

Short communication

Preparation and electrochemical characterization of lithium cobalt oxide nanoparticles by modified sol–gel method

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Received 30 May 2007; received in revised form 13 August 2007; accepted 30 August 2007

Available online 8 September 2007

Abstract

Uniformly distributed nanoparticles of LiCoO₂ have been synthesized through the simple sol–gel method in presence of neutral surfactant (Tween-80). The powders were characterized by X-ray diffractometry, transmission electron microscopy and electrochemical method including charge–discharge cycling performance. The powder calcined at a temperature of 900 °C for 5 h shows pure phase layered LiCoO₂. The results show that the particle size is reduced in presence of surfactant as compared to normal sol–gel method. Also, the sample prepared in presence of surfactant and calcined at 900 °C for 5 h shows the highest initial discharge capacity (106 mAh g^{−1}) with good cycling stability as compared to the sample prepared without surfactant which shows the specific discharge capacity of 50 mAh g^{−1}.

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Keywords: A. Layered compounds; B. Sol–gel chemistry; B. Intercalation reactions; C. X-ray diffraction; D. Electrochemical properties

1. Introduction

Designing nanostructured cathodes in place of conventional materials for lithium rechargeable batteries has become very attractive with a view to improve the performance of lithium rechargeable batteries. Lithium cobalt oxide (LiCoO₂) has been widely studied as a cathode material for lithium ion secondary batteries since it has good capacity, high specific energy, good power rates, low self-discharge, and excellent cycle life [1–3]. LiCoO₂ exhibits two forms viz. hexagonal and cubic structures. These structures are based on the some oxide sublattice, and are distinguished by the spatial arrangements of cations.

Conventionally, LiCoO₂ can be prepared by solid-state reaction at high temperature. The procedure, however, may result in inhomogeneity leading to abnormal grain growth and poor control of stoichiometry. Many advanced chemical processes, such as the sol–gel process [4–7], electrostatic spray decomposition [8,9], hydrothermal [10,11], co-precipitation [12] water-in-oil emulsion method [13], electrostatic spray deposition [14], etc. have been developed to prepare highly active materials of high purity and crystallinity. These methods have the desirable features of operation

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at lower calcination temperature and shorter time for calcinations; however synthesis of particles with size less than 100 nm is generally difficult due to the tendency of particles to agglomerate. It is thus necessary to develop new synthetic methods or even modifications of these existing methods to get the fine and homogeneous distribution of nanoparticles.

Wu et al. [15] have synthesized nanosized LiCoO_2 particles by modified sol–gel method using a surfactant, poly(ethylene oxide)-block-poly(propylene oxide)-block-poly(ethylene oxide) (P123) as a soft template. Chen et. al. [16] have reported LiCoO_2 nanoparticles with shape of thin polygons and size in the range of 20–100 nm by

