

Short communication

Cycling behaviour of LiCoO_2 cathode materials prepared by PAA-assisted sol–gel method for rechargeable lithium batteries

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Abstract

High-temperature LiCoO_2 powders with sub-micron, narrow particle-size distributions, and excellent phase-pure particles are synthesized from molecularly mixed amorphous gel precursors by a sol–gel method. The crystallinity and morphology of the powders are examined by means of X-ray diffraction, Rietveld refinement and scanning electron microscopy, respectively. LiCoO_2 powders using poly(acrylic acid) deliver a high initial discharge capacity of 133 mA h g^{-1} and retain 97% of the initial discharge capacity after 350 cycles in $\text{Li//1 M LiPF}_6\text{-EC/DEC//LiCoO}_2$ cells. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

The layered oxides LiMO_2 ($M = \text{Co, Ni, V}$) have been studied extensively [1–4] as possible cathode materials for 4 V lithium-ion batteries with high specific energy. Of these, the research on the LiCoO_2 is more developed than [5,6] that on other cathode materials because of the simplicity in preparing this material.

LiCoO_2 powders have usually been prepared by grinding and calcination of hydroxides or carbonates such as $\text{LiOH} \cdot \text{H}_2\text{O}$, Li_2CO_3 and CoCO_3 [7]. This method, however, has several disadvantages, namely, inhomogeneity, irregular morphology, larger particle size (i.e., 5 to 10 μm), broader particle-size distribution, and higher temperature and longer period of calcination. It is necessary to obtain uniform particle morphology of sub-micron size with a narrow particle-size distribution in order to achieve batteries with large current capacity and good reliability. Battery performance depends on the LiCoO_2 powders having a high packing density, a high surface area, and good homogeneity [7,8].

Although several solution methods have been developed to increase the physicochemical properties of other oxide systems [9,10], there are few reports of preparing LiCoO_2

powders by a solution method. Nevertheless, it has been reported [11–13] that LiCoO_2 powders can be synthesized by ultrasonic spray decomposition. The sol–gel method, one of the solution methods, can produce a highly reactive, homogeneous powder. This simple method has many advantages, i.e., it produces a powder with high chemical homogeneity powder, good stoichiometric control and active sub-micron size particles in a relatively short processing time at a relatively low temperature.

Recently, the author reported that LiCoO_2 powders with large surface area could be obtained at a relatively low calcination temperature and short time by the amorphous organic precursor process using complexing polyfunctional carboxylic acid, PAA, with proper pH adjustment [14].

In this study, high-temperature (HT)- LiCoO_2 powders with uniform submicron-sized particles are synthesized by a sol–gel method using PAA as a chelating agent at a considerably lower temperature and shorter processing time. The electrochemical performance of the synthesized powders is studied in $\text{Li//1 M LiPF}_6\text{-EC/DEC//LiCoO}_2$ cells, (EC = ethylene carbonate; DEC = diethylcarbonate).

2. Experimental

LiCoO_2 powders were prepared by the PAA-assisted sol–gel method as reported previously [14]. Stoichiometric

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amounts of Li and Co nitrate salts with a cationic ratio of Li:Co = 1:1 were dissolved in distilled water and mixed well with an aqueous solution of poly(acrylic acid) (PAA). The molar ratio of PAA to total metal ions was set at 1. The mixed aqueous solution was adjusted to pH of 1 to 2 by dropwise addition of nitric acid with constant stirring. The resulting solution was evaporated to dryness at 70 to 80°C and calcined at 600 to 800°C for 10 h in air.

Powder X-ray diffraction using $\text{CuK}\alpha$ radiation was used to identify the crystalline phase of the material calcined at various temperatures. Rietveld refinement was then performed on the X-ray diffraction data to obtain the lattice constants. The changes in the particle morphology of the materials during calcination of the gel precursors were examined using a field emission scanning electron microscope (S-4100, Hitachi).

A three-electrode electrochemical cell was used for galvanostatic charge–discharge experiments. The reference and counter electrodes were constructed from the lithium foil (Cyprus). The electrolyte was a 1:1 mixture of EC and DEC containing 1 M LiPF_6 (Mitsubishi Chemical). The cathode was a mixture of 92 wt.% active material, 5 wt.% vulcan XC-72 carbon black, and 3 wt.% PVDF binder. The mixture was then dispersed in NMP and spread on Exmet, followed by pressing and drying at 120°C for 3 h. The cells were assembled in an argon-filled dry box. Charge–discharge cycling was performed galvanostatically at a current density of 1 mA cm^{-2} , with a cut-off voltage of 3.0 to 4.25 V (vs. Li/Li^+).

