

High-resolution images of ultrafine LiCoO_2 powders synthesized by a sol–gel process

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Abstract

The morphology of ultrafine LiCoO_2 powders prepared by a sol–gel process was examined by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The purity and grain size of LiCoO_2 powders was dependent upon the pH value of the sol–gel process. The grain sizes measured by tapping mode AFM were 68, 74 and 100 nm, for samples made in acidic, neutral and basic media, respectively. Compared with grains synthesized using a solid-state high temperature method, which ranged from 5 to 20 μm , the grains synthesized using a low-temperature sol–gel process were at least 70 times smaller. Only products with small grains made in acidic media displayed a pure LiCoO_2 XRD pattern, implying that growth kinetics were favored in non-acidic media. © 1997 Elsevier Science S.A.

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1. Introduction

Due to safety and rechargeability problems associated with the use of lithium metal as the anode in conventional secondary lithium batteries, the concept of a ‘rocking-chair’ battery [1] using an intercalation compound as the anode, has been widely accepted as the main stream of next generation Li-based secondary batteries.

To increase the energy density of a rocking-chair battery, an intercalation compound possessing high open-circuit voltage (OCV) is usually employed as the cathode material. In this respect, LiCoO_2 is an attractive choice because it possesses a high OCV of 4 V. Furthermore, the Li-ion battery system using LiCoO_2 as the cathode is still the only commercially available Li-ion battery system to this date.

The electrochemical properties of LiCoO_2 [2,3] and LiMn_2O_4 [4] compounds synthesized at low temperatures (LT) were very different compared with their high temperature (HT) analogues. The LT- LiCoO_2 and LiMn_2O_4 powders have a higher surface area and smaller grain size, leading to greatly improved cell performance because of better capacity, polarization, and cell reversibility [5].

Tarascon et al. [4] and Barboux et al. [5] found that methods which prepared these metal oxides at HT produced

larger particles with lower cell capacity, but LT methods such as the sol–gel process produced finer particles with higher cell capacity. However, detailed studies on the effects of preparation routes on the morphology and grain size of these metal oxides have not yet been conducted.

In this work, we used the sol–gel process involving new precursors to synthesize LiCoO_2 at LT and analyzed the morphology and grain size of the resulting products prepared under acidic (pH: 3), neutral (pH: 7) and basic (pH: 11) conditions by using scanning electron microscopy (SEM) and atomic force microscopy (AFM) techniques.

2. Experimental

The preparation and characterization of LT- LiCoO_2 is described in detail in Ref. 6. Briefly, the starting materials, $(\text{C}_5\text{H}_7\text{O}_2)_3\text{Co}$ and LiNO_3 were stoichiometrically mixed and dissolved in ethanol. The pH values were controlled by adding a NH_4OH solution while stirring vigorously. Gelatinous precipitates were formed instantaneously. The mixture was left standing until the solvents were evaporated. The slurries were heated at 500 °C for 12 h in ambient atmosphere yielding a black homogeneous solid product.

SEM was carried out using a Hitachi S-2300 microscope. To prepare samples for SEM analysis, once the powders were sufficiently dried, they were attached to a circular metal plate

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with double-sided tape. An ion coater was used for vacuum gold plating.

The samples for AFM analysis were prepared in a sealed box with a small opening on one side. The glass slides (1 cm × 1 cm) were washed thoroughly with deionized water. After drying, the slides were coated with a very thin layer of glue and placed in a sealed box with the loose powders sitting above on a plate near the small opening. Using a pipette

attached to the opening, the particles were blown to land evenly on the glass slides. A tapping mode AFM was used for the investigation in this work.

The morphology of the cathode powders was monitored with a tapping mode AFM (Digital Instruments, Nano-Scope^{III}, 125 μm AFM scanning head). The material of the tapping mode AFM cantilevers (Digital Instruments) was an etched single crystal of n-type silicon. The tip had a 10 nm