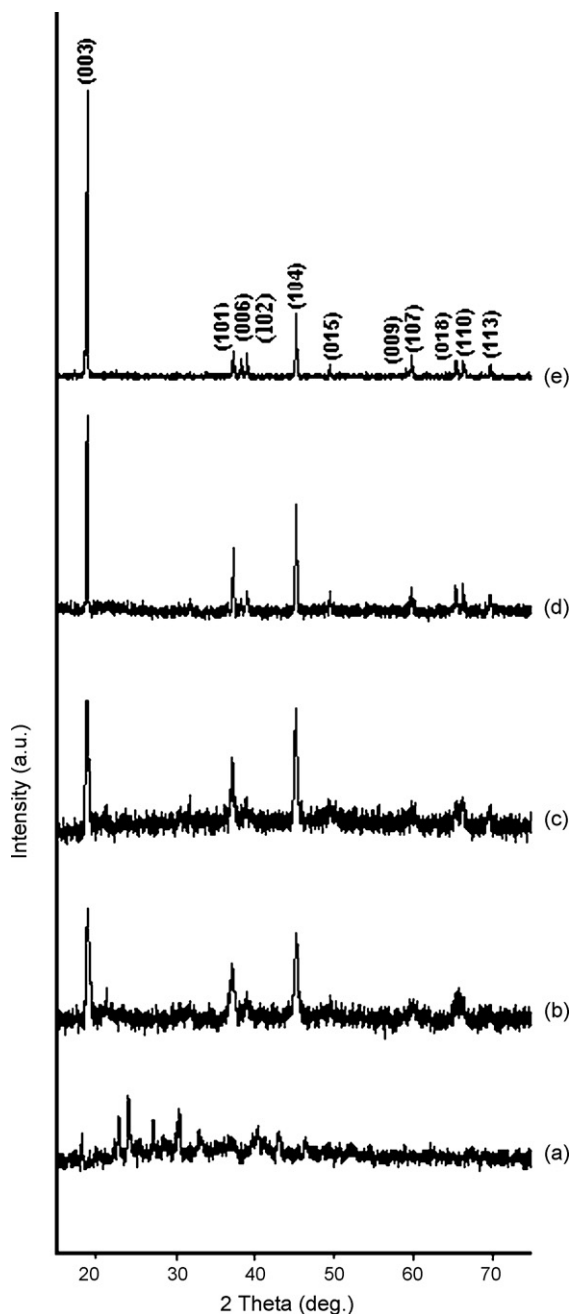


Fig. 1. XRD patterns of sample calcined at various temperatures for 5 h. (a) Precursor dried at 100 °C, (b) 300 °C, (c) 500 °C, (d) 700 °C and (e) 900 °C.

co-precipitation method in ethanol with mechanical stirring. The problem herein is that the nanoparticles of LiCoO_2 prepared by this method get agglomerated and thereby it becomes hard to disperse and mix them with carbon black and binder to produce the cathode. Hence, the contact resistance of a cathode using these nanoparticles is much higher than that of the commercial one, leading to the pronounced capacity fading. In lithium batteries the cathode performance is affected by particle size and crystalline phase of material. Sheu et al. [17] have shown that smaller particle size distribution resulted in better cycle stability. Recently, Predoana et al. [18] have studied electrochemical properties of LiCoO_2 prepared by sol–gel method using citric acid as a chelating agent. Li et al. [19] have synthesized different lithiated transition metal oxide nanotubes and their electrochemical measurement showed that nanotube electrode could be charged and discharged reversibly with high capacities and good rate capabilities.

In this paper, we report a new sol–gel method of synthesizing nano-sized LiCoO_2 particles in presence of neutral surfactant and examine the electrochemical properties of these nanoparticles.

2. Experimental

Analytical grade cobalt nitrate, lithium carbonate, citric acid and Tween-80 are used as starting materials. To begin with surfactant (0.05 M) was dissolved in 300 ml distilled water, followed by slow addition of 25.24 g (0.4 M) of citric acid under stirring condition. This is followed by the appropriate amount of additions of cobalt nitrate and lithium carbonate such that the citric acid:Li:Co molar ratio 4:2:1 is maintained. After the effervescence stops clear pink colored acidic solution is formed which is brought to the pH 7.5 by drop wise addition of 5 M NH_4OH solution. This pink colored solution is kept at 80 °C under reflux and under continuous stirred condition for 2 h. The clear liquor so obtained is then kept at 110 °C for the formation of gel. This gel is dried by keeping it at the same temperature for some more time. The Powder obtained is washed several times with methanol–acetone mixture to remove excess organic, inorganic or unreacted material and is then calcined at various temperatures for 5 h. We have also synthesized a sample without surfactant (normal sol–gel) by this method for comparison with sample prepared in the presence of Tween-80.

