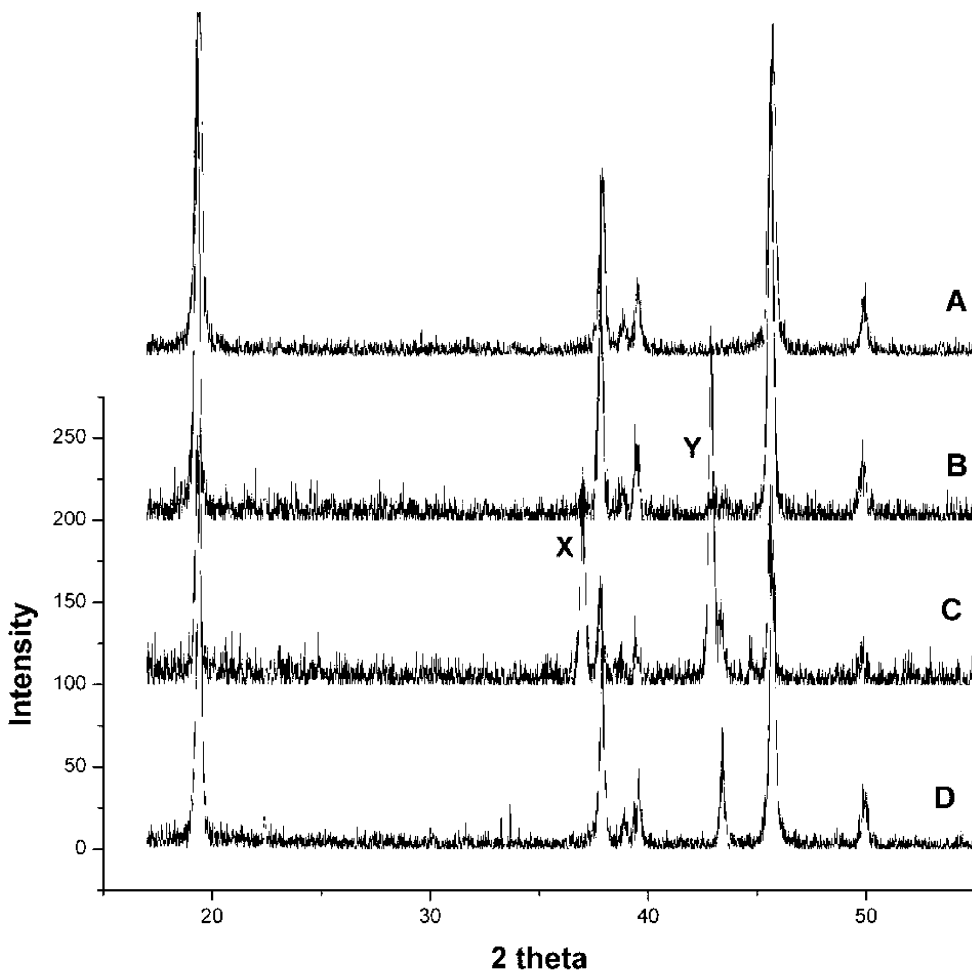


Fig. 5. XRD tracking of LiCoO_2 decomposition due to mechanical processing (MP) between thermal processing stages: (A) test sample [$T_{\text{proc.}} = 400^\circ\text{C}$ (10 h) + 800°C (8 h)]; (B) 400°C + MP (600 rpm, 2.5 h) + 800°C (8 h); (C) 400°C + MP (600 rpm, 12 h) + 800°C (8 h); (D) sample C + 800°C (16 h). X— Co_3O_4 ; Y— $\text{Li}_{1.5}\text{Co}_3\text{O}_4$.

the strong interference of local melting during thermolysis on the morphological evolution and to the impossibility to apply intense mechanical processing to the final oxide powder. At the same time the response of the system to the modification of the aggregate structure of intermediates is rather predictable. It makes reasonable the application of powder engineering methods to other modern cathode materials based on complex oxides of lithium. Taking into account the similar character of particle micromorphology evolution during thermal decomposition, proposed methods of particle size modification can be successfully combined with a large number of various chemical synthesis methods involving the thermolysis of salt precursors.

Acknowledgements

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