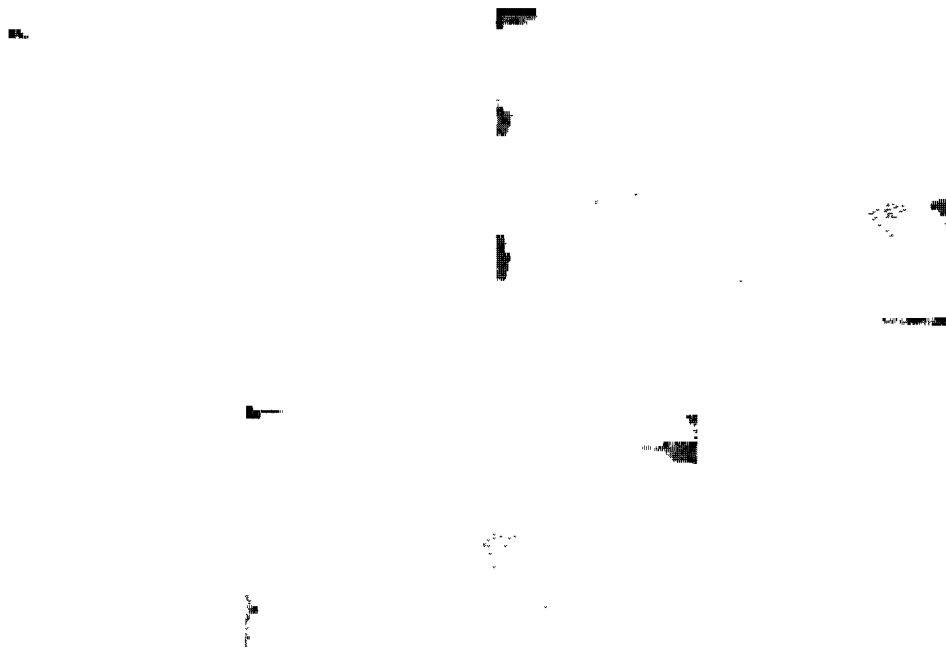


Fig. 1. SEM of LiCoO₂ powders synthesized from a sol-gel process in: (a) acidic medium, pH=3; (b) neutral medium, pH=7, and (c) basic medium, pH 11.

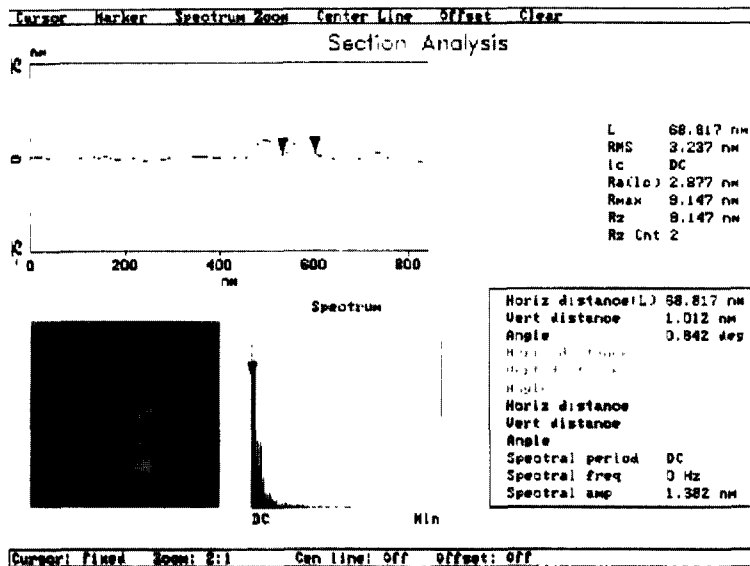


Fig. 2. Sectional profile analysis for AFM images of LiCoO₂ powders prepared in an acidic medium, pH: 3.

radius of curvature and 35° interior angle. Images were captured at a rate of 0.25 frame/min. Following each experiment, images were obtained from different areas on the sample surface to improve the reliability of the images.

3. Results and discussion

Although the SEM used in this study was not high resolution, providing only a $10\times k$ magnification, it did confirm that the samples produced using the sol–gel process were amorphous. As shown in Fig. 1(a), samples prepared under acidic conditions possessed the least amount of aggregates. However, clusters of particles were most readily formed using

a sol–gel process under basic conditions. A bulky aggregate stands out at the bottom of Fig. 1(c).

To relate to the results of the SEM analysis, further morphology studies of LiCoO_2 were performed with a tapping mode AFM expanding the magnification of LiCoO_2 particle size to the nanometer scale. When the scan scale was $1\ \mu\text{m}$, the location of individual grains could be seen clearly. The roughness of mean square of the blank substrate with a very thin layer of glue was observed from AFM to be 0.53 nm. Since the substrate is so smooth that the LiCoO_2 particles on the substrate can be easily distinguished. Tapping mode AFM was used to measure the height profile of each grain. The path of the probe is indicated by a line in each photograph (Figs. 2–4) and the individual grains are marked by arrows.

