

LiCoO₂ thin film cathodes grown by sol–gel method

Vaishali Patil · Arun Patil · Ji-Won Choi ·
Yoon-Pyo Lee · Young Soo Yoon · Hyun-Jai Kim ·
Seok-Jin Yoon

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Abstract Lithiated layered transitional metal oxide materials of the LiMO₂ type and especially LiCoO₂ presents interesting specific properties as high energy density, long cycle life and constant discharging properties in a wide range of working conditions as well as a good safety. These properties made these materials excellent candidates as active compounds for high capacity cathode materials for rechargeable lithium batteries. LiCoO₂ is the most common lithium storage material for lithium rechargeable batteries, used widely to power portable electronic devices. Operation of lithium rechargeable batteries is dependent on reversible lithium insertion and extraction processes into and from the host materials of lithium storage. In this study, LiCoO₂ thin films were prepared by the sol–gel spin coating technique using metal acetate and citric acid as starting materials. Citric acid acts as a chelating agent, which promotes the preliminary reaction between lithium and cobalt and suppresses the precipitation of acetates. The sol–gel method is well known as one of promising thin-film preparation methods, which has good advantages such as low fabrication cost, relatively easy stoichiometry control, high

deposition rate and also known as a low-temperature synthesis method for various ceramics. In addition, the crystal phases involved in the thin film can also be controlled by changing the chemical compositions of the sol. The crystallinity, microstructure and electrochemical properties of final films are also studied by XRD, SEM, AFM and galvanostatic charge/discharge cycling test. Films heat-treated under appropriate conditions exhibit high capacity and good crystallinity so those films are considered to be candidates as cathodes for thin-film micro batteries.

Keywords LiCoO₂ thin films · Sol–gel · Characterization

1 Introduction

Lithium-based layered transition metal oxides like LiMO₂ (where M is a 3d transition metal such as Ni, Co, Mn, Al, and V) have attracted a worldwide great interest in the last period of time [1–4]. Their specific properties such as high energy density, long cycle life, good safety, constant discharging properties and wide range of working temperatures made them excellent candidates as active compounds for high capacity cathode materials for rechargeable lithium batteries. The usual structure of these materials is similar with sodium chloride lattice with the cations filling the octahedral interstices and oxygen atoms situated in close packed sites. In most of the cases in LiMO₂ oxides, the cations are arranged in an ordered structure that presents tunnels that permit the intercalation and deintercalation of the lithium ions during the recharge process, promoting it by this [5–8]. Among these oxides many research groups are investigating LiCoO₂ thin films for use as a cathode material in microbatteries. Solid-state thin-film microbatteries have been studied for various applications [5–19].

V. Patil · A. Patil · J.-W. Choi · H.-J. Kim · S.-J. Yoon (✉)
Thin Film Materials Research Center,
Korea Institute of Science and Technology,
Seoul 136-791, South Korea
e-mail: sjyoon@kist.re.kr

Y.-P. Lee
Thermal/Flow Control Research Center,
Korea Institute of Science and Technology,
Seoul 136-791, South Korea

Y. S. Yoon
Department of Advanced Technology Fusion,
Konkuk University,
Seoul 143-701, South Korea

Two of the more interesting applications of microbatteries is monolithic hybridization with complementary metal oxide semiconductor random access memory (CMOS-RAM) or combined with solar cells. In addition, these batteries can be adapted to microelectronics, sensor technology and high-temperature semiconductor electronics [13]. Various methods are employed for the preparation of LiCoO_2 thin films such as sputtering [5–7], electron beam evaporation [8–9], pulse-laser deposition [10] and CVD [11, 12]. These methods, however, have several disadvantages such as difficulty in controlling the stoichiometry, long deposition times and high costs for fabrication. We adopted the sol–gel method as an alternative approach to overcome these problems. This method offers advantages such as excellent control of stoichiometry, easy control of crystallinity, density and microstructure. Moreover, the fabrication cost is relatively low and the deposition rate is high.

In this study, LiCoO_2 thin films were synthesized using citric acid as a chelating agent and their structural and electrochemical properties were studied by X-ray diffraction (XRD), electrochemical voltage spectroscopy, cyclic voltammetry, and galvanostatic charge discharge experiments.

