

Short communication

Novel solution-combustion synthesis of LiCoO_2 and its characterization as cathode material for lithium-ion cells

Shalini Rodrigues^a, N. Munichandraiah^{b,*}, A.K. Shukla^a

^a*Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore - 560012, India*

^b*Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore - 560012, India*

Received 22 January 2001; accepted 19 March 2001

Abstract

Lithium cobalt oxide (LiCoO_2) which is being widely used as cathode material in lithium-ion batteries is synthesized by a novel solution-combustion procedure. In this synthesis, a solution mixture of $\text{Co}(\text{NO}_3)_2$, Li_2CO_3 and diformyl hydrazine fuel is heated to ignite at 350°C . This is accompanied by decomposition of cobalt nitrate and lithium carbonate to form LiCoO_2 within a few minutes, which is annealed at 850°C for 6 h to obtain an ordered-crystalline layered compound. The powder X-ray diffraction pattern of the prepared LiCoO_2 shows a hexagonal cell with $a = 2.81$ and $c = 13.83$ Å. Electrodes made with LiCoO_2 , acetylene black and poly(vinylidene fluoride) yield a discharge capacity of ~ 120 mAh g^{-1} with good Faradaic efficiency over several charge–discharge cycles. Cyclic voltammetric and ac impedance data also corroborate the electrochemical activity of LiCoO_2 synthesized in the present study. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Li-ion cell; Lithium cobalt oxide; Combustion synthesis; Charge–discharge cycling

1. Introduction

The reversible electrochemical intercalation and de-intercalation of Li^+ ions in a layered LiCoO_2 framework first demonstrated by Goodenough et al. [1] in 1980 laid the foundation of lithium-ion battery technology in the following years [2]. The subsequent development of a lithium-ion battery with a specific energy of about 120 Wh kg^{-1} which utilizes layered intercalation-compounds as the active materials for both its positive and negative electrodes has intensified research on the synthesis of LiCoO_2 and related transition-metal oxide frameworks. In particular, the search for synthetic methods for preparing the oxide in its appropriate crystallographic form by easy and rapid routes has assumed primary importance. Conventionally, LiCoO_2 sample is synthesized by heating a palletized mixture of lithium carbonate and cobalt carbonate in air at 900°C for 60 h with repeated, intermittent, grinding and heating [1].

To obtain rapid as well as low-temperature synthetic routes, several methods have been reported in the literature [3–10] as follows. Acetate precursors have been employed to make an aqueous gelatinous precipitate which is dried at 150°C followed by heating at 300°C for 12 h [3]. Carbonates

of Li and Co have been mixed and air heated at 400°C for 2–5 days [4]. An aqueous solution of nitrates has been spray-dried and heated at 400°C up to 9 days [5]. A gelatinous precipitate obtained by mixing solutions of LiOH , NH_4OH and $\text{Co}(\text{NO}_3)_2$ has been dried and heated at 400°C for 2 h [6]. A palletized mixture of LiOH and CoOOH has been heated in an autoclave at 100°C for 3 days [7]. A complex, formed between humic acid and LiOH has been mixed with $\text{Co}(\text{NO}_3)_2$ to make a gel followed by heating for 6 h at 350°C and then for 12 h at 450°C [8]. A microwave method has also been reported for LiCoO_2 synthesis [9]. In a super-critical water synthesis procedure, LiOH and $\text{Co}(\text{NO}_3)_2$ were mixed in a reactor at 450°C to prepare LiCoO_2 within 1 min [10]. In the present study, LiCoO_2 is prepared by a solution-combustion route which takes about 5 min with an ignition temperature as low as about 350°C . The compound is found suitable for reversible positive electrodes with discharge capacities between 110 and 120 mAh g^{-1} .

2. Experimental

Analar grade Li_2CO_3 , LiPF_6 , $\text{Co}(\text{NO}_3)_2$, ethylene carbonate, dimethyl carbonate and lithium ribbon (0.7 mm thickness) were purchased from Aldrich. Diformyl hydrazine

* Corresponding author. Tel.: +91-80-309-2828; fax: +91-80-360-0683. E-mail address: muni@ipc.iisc.ernet.in (N. Munichandraiah).