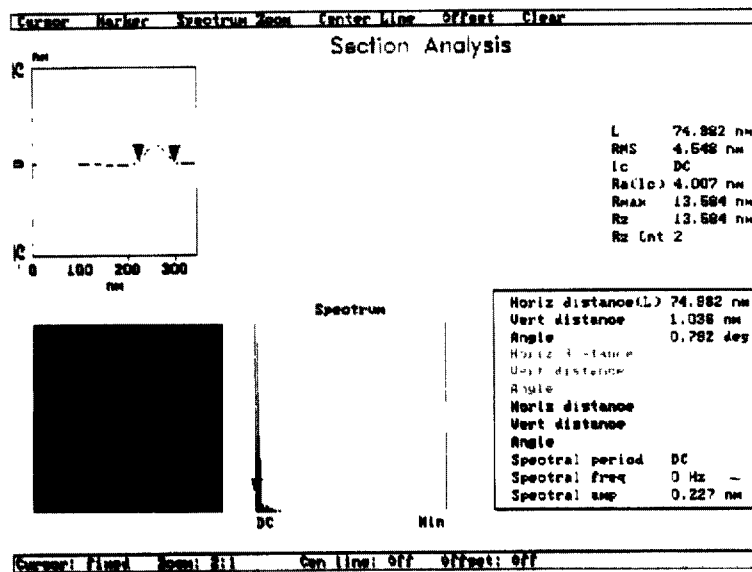


Fig. 3. Sectional profile analysis for AFM images of LiCoO_2 powders prepared in a neutral medium, pH: 7.

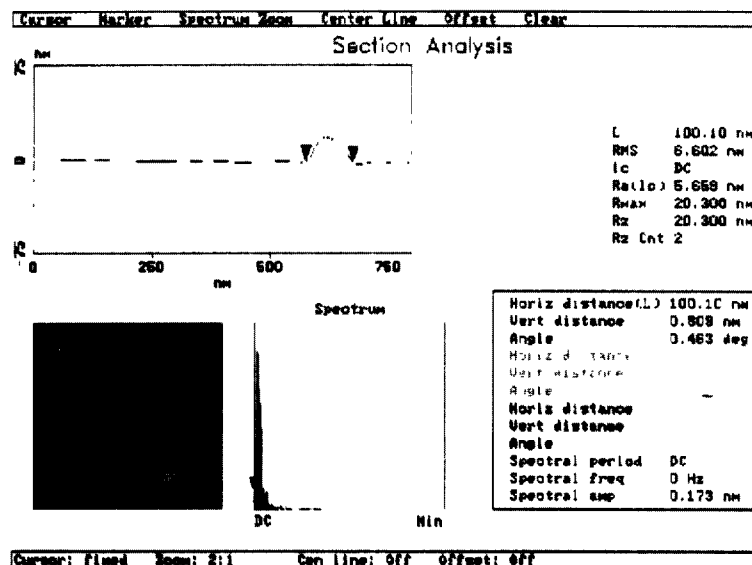


Fig. 4. Sectional profile analysis for AFM images of LiCoO_2 powders prepared in a basic medium, pH: 11.