2 Experimental

2.1 Preparation of thin films

LiCoO_2 thin films were prepared on platinum coated silicon wafers by using sol–gel spin coating method. Lithium acetate and cobalt acetate were used as raw materials. These two acetates were mixed in the molar ratio 1.1:1 and dissolved in methanol together with optimized amount of citric acid. Citric acid acts as a chelating agent, which promotes the preliminary reaction between lithium and

cobalt and suppresses the precipitation of acetates. But excessive addition of citric acid causes cracks in the film surface. This mixture was stirred for 20 h to get homogeneous coating solution. The volume of methanol was reduced by heating sol at 60 °C (Fig. 1). The prepared sol was coated on platinum coated silicon wafer using spin coating method. The solution was spin coated on the substrate at 3,000 rpm for 30 s. After drying, the sol was converted to gel and then heated at 750 °C for 10 min in air. The purpose of the drying process is to evaporate the solvents and the organic materials from the solutes. This process was repeated for four times to get sufficiently thick film. At the final deposition, heat treatment was performed at 750 °C for 1 h.

2.2 Structural characterization

The prepared thin films were analyzed by X-ray diffraction (XRD) with $\text{CuK}\alpha$ (50 kV and 300 mA) at a scan rate of 8°min^{-1} in the 2θ range from 10° to 100° . The morphologies of surface and cross sections of the thin films were observed with scanning electron microscopy. The rms roughness of as deposited thin films was determined by atomic force microscopy studies.

2.3 Electrochemical characterization

All electrochemical measurements were carried out on the Li/LiCoO_2 cells assembled in beakers in the glove box. A LiCoO_2 thin film with 1 cm^2 active area was used as the cathode and a lithium metal foil was used as the anode. One molar of LiClO_4 in propylene carbonate solution was used as the liquid electrolyte. To examine the electrochemical behavior of LiCoO_2 thin film cathodes, galvanostatic charge–discharge cycling tests were carried out between 3 and 4.2 V. To examine the rate capability of LiCoO_2 thin film cathodes, the cell was cycled between 3 and 4.2 V.

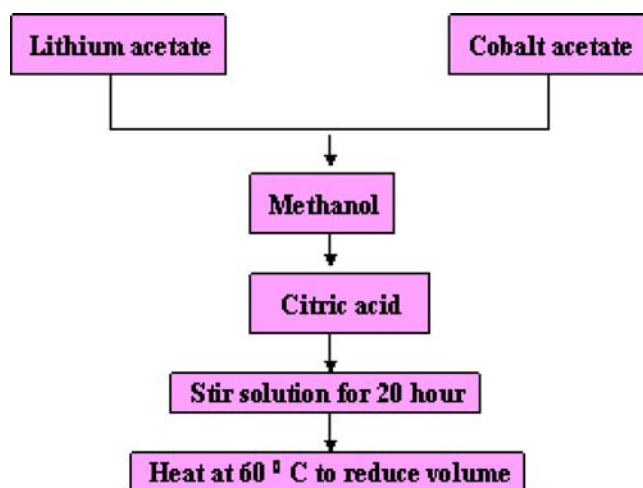


Fig. 1 Schematic diagram showing preparation of sol

3 Results and discussion

The layered LiCoO_2 intercalation host can be derived from the rock salt structure. The structure is rhombohedral (space group $R3m$) with cobalt and lithium alternately occupying octahedral sites between adjacent close-packed planes of oxygen. Approximately half of the lithium can reversibly be extracted and re-inserted electrochemically, before any structural degradation occurs. Diffusion of lithium proceeds through a vacancy hopping mechanism within the lithium plane and is thus strictly two-dimensional. The high cycling stability of LiCoO_2 and its high cell potential against lithium makes it an attractive intercalation electrode for micro-scale power supplies.

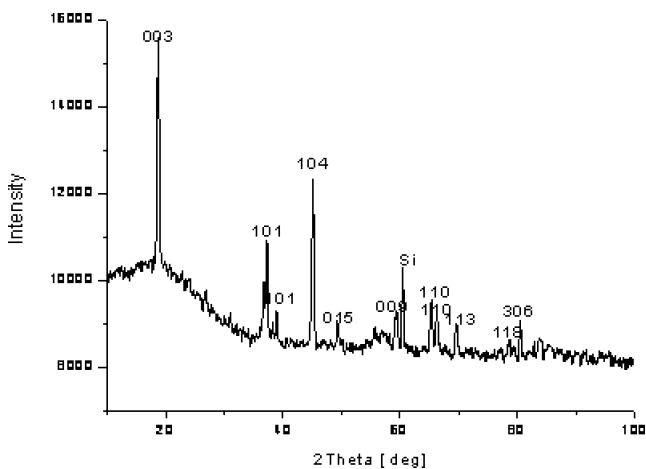


Fig. 2 X-ray diffraction pattern of LiCoO₂ thin films prepared on Pt substrate by sol-gel method

