

# Fabrication of $\text{LiCoO}_2$ thin films by sol–gel method and characterisation as positive electrodes for $\text{Li}/\text{LiCoO}_2$ cells

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## Abstract

$\text{LiCoO}_2$  thin films are receiving attention as positive electrodes (cathodes) for thin-film microbatteries. In this study,  $\text{LiCoO}_2$  thin films are fabricated by a sol–gel spin-coating method and a post-annealing process. The thermal decomposition behaviour of the precursor is investigated by thermogravimetry/differential thermal analysis TG/DTA and mass spectroscopy. The crystallinity, microstructure and electrochemical properties of the final films are also studied by X-ray diffraction (XRD), scanning electron microscopy (SEM) and galvanostatic charge-discharge cycling tests. Films heat-treated under appropriate conditions exhibit high capacity and good crystallinity and are therefore considered to be candidates as cathodes for thin-film microbatteries. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:**  $\text{LiCoO}_2$ ; Thin film; Microbattery; Sol–gel spin-coating method; Annealing

## 1. Introduction

In recent years, thin-film solid-state microbatteries have been studied for various applications. Because of the reduced current and power requirements of electronic devices, such microbatteries have the following applications, monolithic hybridisation with complementary metal oxide semiconductor random access memory (CMOS-RAM), back-up power for computer memory chips, small sensors, hazard cards. High-voltage materials such as  $\text{LiCoO}_2$ ,  $\text{LiNiO}_2$  and  $\text{LiMn}_2\text{O}_4$  are being developed for use as positive electrodes (cathodes) in rechargeable lithium batteries [1–3]. The fabrication of  $\text{LiCoO}_2$  as thin-film cathodes for application in all solid-state microbatteries has been a particularly active field of research due to the excellent electrochemical properties and ease of manufacture of this material [4–6].

To date, thin films of the cathode materials have been fabricated by electron beam evaporation [7], pulsed laser ablation [8], sputtering [4–6], and electrostatic spray deposition [9]. By contrast, there have been few reports of the fabrication of  $\text{LiCoO}_2$  thin films by the sol–gel method using

a spin coater. The sol–gel method offers the following advantages: easy doping; low cost and high deposition rate; easy control of crystallinity and microstructure; good control of stoichiometry.

$\text{LiMn}_2\text{O}_4$  thin films fabricated by a sol–gel method have exhibited excellent properties [10]. Thus, we have now obtained  $\text{LiCoO}_2$  thin films by means of annealing conditions after depositing them by the sol–gel method, using a spin coater. The same spin-coating method was used but the appropriate fabrication conditions for  $\text{LiCoO}_2$  thin films are much different from that of  $\text{LiMn}_2\text{O}_4$  thin films. The effect of the annealing temperature on the electrochemical properties, the crystallinity and the microstructure of the  $\text{LiCoO}_2$  thin films has been investigated. The  $\text{LiCoO}_2$  thin film which has the best electrochemical properties will be used as a cathode for an all solid-state microbattery in future studies.

## 2. Experimental

Making a solution with good wetting properties on the substrate proved to be the most difficult problem in fabrication of  $\text{LiCoO}_2$  thin films. Generally, such films are deposited on a metal current-collector.  $\text{LiCH}_3\text{CO}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{LiCH}_3\text{CO}-\text{CHCOCH}_3$  (lithium acetylacetonate) and  $\text{LiNO}_3$

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were tested as solutes of lithium sources and  $\text{Co}(\text{CH}_3\text{CO}_2)_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{Co}(\text{CH}_3\text{COCH}=\text{COCH}_3)_3$  (Cobalt acetylacetonate),  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  as solutes of cobalt sources. Ethanol, 2-propanol, 1-butanol, 2-methoxyethanol were examined as solvents. Most combinations of these materials, however, have low solubility or poor wetting properties.  $\text{LiCH}_3\text{Co}-\text{CHCOCH}_3$  and  $\text{Co}(\text{CH}_3\text{CO}_2)_2 \cdot 4\text{H}_2\text{O}$  were chosen as solutes and a mixture of 2-methoxyethanol and acetic acid as the solvent. The resulting solution exhibited quite good wetting properties and solubilities, and thus it was possible to fabricate a  $\text{LiCoO}_2$  thin film. The ratio of Li:Co was adjusted to 1:2. The precursor solution was stirred for 10 h with a magnetic stirrer in a nitrogen atmosphere. The precursor powder was prepared from the solution by an ageing process at  $80^\circ\text{C}$  for 48 h. The thermal decomposition behaviour of the powder was investigated by means of thermogravimetry (TG)/differential thermal analysis (DTA) and mass spectroscopy analysis.