(DFH) was prepared by drop-wise addition of formaldehyde to a stoichiometric quantity of hydrazine hydrochloride at 0°C following the procedure reported by Ainsworth and Jones [11]. LiCoO₂ was synthesized as follows. A solution mixture of Co(NO₃)₂ and Li₂CO₃ was prepared by dissolving the respective compounds in a minimum amount of water by taking 10–25% excess of Li₂CO₃ than the stoichiometric requirement. The excess of Li₂CO₃ was required to compensate evaporation loss of Li as Li₂O. DFH fuel was added in a weight ratio of 20% to the solution and stirred thoroughly to make a uniform, syrupy liquid. In a typical composition, the mass ratio of Co(NO₃)₂, Li₂CO₃ and DFH is 2:0.6:0.4. The solution mixture was transferred to a wide-mouthed petri dish and introduced into a furnace which was preheated to 350°C. Within a few seconds, the fuel ignited with froth and fumes that lasted for about 5 min. The solid residue in the petri dish was cooled to ambient temperature, washed with methanol, and dried in air. The powder X-ray diffraction (XRD) pattern of the product confirmed that it was LiCoO₂.

For the purpose of electrochemical characterization, LiCoO₂ electrodes were prepared on an aluminium foil substrate. The foil (0.1 mm thick) was cut into rectangular shape (20 mm × 5 mm) with a tag for electrical connections, polished with successive grades of emery paper to a uniform and smooth finish, washed copiously with doubly-distilled water, etched for about 2 min in dilute HCl solution, washed again, rinsed with acetone, and finally dried in air. LiCoO₂ (80 wt.%), acetylene black (10 wt.%) and PVDF (10 wt.%) were mixed together with a minimum volume of *n*-methylpyrrolidinone to form a syrupy mixture which was spread on the pretreated aluminium foil and allowed to dry at 80°C under vacuum. Spreading and drying was repeated three times, and finally dried at 80°C for 12 h under vacuum. The electrode thus prepared was compacted at 50 kN cm⁻² pressure and vacuum heated for about 3 days prior to transferring into an argon-filled dry box. Cells were assembled in airtight polypropylene rectangular containers in a three-electrode configuration which used lithium metal as both the counter and the reference electrodes. A Celgard inter-electrode separator was used. The electrolyte was 1 M LiPF₆ in ethylene carbonate and dimethyl carbonate mixture (1:1). The solvents were distilled three times in an argon atmosphere and repeatedly treated with 4 Å molecular sieves prior to preparation of the electrolyte.

XRD patterns of the samples were recorded on a Jeol (JDX-8P) diffractometer and the microscopic nature was observed by means of a Jeol (JSM-5600 LV) scanning electron microscope. The cyclic voltammetric behaviour of the electrodes was recorded with an Autolab potentiostat (AUT 30). Electrochemical impedance spectra were measured in the frequency range 100 kHz to 10 mHz with an excitation signal of 5 mV by means of an EG&G PARC-6390 electrochemical impedance analyzer. Galvanostatic charge and discharge data on the electrodes were obtained using a galvanostatic circuit which comprised a regulated

dc power source, a high resistance and an ammeter in series with the cell. A digital multimeter of high input-impedance was used to measure the electrode potential.

3. Results and discussion

Metal oxides are reportedly synthesized much faster by solution-combustion than by conventional, high-temperature, solid-state synthesis [12,13]. The procedure requires addition of a mild fuel to the metal nitrate solution and ignition of this fuel at an appropriate temperature, usually around 350°C. During the course of fuel burning, decomposition of nitrate and oxidation of the metal ion takes place simultaneously and results in the formation of the metal oxide. As the process is accompanied by large quantities of gases (CO₂, NO, NO₂ and H₂O) the oxides are produced in fine particles with a high surface area. For the preparation of LiCoO₂, a solution mixture of Li₂CO₃, Co(NO₃)₂ and DFH fuel is combusted at 350°C. The solution mixture catches fire, copious fumes are emitted, and a solid residue remains in the container during the process which lasts for a few minutes. A scanning electron micrograph of the LiCoO₂ shows a uniform distribution with a particle size which ranges from 2–5 μm, as shown in Fig. 1.