3. Results and discussion

The X-ray diffraction (XRD) patterns for materials calcined at various temperatures for 10 h in air are presented in Fig. 1. The HT- LiCoO_2 powders have a single

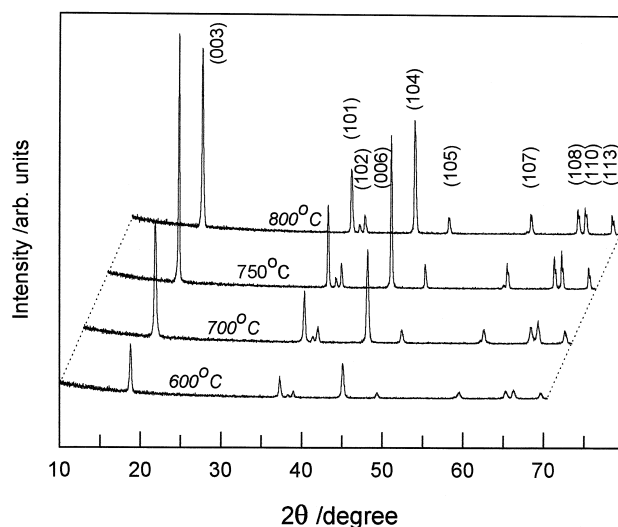


Fig. 1. X-ray diffraction patterns for gel derived materials calcined at various temperatures.

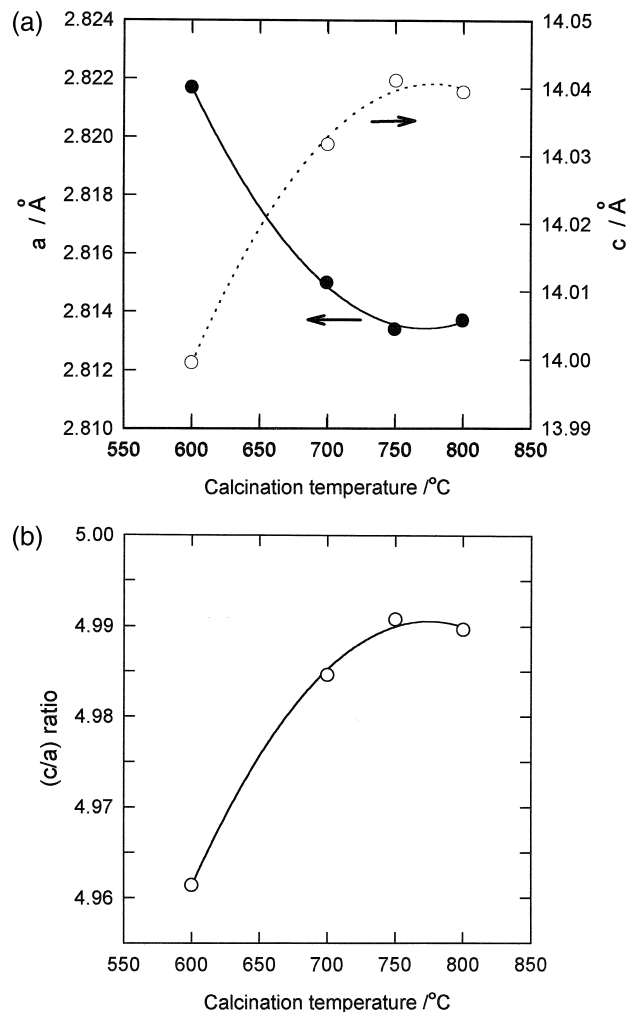


Fig. 2. Dependence of (a) hexagonal lattice constants a and c and (b) c/a ratio of LiCoO_2 powders on calcination temperature.

phase over the whole temperature range and all diffraction peaks can be indexed by assuming the structure to be a hexagonal lattice of the $\alpha\text{-NaFeO}_2$ type. The diffraction peaks are much sharper, and the width of the peaks is much narrower, on increasing the calcination temperature. This indicates an increase in crystallinity and a gradual growth in the average particle size. Similar results have already been reported for LiCoO_2 powders synthesized at lower temperatures [14]. It is inferred from the above results that the materials derived from the gel precursor are of atomic scale and homogeneously mixed with each other and, thus, have high sinterability.