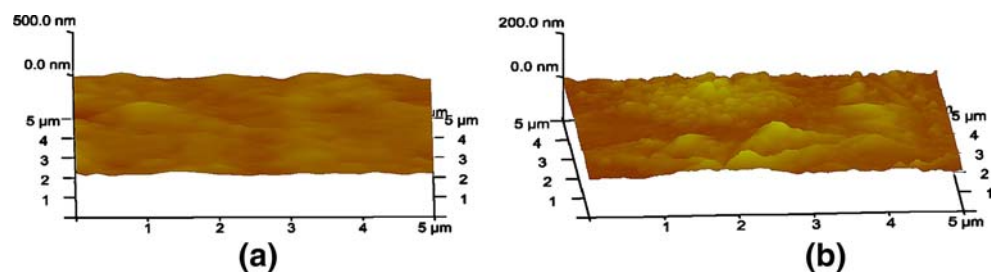
3.1 X-ray diffraction characterization

The structural identification of the films was performed at room temperature by an X-ray diffraction (XRD) analysis. Figure 2 shows the XRD patterns of LiCoO₂ thin films deposited on platinum coated silicon wafers. LiCoO₂ thin film shows the strongest (003) peak at 18.72°. Besides the main peak of the LiCoO₂ thin film, minor peaks indexed as (101), (104), (015), (009), (110), (113) at 36.71°, 45.09°, 49.26°, 59.47°, 65.32°, 69.62° can be seen as well. Considering the intensity and position of the Bragg peaks, it is well known that patterns of the rhombohedral unit cell (R3m space group) can be indexed in the hexagonal system. This material exhibits the classical layered structure generally found for the most LiMO₂ oxides isomorphous with α -NaFeO₂. Unit-cell parameters are $a=2.815^\circ\text{A}$ and $c=14.03^\circ\text{A}$. These values are close to those reported in the JCPDS data [20]. Using the Scherrer formula, the particle size of LiCoO₂ nanocrystals was calculated 20.56 nm from FWHM (full width half maximum) of (003) reflection

$$\bar{D} = \frac{\lambda}{B \cos \theta} \quad (1)$$

where λ is the X-ray wavelength, B the angular line width at the half maximum intensity and θ the Bragg's angle.

Fig. 3 AFM representation of the surface of LiCoO₂ thin films: (a) before cycling, (b) after cycling



3.2 Atomic force microscopy studies

Typical three dimensional AFM images at $5 \times 5 \mu\text{m}$ scale of the surface topography of the LiCoO₂ thin films deposited using citric acid as chelating agents before cycling are shown in Fig. 3(a). AFM studies show coarse grains and rough surface morphology. The root mean square (rms) roughness of LiCoO₂ thin films is 15.8 nm. The surface roughness will induce a big surface area, which is favorable for lithium intercalation and deintercalation due to bigger area contacted with liquid electrolyte.

Figure 3(b) shows AFM images of LiCoO₂ thin films after cycling. Due to constant charging and discharging cycles the structure of LiCoO₂ thin films distorted and roughness increases to 22.3 nm.

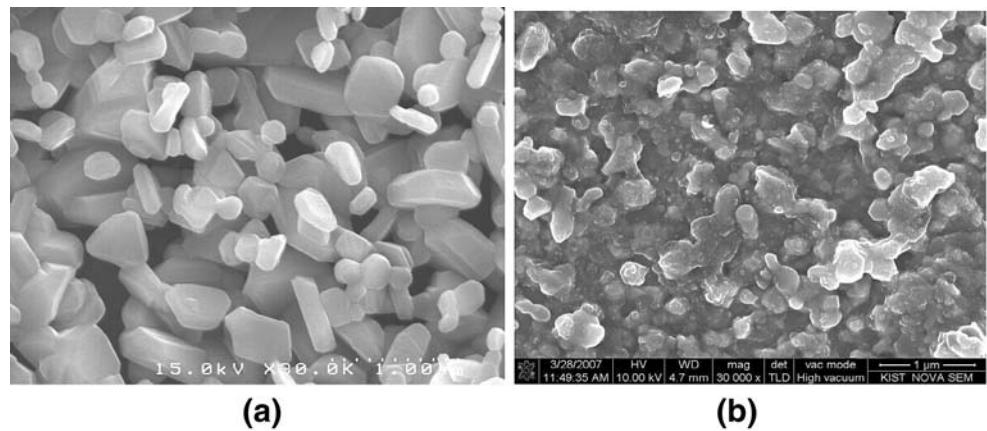
3.3 Scanning electron microscopy studies