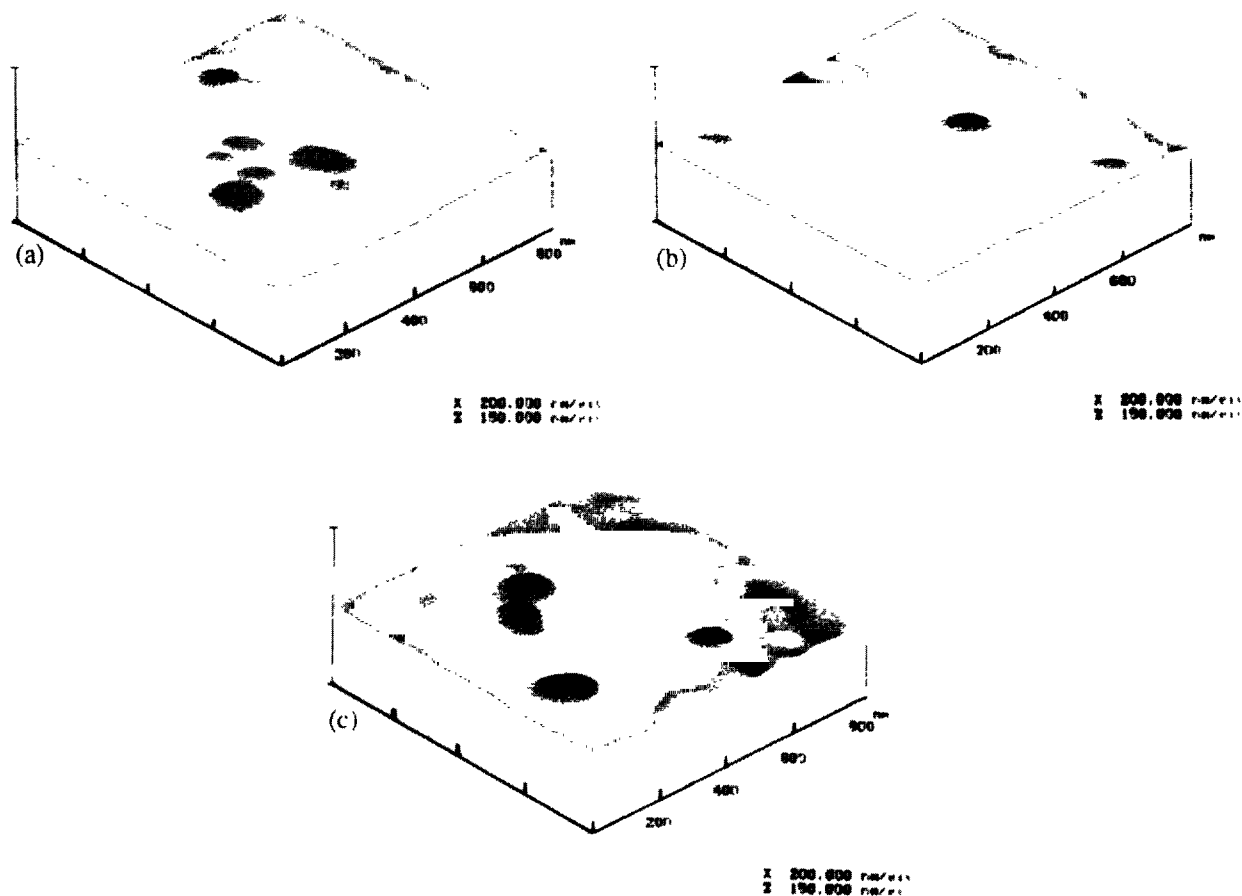


Fig. 5. 800 nm \times 800 nm AFM images of LiCoO_2 powders obtained from a sol–gel process under different pH conditions. (a) pH: 3; (b) pH: 7, and (c) pH: 11

The grain size was approximated by doubling the distance between each peak and trough or measuring the distance between two neighboring troughs.

As indicated by L or the horizontal distance in Figs. 2–4, the grain sizes for samples prepared under acidic, neutral and basic conditions were approximately 68, 74, and 100 nm, respectively. A three-dimensional AFM image of these samples in Fig. 5 illustrates the marked differences in particle size. The particle tips of samples prepared in acidic media are much smaller and more defined than samples prepared in neutral or basic media. Two series of AFM studies were conducted. The measurements obtained were almost identical in both cases.

Furthermore, the XRD patterns of samples prepared under acidic conditions closely match that of pure LiCoO_2 . However, XRD patterns for samples prepared under neutral or basic conditions displayed extra peaks indicative of impurities [6]. This finding is interesting because it implies that the grain size and purity of LiCoO_2 powders is dependent upon the pH value of the sol–gel process. In addition, the grain growth kinetics of LiCoO_2 in the sol–gel process were more favored under neutral and basic conditions. Due to page lim-

itations, details of the cell performance with these ultrafine LiCoO_2 will be reported elsewhere [6].

4. Conclusions

The results regarding the morphology and grain size of ultrafine LiCoO_2 powders prepared by a sol–gel process were consistent using SEM and high resolution tapping mode AFM. Compared with grains prepared using a solid-state high-temperature method, which ranged from 5 to 20 μm , the grains prepared using a sol–gel process were many times smaller. Interestingly, only products with small grains made in acidic media showed an XRD pattern consistent with pure LiCoO_2 , implying that growth kinetics were favored in non-acidic media.

Acknowledgements

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