The lattice constants (a and c) and the c/a ratio of the hexagonal structure are shown in Fig. 2 as a function of calcination temperature. While the lattice constant a decreases with increasing calcination temperature, the lattice constant c and the c/a ratio increase. These findings suggest that the expansion of the c -axis is due to stabilization of the layered structure by a decrease in the electrostatic binding energy, by which the crystallinity of the

LiCoO_2 powder increases with increasing calcination temperature [15]. The hexagonal lattice constants a , c , and the c/a ratio for LiCoO_2 powder calcined at 750°C are 2.8134 Å, 14.0411 Å and 4.9908, respectively. These values are in good agreement with the values reported by Gummow et al. [16] namely, 2.8179 Å (a), 14.0597 Å (c), and 4.99 (c/a ratio).

Scanning electron micrographs of powders calcined at 750 and 800°C for 10 h in air are shown in Fig. 3. The powders calcined at 750°C consist of monodispersed rectangular particulates of size $0.5\ \mu\text{m}$. As the calcination temperature is increased, the growth kinetics are favoured

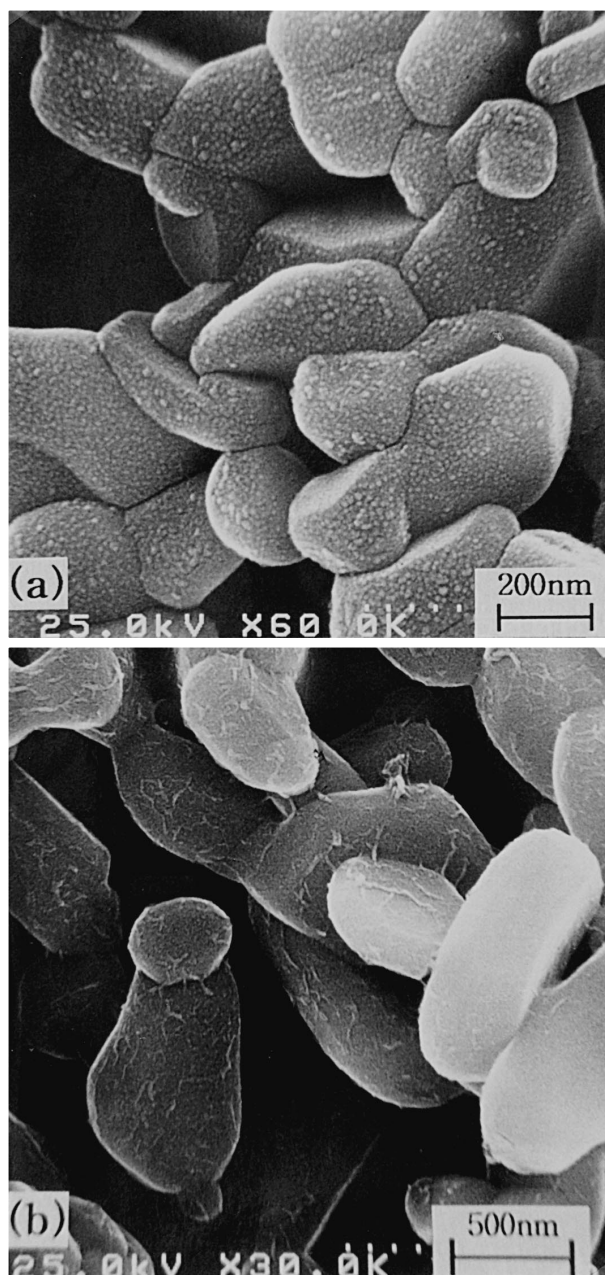


Fig. 3. Scanning electron micrographs of LiCoO_2 powders calcined at (a) 750°C and (b) 850°C .