Figure 4(a) shows a cross sectional SEM image of LiCoO₂ thin film. The morphology of thin films is dense. The thickness of the films is estimated to be 2 μm . The scanning electron micrographs of LiCoO₂ before cycling and after cycling showed in Fig. 4(a) and (b). Scanning electron microscopy image shows the well defined hexagonal grains are formed at high temperature and grains are compactly arranged. Figure 4(b) shows SEM image after cycling. The LiCoO₂ thin film electrode is cycled between 3.0 and 4.2 V in the cell containing LiClO₄ as solute and PC as electrolyte with lithium metal as an anode. When LiCoO₂ thin film electrode is cycled, the surface is covered with the SEI layer which is the oxidation product of electrolyte including solvent and salt anion. The new SEI layer is formed constantly on the surface of LiCoO₂ thin film in each cycle. This causes increase of cathode polarization which degrades the electrochemical performance of the LiCoO₂ thin film.

3.4 Electrochemical characterization

LiCoO₂ films grown onto platinum coated silicon wafers annealed at 750 °C were used as cathode materials and tested in lithium microbatteries with 1 M LiClO₄ in

Fig. 4 SEM micrographs of LiCoO₂ thin films: (a) before cycling, (b) after cycling



propylene carbonate as an electrolyte. Cyclic voltammetry (CV) measurements have been carried out at sweep rate of 0.2 mVs^{-1} . Figure 5 shows the cyclic voltammogram for a Li/LiCoO₂ cell. There are two sets of well-defined current peaks observed in the CV diagram corresponding to the oxidation and reduction reaction; they are located at 3.82 and 3.78 V for the LiCoO₂ film. The main lithium intercalation and deintercalation peaks with the same peak potential separation of 40 mV, indicating that these samples have basically the same thermodynamic reversibility for intercalation and deintercalation of Li ions. It should be remarked that the fully intercalated phase is not recovered during the first discharge. This could be probably assigned to a kinetic problem especially as the phase Li_xCoO₂ is a poor electronic conductor. These peaks are slightly shifted toward lower potentials for films. These CV features are associated with the redox process of Co³⁺ to Co⁴⁺ and vice-versa, when lithium is extracted from, and inserted into the Li_xCoO₂ phase. The redox couple with a mid-peak potential of about 3.8 V is considered to be a single-phase insertion/deinsertion reaction of lithium ions in LiCoO₂ [21, 22]. The specific capacity and cyclability of the LiCoO₂ thin films

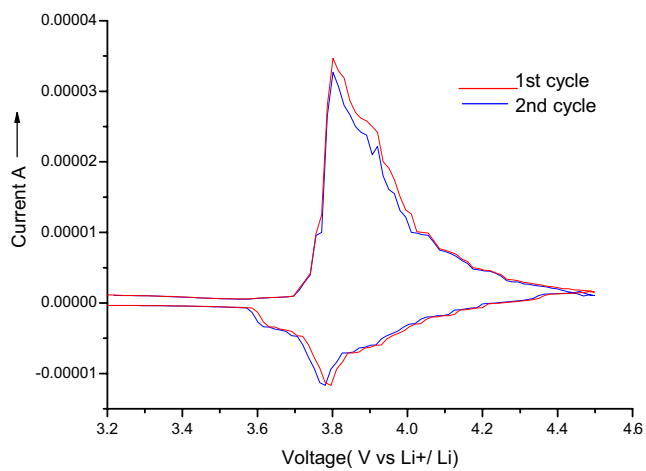


Fig. 5 Cyclic voltammograms of LiCoO₂ thin films

were determined by cycling test cells at a constant current density between 4.2 and 3.0 V. Figure 6 shows the discharge capacity versus cycle number of LiCoO₂ thin film. Initially LiCoO₂ delivered 110 mAhg^{-1} discharge capacity; but the capacity slowly declined with increase in cycling and remained at 75 mAhg^{-1} .

4 Conclusion

Many advances have been made in battery technology in recent years; however the practicality of systems is highly dependent upon the performance of positive electrodes. Despite the commercial success of LiCoO₂, many problems remain in the use of the lithiated cobaltates. The sol-gel process is an attractive method to synthesize LiCoO₂ cathode materials for lithium-ion batteries, and requires a much lower calcination temperature and shorter calcination time than the solid-state reaction. LiCoO₂ thin films were deposited on the Pt current collector by a sol-gel method using a spin coating and an annealing process. Citric acid acts as a chelating agent in making a gel LiCoO₂. XRD