A Si(100) wafer covered with  $1000 \text{ \AA}$  of  $\text{SiO}_2$  was used as the substrate. A Pt ( $1000 \text{ \AA}$ ) current-collector and Ti ( $500 \text{ \AA}$ ) buffer layer was deposited on the  $\text{SiO}_2/\text{Si}$  wafer by RF-magnetic sputtering.  $\text{LiCoO}_2$  thin films were deposited on the Pt/Ti/ $\text{SiO}_2/\text{Si}$  substrate by means of a spin-coating technique. The solution was spin coated on the substrate at 3000 rpm for 30 s. The purpose of the drying process is was to evaporate the solvents and the organic

materials from the solutes. The above process was repeated eight times and produced the “as-deposited” films. These films were annealed at  $600\text{--}750^\circ\text{C}$  in an oxygen atmosphere for 10 min. The final film thickness (measured by  $\alpha$ -step) was about  $2000 \text{ \AA}$ . X-ray diffraction (XRD) analysis using  $\text{Cu K}\alpha$  radiation was performed on the final films to identify the crystalline phase. The morphology and surface roughness of the final film were observed with scanning electron microscopy (SEM) and atomic force microscopy (AFM), respectively. The electrochemical properties of  $\text{LiCoO}_2$  thin films were investigated in a beaker-type cell which comprised a cathode, a reference electrode, an anode of Li foil (Cyprus Foote Mineral) and an electrolyte of 1 M  $\text{LiClO}_4$  in propylene carbonate (PC) solution. Charge–discharge cycling tests were performed galvanostatically at a constant current density of  $100 \mu\text{A}/\text{cm}^2$ . All the experiments were carried out in a dry box filled with argon.

### 3. Results and discussion

#### 3.1. Decomposition behaviour of $\text{LiCoO}_2$ precursor

The properties of thin films made by the sol–gel spin-coating method are known to be sensitive to the dry temperature. Thus, it is very important to determine the dry