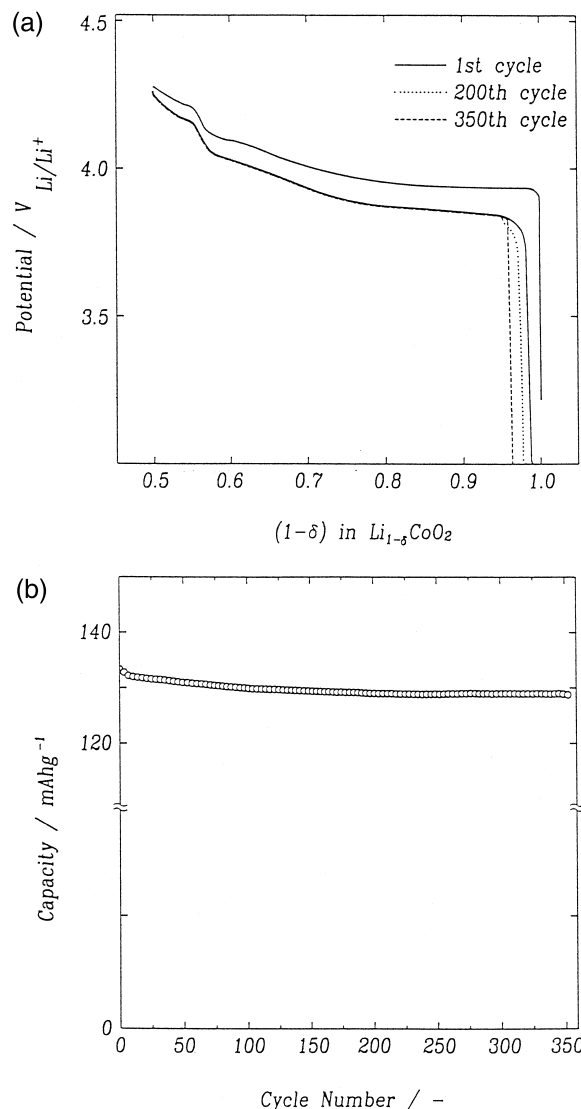


Fig. 4. (a) Cycling charge–discharge curves and (b) variation of specific discharge capacity with number of cycles for $\text{Li}/1\ \text{M LiPF}_6\text{-EC/DEC//LiCoO}_2$ cells using LiCoO_2 powders calcined at 750°C . Cycling was carried out galvanostatically at a constant charge–discharge current density of $1\ \text{mA cm}^{-2}$ between 3.0 and 4.25 V.

and thus the agglomerated spherical particles change to larger particulates. When the gel precursors are heated at 800°C , the size of the particulates increases to $1\ \mu\text{m}$ and there is a fairly narrow particle-size distribution.

In order to study the electrochemical performance of the synthesized materials, cathodes were fabricated using the powders calcined at 750°C . The charge–discharge behaviour is shown in Fig. 4 along with the discharge capacities after a given number of cycles for $\text{Li}/1\ \text{M LiPF}_6\text{-EC/DEC//LiCoO}_2$ cells at a constant charge–discharge current density of $1\ \text{mA cm}^{-2}$. The charge–discharge curves have two distinct plateaux, which is indicative of a well-crystallized HT- LiCoO_2 structure [17,18]. There is no change in the curves after 350 cycles. Also, the polarization (i.e., half of the difference in voltage between

the charge and discharge curves) is very low and does not increase with cycling up to 350 cycles. Initially, the LiCoO₂ electrode delivered 133 mA h g⁻¹. The discharge capacity slowly decreased with cycling and remained at about 129 mA h g⁻¹ up to the 350th cycle, which is 97% of initial capacity. It is well known that the contact resistance between LiCoO₂, the binder (PVDF), and the carbon within the composite cathode must remain as small as possible in order to obtain good cycleability [19]. The change in the LiCoO₂ lattice which results in considerable strain on these interface is believed to deteriorate the electrical contact between the surfaces of the insertion-material particles and hence decrease the capacity of the cathode during repeated charge–discharge cycling [19]. This phenomenon is severe with LiCoO₂ powders which have a broad particle size-distribution. Therefore, the observed excellent cycleability must result from good contact between the composite cathode interfaces (LiCoO₂/binder/carbon) that is due to the narrow particle-size distribution and the high homogeneity of the LiCoO₂ cathodes. Thus, the PAA-assisted sol–gel method is a very attractive method for synthesizing LiCoO₂-based cathode materials for lithium secondary batteries.

4. Conclusions

HT-LiCoO₂ powders with submicron, monodispersed, and highly homogeneous particles have been synthesized by a sol–gel method which uses an aqueous solution of metal nitrate containing PAA as chelating agent. It is seen that as the calcination temperature increases, the crystallinity of the powders increases and the optimal calcination temperature is 750°C. PAA-assisted LiCoO₂ powders calcined at 750°C initially deliver a discharge capacity of

133 mA h g⁻¹. The capacity remains about 129 mA h g⁻¹ after 350 cycles, and thus shows excellent rechargeability in Li//1 M LiPF₆-EC/DEC//LiCoO₂ cells cycled between 3.0 and 4.25 V.

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