The XRD pattern of the as-synthesized sample of LiCoO₂ indicates an amorphous phase of the compound. Subsequent to annealing at 850°C for about 6 h, however, an ordered-crystalline XRD pattern was obtained, as shown in Fig. 2. The cell parameters obtained by indexing the peaks to a hexagonal cell are $a = 2.81$, $c = 13.83$ Å, $V = 94.87$ Å³, and $c/a = 4.91$. These values are comparable with those reported in the literature [6]. The excess Li₂CO₃ used for synthesis was found to be absent in the XRD pattern. It is thus evident that the layered LiCoO₂ which is identical in crystal phase to that reported in the literature is obtained by the solution-combustion route. Analysis of several sample

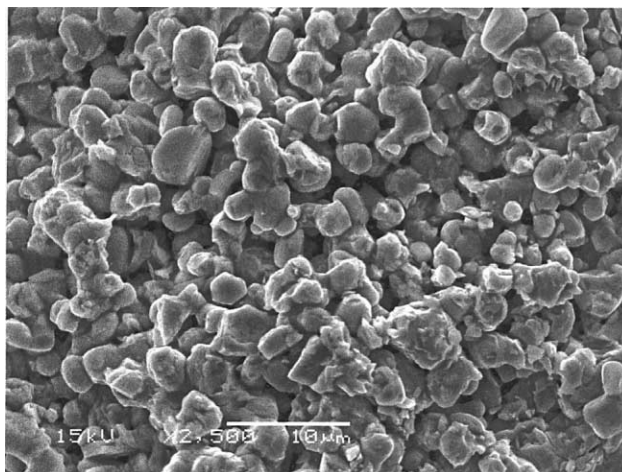


Fig. 1. Scanning electron micrograph of LiCoO₂.

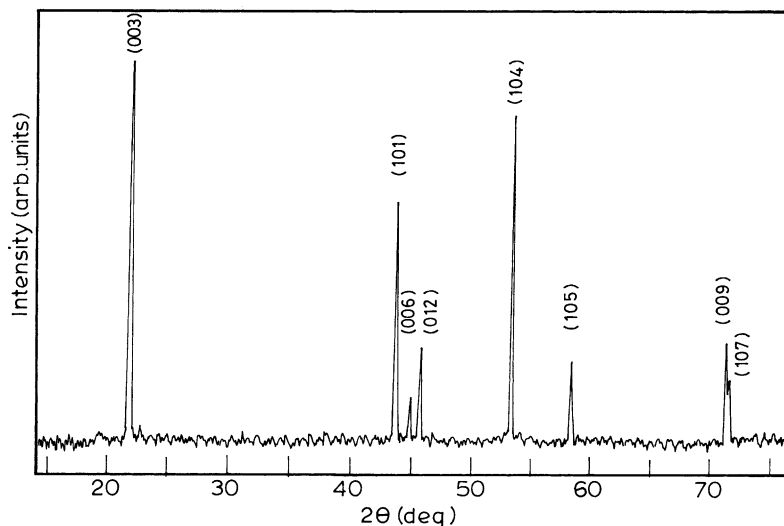


Fig. 2. Powder XRD pattern of LiCoO_2 (Co $K\alpha$ radiation).

oxides for lithium content revealed a value of $x = 0.98\text{--}1.00$ for Li_xCoO_2 which suggests a high degree of intercalated lithium.

A cyclic voltammogram of LiCoO_2 in 1 M LiPF_6 electrolyte between 3 and 4.6 V versus Li/Li^+ electrode is given in Fig. 3. An anodic peak appears at 4.1 V versus Li/Li^+ during the forward scan and a cathodic peak at 3.8 V versus Li/Li^+ during the reverse scan. The voltammogram suggests that LiCoO_2 prepared in the present study exhibits electrochemical activity.

The Li/LiCoO_2 cells were subjected to charge–discharge cycles at the C_{10} rate between 3 and 4.2 V. Typical charge–discharge curves showing the variation of LiCoO_2 electrode potential are presented in Fig. 4. The discharge capacity calculated from Fig. 4 is 120 mAh g^{-1} of LiCoO_2 which is comparable with values between 80 and 130 mAh g^{-1} reported in the literature [4,8]. The cycle-life data obtained

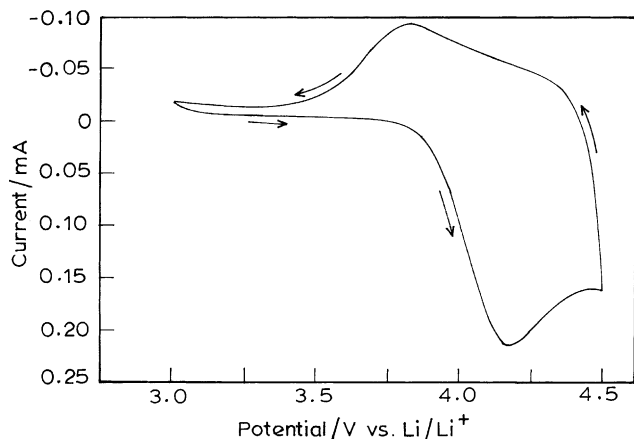


Fig. 3. Cyclic voltammogram of LiCoO_2 in 1 M LiPF_6 electrolyte of ethylene carbonate and dimethyl carbonate. Scan rate = 0.05 mV s^{-1} , electrode area = 2 cm^2 .