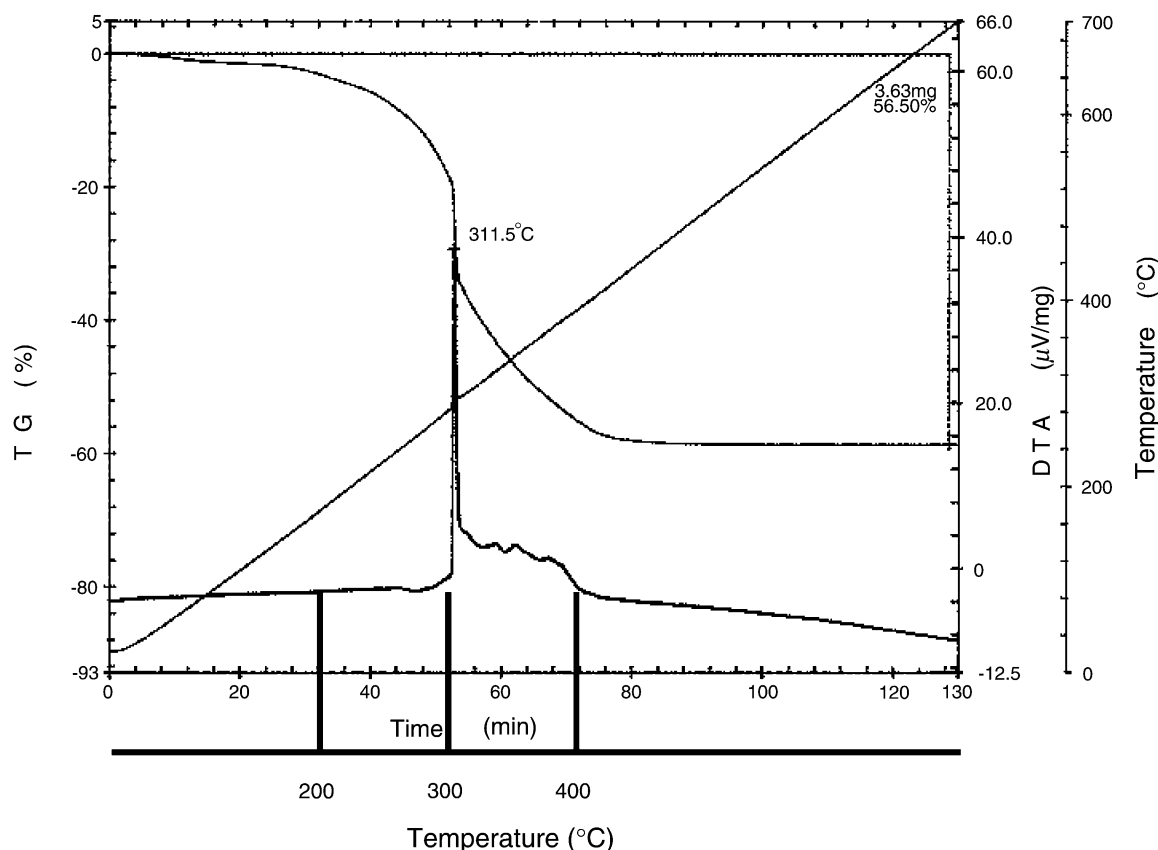


Fig. 1. TG–DTA curve for  $\text{LiCoO}_2$  precursor powder.

condition before proceeding to the next process. In this study, the dry condition was determined by the decomposition behaviour of the  $\text{LiCoO}_2$  precursor. The TG and DTA results for the  $\text{LiCoO}_2$  precursor are shown in Fig. 1. The TG curve indicates a gradually increased weight loss associated with the removal of absorbed water and solvents from the start point to  $260^\circ\text{C}$ . There is an abrupt, large weight loss at  $300^\circ\text{C}$  due to the decomposition of the organic constituents

of the precursor powder and this decomposition continues to  $400^\circ\text{C}$ . The exothermic peak at  $311.5^\circ\text{C}$  and small peaks above that temperature are related to the decomposition of the precursor.

Mass spectroscopy was used to obtain more information about the decomposition behaviour. The total intensity of the evaporated mass from the  $\text{LiCoO}_2$  precursor is shown in Fig. 2a. Peaks of relatively high intensity are detected at

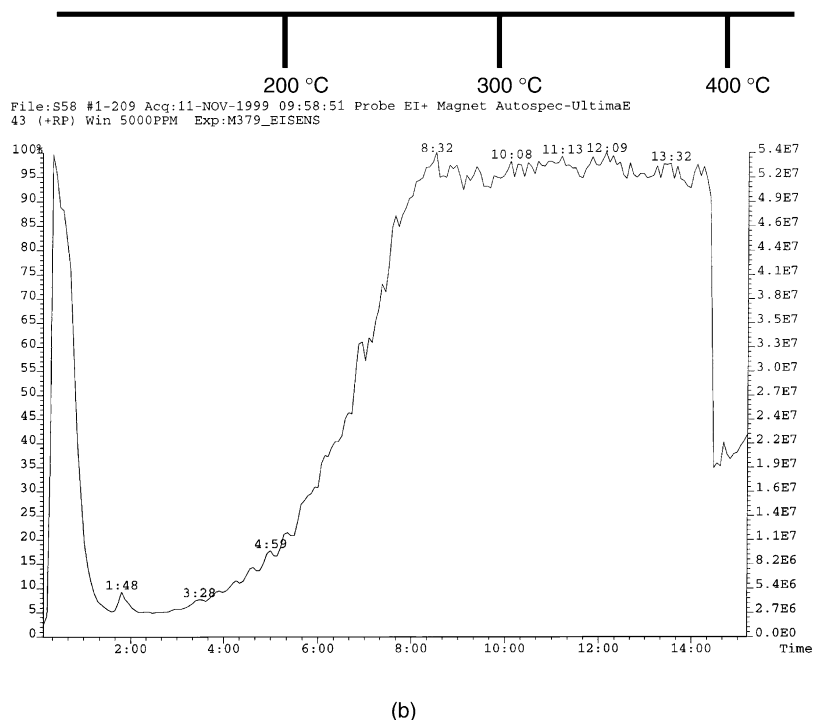
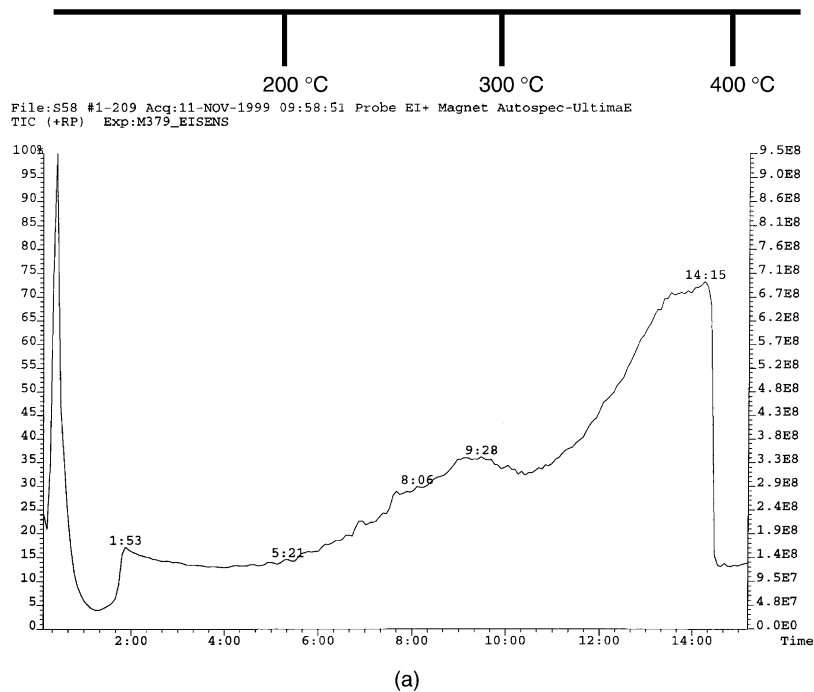