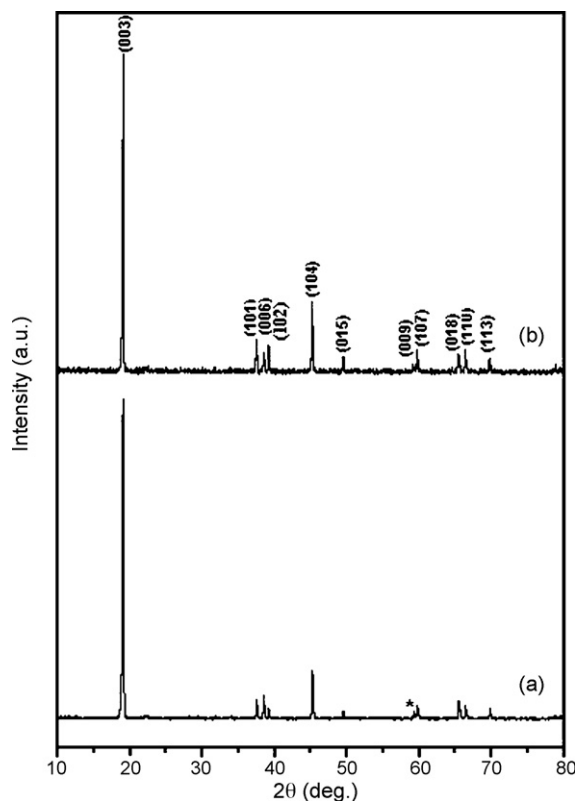


Fig. 2. XRD patterns of samples calcined at 900 °C for 5 h. (a) Normal sol–gel and (b) sol–gel with Tween 80.

3. Results and discussion

The phases present in the calcined samples were identified with X-ray diffractometer (XRD) (Powder XRD PW 1830, using Cu K α radiation with 40 kV, 30 mA at scanning rate of 5°/min). The X-ray diffraction pattern of materials prepared in presence of surfactant and calcined at various temperatures at 300, 500, 700, and 900 °C for 5 h are presented in Fig. 1. The formation of pure phase LiCoO₂ starts from 700 °C. It can be observed from Fig. 1e that all the diffraction peaks can be indexed to the hexagonal α -NaFeO₂ lattice structure. On increasing the calcination temperatures, the diffraction peaks becomes much sharper and the width of the peaks much narrower which indicates the growth of average particle size and an increase in crystallinity.

The X-ray diffraction spectra were used for determining the mean diameter of the particles (D) using the Scherrer formula

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (1)$$

where D is the crystallite size, k is the Scherrer constant usually taken as 0.89, λ is the wavelength of the X-ray radiation (0.15418 nm for Cu K α), and β is the full width half maximum (FWHM) of the diffraction peak measured at 2θ . The estimated crystallite size of the sample (prepared in presence of surfactant and calcined at 900 °C) from line broadening of the most intense diffraction peak (0 0 3) plane is approximately 6 nm.

Fig. 2 shows the XRD patterns of samples synthesized by normal sol–gel (Fig. 2a) and sol–gel with surfactant (Fig. 2b). From the pattern of samples it can be seen that no peaks of any impurities were found in the sample prepared by sol–gel in presence of surfactant, indicating that the nanocrystallite obtained via this synthesis method consist of