during repeated cycling of the electrodes are shown in Fig. 5. An average capacity value of 120 mAh g^{-1} is maintained over more than 20 charge–discharge cycles. The coulombic efficiency of discharge is found to be about 81% when averaged over 20 cycles. In Fig. 6, the impedance spectra of a freshly assembled Li/LiCoO_2 cell in discharge state and subsequent to its charging are shown. The spectrum shown in Fig. 6(a) is characterized by a high-frequency small semicircle followed by the low-frequency data in the form of an incomplete large semicircle. Subsequent to the charging of the cell, the high-frequency semicircle becomes smaller in size and the low-frequency data show tendency to form a semicircle as shown in Fig. 6(b). The cell resistance

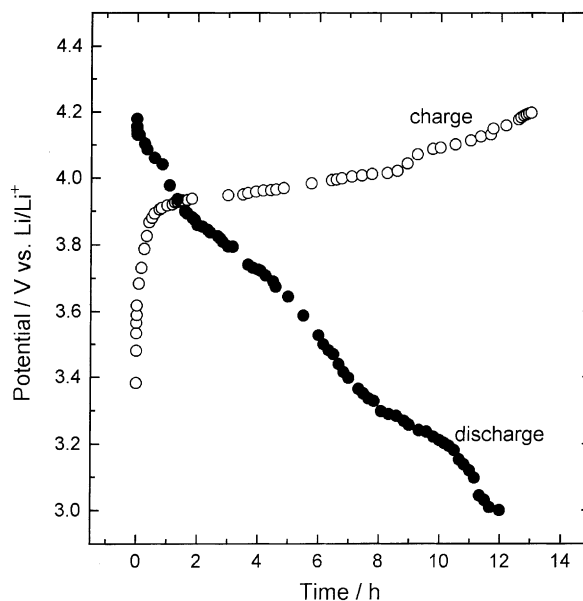


Fig. 4. Variation of LiCoO_2 electrode potential during charge–discharge at C_{10} rate.

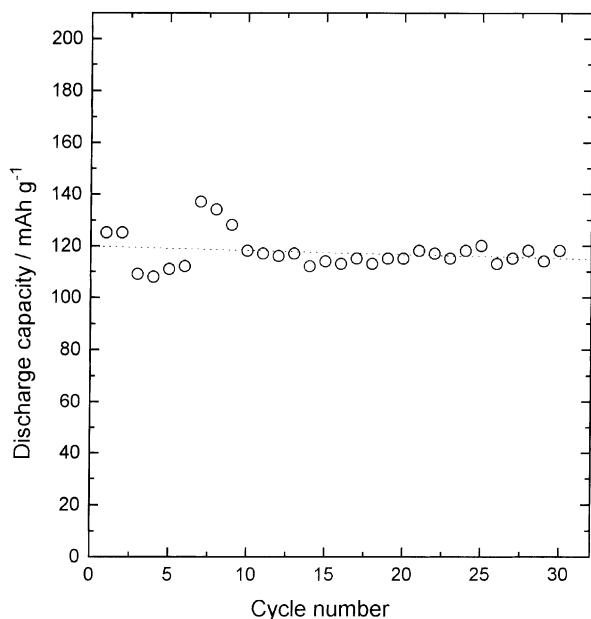


Fig. 5. Cycle-life data of LiCoO₂ electrode at C₁₀ rate.