Fig. 2. Mass spectroscopy analysis of  $\text{LiCoO}_2$  precursor powder: (a) total intensity; (b)  $\text{CH}_3\text{CO}$  intensity; (c)  $\text{CH}_3\text{CO}_2$  intensity; (d)  $\text{CO}_3$  intensity.

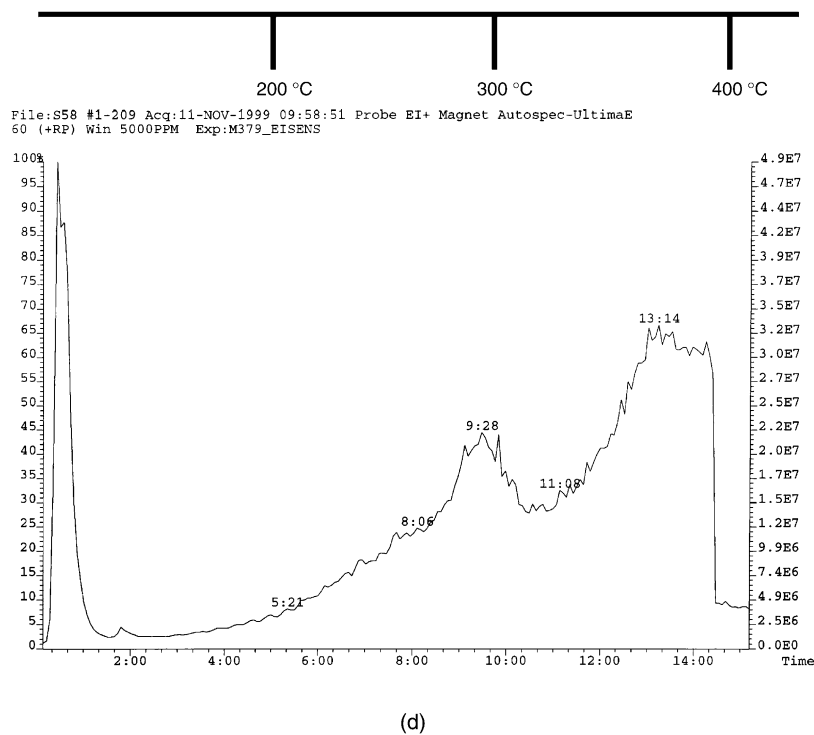
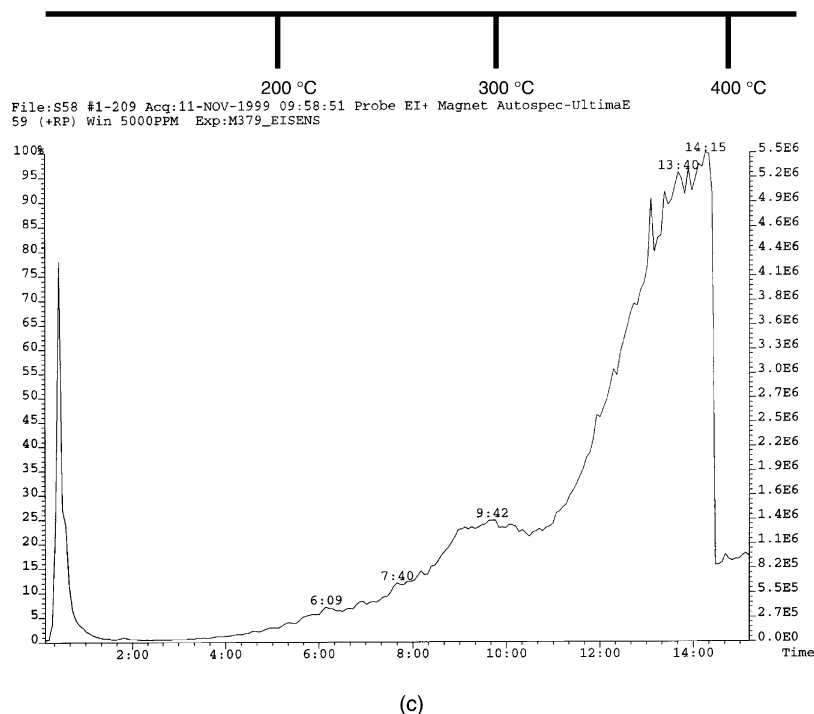