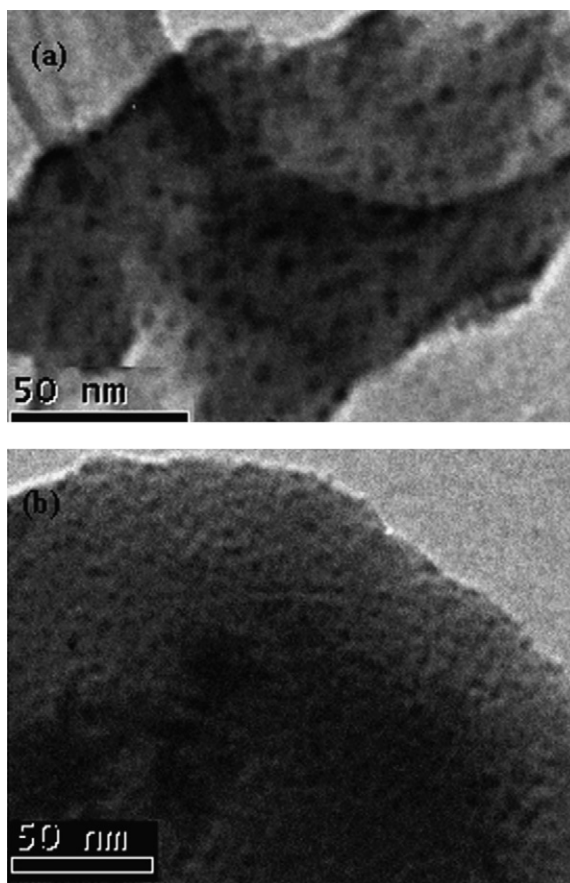


Fig. 3. TEM analysis of LiCoO₂ sample prepared (a) normal sol–gel and (b) sol–gel in presence of Tween 80.

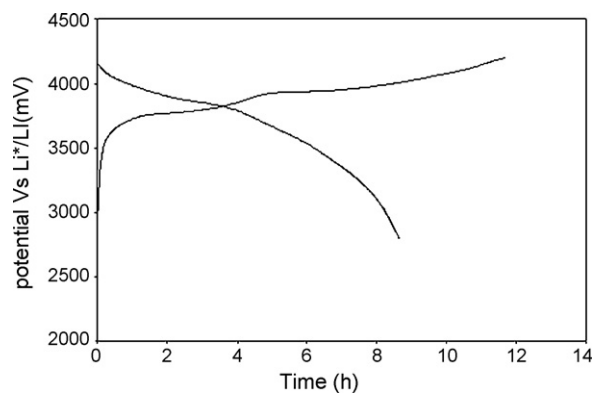


Fig. 4. First charge/discharge curves of LiCoO_2 prepared in presence of surfactant and calcined at 900°C for 5 h.

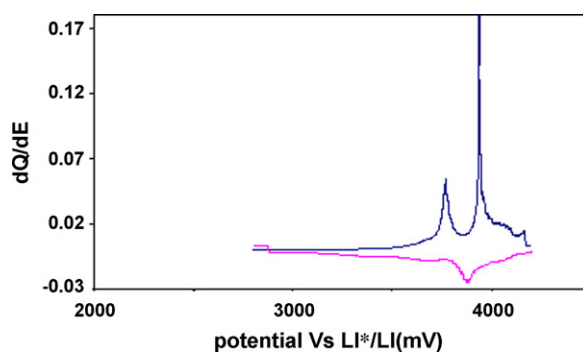


Fig. 5. Differential capacity–voltage dependences for cathode material LiCoO_2 .

ultrapure phase; the sample prepared by normal sol–gel method however shows a impurity peak*. One more interesting difference is that the sequence of intensities of (1 0 1), (0 0 6) and (0 1 2) diffraction peaks is totally opposite in both the samples. One more interesting observation is that in Fig. 2a (0 0 6) peak intensity is more than 1 0 2 peak. This observation could be ascribed to the inhomogeneous distribution of lithium in the 3a sites. Both the patterns show clearly the peak splitting between (1 0 8) and (1 1 0) peaks and confirms the formation of layer structure of lithium cobalt oxide.

The transmission electron microscopy images of LiCoO_2 powder calcined at 900°C prepared by sol–gel method in presence of surfactant is shown in Fig. 3. The average particle size of lithium cobalt oxide powder prepared by normal sol–gel method (Fig. 3a) and sol–gel in presence of Tween 80 (Fig. 3b) are approximately of 8 and 5 nm in diameter,