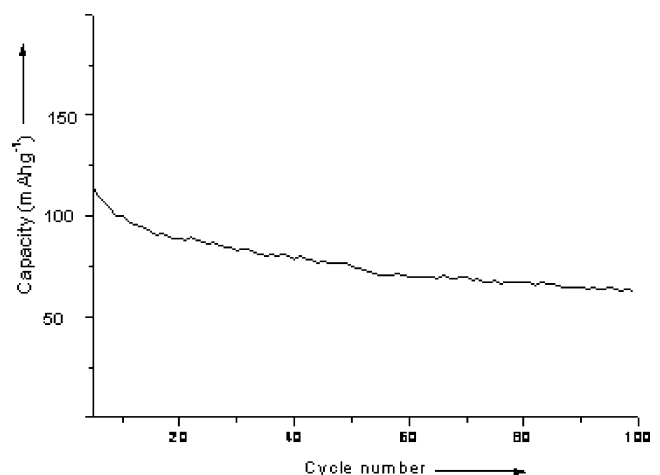


Fig. 6 Change in discharge capacity with cycle numbers of LiCoO₂ thin film cathode

studies show that LiCoO_2 thin films prepared show rhombohedral structure in hexagonal lattice. Surface roughness (RMS) of LiCoO_2 thin films after cycling is 22.3 nm which confirms distortion of hexagonal structure after cycling. LiCoO_2 showed no change of potential separation in the main oxidation and reduction peaks which indicate that these samples have basically the same thermodynamic reversibility for intercalation and deintercalation of Li ions. From these results, LiCoO_2 thin films prepared by the sol-gel method may be candidates to serve as cathodes in all solid-state thin film microbatteries.

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References

1. Y.A. Jeon, S.K. Kim, Y.S. Kim, D.H. Won, B.I. Kim, K.S. No, *J. Electroceram.* **17**, 667 (2006)
2. X.J. Zhu, H.X. Liu, X.Y. Gan, M.H. Cao, J. Zhou, W. Chen, Q. Xu, S.X. Ouyang, *J. Electroceram.* **17**, 645 (2006)
3. H.S. Kim, S.I. Kim, C.W. Lee, S.I. Moon, *J. Electroceram.* **17**, 673 (2006)
4. M.S. Park, S.H. Hyun, S.C. Nam, *J. Electroceram.* **17**, 651 (2006)
5. H. Wang, Y.I. Jang, B. Huang, D.R. Sadoway, Y.M. Chiang, *J. Electrochem. Soc.* **146**, 473 (1999)
6. W.S. Yoon, K.K. Lee, K.B. Kim, *J. Electrochem. Soc.* **147**(6), 2023 (2000)
7. G.T. Fey, D.L. Huang, *Electrochim. Acta* **45**, 295 (1999)
8. M.N. Obrovac, O. Mao, J.R. Dahn, *Solid State Ion.* **112**, 9 (1998)
9. J.B. Bates, G.R. Gruzalski, N.J. Dudney, C.F. Luck, X. Yu, *Solid State Ion.* **70/71**, 619 (1994)
10. K.H. Hwang, S.H. Lee, S.K. Joo, *J. Power Sources* **54**, 224 (1995)
11. K.H. Hwang, S.H. Lee, S.K. Joo, *J. Electrochem. Soc.* **141**, 3296 (1994)
12. J.B. Bates, N.J. Dudney, D.C. Lubben, G.R. Gruzalski, B.S. Kwak, X. Yu, R.A. Zuhr, *J. Power Sources* **54**, 58 (1995)
13. S.J. Lee, J.K. Lee, D.W. Kim, H.K. Baik, *J. Electrochem. Soc.* **143**, L268 (1996)
14. K.A. Striebel, C.Z. Deng, S.J. Wen, E.J. Cairns, *J. Electrochem. Soc.* **143**, 1821 (1996)
15. P. Fragnaud, R. Nagarajan, K.M. Schleich, D. Vujic, *J. Power Sources* **54**, 362 (1995)
16. P. Fragnaud, D.M. Schleich, *Sens. Actuators, A, Phys.* **51**, 21 (1995)
17. S.D. Jones, J.R. Akridge, *J. Power Sources* **54**, 63 (1995)
18. S.D. Jones, J.R. Akridge, F.K. Shokoohi, *Solid State Ion.* **69**, 357 (1994)
19. L. Chen, J. Schoonman, *Solid State Ion* **67**, 17 (1994)
20. JCPDS data file 16-0427
21. H. Xia, L. Lu, G. Ceder, *J. Alloys Compd.* **417**, 304 (2006)
22. W. Huang, R. French, *Solid State Ion.* **86**, 395 (1996)