Fig. 2. (Continued).

300–380°C, which means that most of the weight loss occurs in this range. This observation agrees with those of TG and DTA. The following compounds were detected, CO<sub>2</sub>, CO<sub>3</sub>, CH<sub>3</sub>CO, CH<sub>3</sub>CO<sub>2</sub>, CH<sub>3</sub>CO and CH<sub>3</sub>CO<sub>2</sub> are related to the decomposition of lithium acetylacetonate and cobalt acetate, respectively. CO<sub>3</sub> is due to the decomposition of both. The intensity of CH<sub>3</sub>CO detected at 260–380°C is large and

constant as shown in Fig. 2b. CH<sub>3</sub>CO<sub>2</sub> (Fig. 2c) has peaks at 340–380°C and CO<sub>3</sub> (Fig. 2d) has peaks similar to that of the total intensity. From these results, it can be concluded that the decomposition of lithium acetylacetonate and cobalt acetate continues to 400°C. In fact, most of the decomposition of cobalt acetate occurs above 340°C. The organic materials which originate from the decomposition of

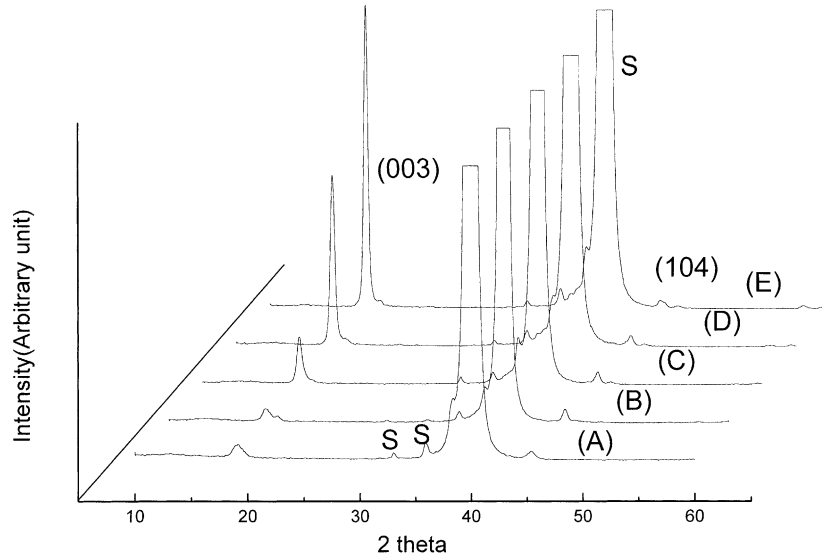


Fig. 3. XRD patterns of (A) as-deposited film; LiCoO<sub>2</sub> films annealed at (B) 600°C; (C) 650°C; (D) 700°C and (E) 750°C.