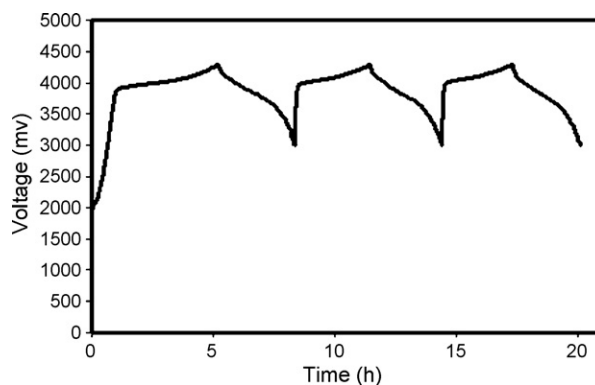


Fig. 6. Cycling performance of a LiCoO_2 .

Table 1
Cycling capacity data of nano sized LiCoO₂

Cycle no.	Charge capacity (mAh g ⁻¹)	Discharge capacity (mAh g ⁻¹)
1	173	106
2	111	104
3	107	103

respectively. Fig. 3a shows agglomerated and heterogeneous particle size distribution while Fig. 3b shows homogeneous particle size distribution.

Standard 2016 coin cells were assembled using lithium metal as anode, a Celgard 2400 separator and 1 M solution of LiPF₆ in a 50:50 (v/v) mixture of ethylene carbonate and diethyl carbonate. Cathodes were 1.8 cm diameter disc, slurry-coated with an 80:15:5 mixture of the cathode active powder, acetylene black and poly-vinylidene fluoride in *N*-methyl-2-pyrrolidone. Cathode active material loadings in the samples varied from 0.004 to 0.0045 g. Charge–discharge studies were performed using an in-house cycling unit between 4.25 and 3.0 V at *C*/10 rate.

Materials made as described above, have been cycled in 2016 type coin cells. Results are shown in Figs. 4–6. The first charge/discharge behavior is presented in Fig. 4. It can be clearly seen that the curves depict typical LiCoO₂ pattern with a large plateau around 3.8–4 V. The large irreversible capacity in the first cycle can be assigned to the formation stage. Fig. 5 presents the differential capacity curves and as observed above large discharge capacity peak is located around 3.85 V corresponding to the hexagonal phase. Fig. 6 depicts the specific capacity curves of the nanosized pristine LiCoO₂ synthesized through sol–gel in presence of surfactant method for three cycles. As can be seen from the cycling curves, the average operating voltage is around 4 V. Further, it can be seen that LiCoO₂ delivers the charge and discharge capacities of 173 and 106 mAh g⁻¹, respectively, for the first cycle at a current rate of *C*/10 in the voltage range of 3–4.25 V. Even though, the cells exhibit large irreversible capacity in the first cycle the electrodes show a stable charge/discharge behavior with high coulombic efficiency (90%) in the subsequent cycles and corresponding to ~0.4–0.45 (Table 1) of lithium extraction during the charging/discharging process. These behaviors confirm the purity of our synthesized sample as evidence by XRD. However, the sample prepared without surfactant shows less discharge capacity (50 mAh g⁻¹), which may be due to impurity present in the layered structure and heterogeneous particle size distribution. Better layered structure will give higher charge/discharge capacity since during charge/discharge processes lithium ions can deintercalate/intercalate in the layered space. We may thus conclude that sol–gel derived nano-sized LiCoO₂ could be a potential cathode material for Lithium rechargeable batteries exhibiting high specific capacity.

4. Conclusion

The nano-sized LiCoO₂ synthesized by modified sol–gel method in presence of nonionic surfactant gives improvements in cycling capacity compared to nano-sized LiCoO₂ sample synthesized by normal sol–gel method. Tween 80 plays an important role in the synthesis of lithium cobaltite nanoparticles. This enhanced capacity of the sample may be attributed to homogeneous particle size and pure phase LiCoO₂ nanoparticles compared to normal sol–gel sample.

Acknowledgement

Financial assistance under SERC Fast Track (for R.B. Khomane) from Department of Science and Technology (DST), New Delhi, India, is gratefully acknowledged.

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