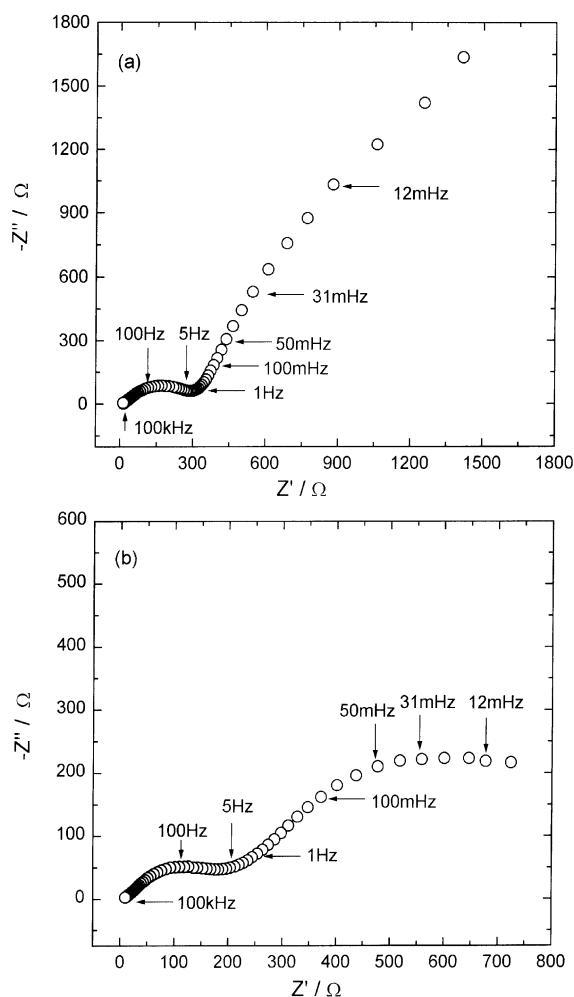


Fig. 6. Electrochemical impedance spectrum of Li/LiCoO₂ cell, (a) as assembled; (b) after charging to 4.2 V.

thus becomes much smaller after the Li/LiCoO₂ cell is charged. This study is in agreement with ac impedance studies of commercial lithium-ion cells and LiCoO₂ electrodes, in which the presence of a pair of semicircles due to the LiCoO₂ positive electrode and a decrease of cell impedance with an increase of state-of-charge are reported [14,15]. These results further support the electrochemical suitability of LiCoO₂ prepared by the solution-combustion synthesis.

4. Conclusions

Lithium cobalt oxide is synthesized by heating a solution mixture of Co(NO₃)₂, Li₂CO₃ and DFH at 350°C. The product forms within a few minutes, which is annealed at 850°C for 6 h to obtain an ordered-crystalline layered compound. The powder XRD pattern of the prepared LiCoO₂ indicates a hexagonal cell. Electrodes made with LiCoO₂, acetylene black and poly(vinylidene fluoride) yield a discharge capacity of ~120 mAh g⁻¹ with good Faradaic efficiency over several charge–discharge cycles. Cyclic voltammetric and ac impedance data also corroborate the electrochemical activity of LiCoO₂ synthesized in the present study.

Acknowledgements

Financial support from Ministry of Non-conventional Energy Sources, Government of India, New Delhi is gratefully acknowledged.

References

- [1] K. Mizushima, P.C. Jones, P.J. Wiseman, J.B. Goodenough, *Mater. Res. Bull.* 15 (1980) 783.
- [2] B. Serosati, *J. Electrochem. Soc.* 139 (1992) 2776.
- [3] P. Barboux, J.M. Tarascon, F.K. Shokoohi, *J. Solid State Chem.* 94 (1991) 185.
- [4] R.J. Gummow, M.J. Thackeray, *Solid State Ionics* 53–56 (1992) 681.
- [5] E. Rossen, J.N. Reimers, J.R. Dahn, *Solid State Ionics* 62 (1993) 53.
- [6] B. Gracia, P. Barboux, F. Ribot, A. Kahn-Harari, L. Mazerolles, N. Baffier, *Solid State Ionics* 80 (1995) 111.
- [7] G.G. Amatucci, J.M. Tarascon, D. Larcher, L.C. Klein, *Solid State Ionics* 84 (1996) 169.
- [8] E.-D. Jeong, M.-S. Won, Y.-B. Shim, *J. Power Sources* 70 (1998) 70.
- [9] H. Yan, X. Huang, H. Li, L. Chen, *Solid State Ionics* 113–115 (1998) 11.
- [10] K. Kanamura, A. Goto, R.Y. Ho, T. Umegaki, K. Toyoshima, K.-i. Okada, Y. Hakuta, T. Adschiri, K. Arai, *Electrochem. Solid State Lett.* 3 (2000) 256.
- [11] C. Ainsworth, P.G. Jones, *J. Am. Chem. Soc.* 77 (1955) 621.
- [12] K.C. Patil, *Bull. Mat. Sci.* 16 (1993) 533.
- [13] N. Arul Dhas, K.C. Patil, *Ceramic Int.* 20 (1994) 57.
- [14] S. Rodrigues, N. Munichandraiah, A.K. Shukla, *J. Solid State Electrochem.* 3 (1999) 397.
- [15] M.G.S.R. Thomas, P.G. Bruce, J.B. Goodenough, *Solid State Ionics* 18/19 (1986) 794.