precursors will be entirely removed if a high dry temperature such as 400°C is employed. In this study, however, 400°C was not adopted as the dry temperature since a large stress is generated from the difference in the thermal expansion coefficient between the LiCoO<sub>2</sub> thin film and the substrate. Therefore, 380°C was chosen as the dry temperature. Thin films dried at 260, 300 and 340°C were also examined to determine the relationship between dry temperature and the properties of thin films. The results will be published elsewhere.

### 3.2. Analysis of crystallinity, microstructure and electrochemical property of films

As-deposited films (dried at 380°C) were annealed at 600, 650, 700 and 750°C in O<sub>2</sub> flowing for 10 min. X-ray diffraction patterns for as-deposited and annealed film are given in Fig. 3. The peaks marked S are the peaks of the substrate. The (0 0 3) and (1 0 4) peaks of LiCoO<sub>2</sub> are observed in all films, which means that all films, including the as-deposited film, have a crystalline LiCoO<sub>2</sub> phase. The

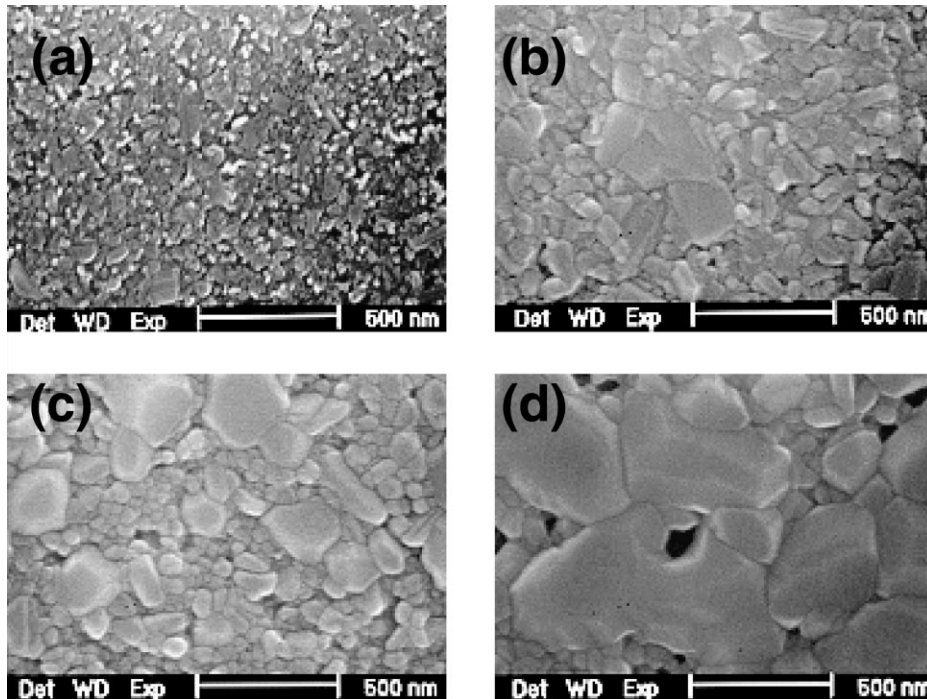


Fig. 4. Electron micrographs of LiCoO<sub>2</sub> films annealed at (a) 600°C; (b) 650°C; (c) 700°C and (d) 750°C.

crystallinity increases as the annealing temperature increases. The as-deposited and 600°C annealed films have poor crystallinities compared with other thin films. So the as-deposited and 600°C annealed films are considered to have unstable  $\text{LiCoO}_2$  frameworks.

The surface morphologies of  $\text{LiCoO}_2$  thin films annealed at 600–750°C are given in Fig. 4. On increasing the annealing temperature, the grain size of the film increases. The grain size at 650°C is about 0.1  $\mu\text{m}$  and that at 700°C is almost same. For films annealed at 750°C, the grain size increases up to 0.4  $\mu\text{m}$  and many pores are observed. This porous structure has an advantage when using a liquid electrolyte since it has large contact area with electrolyte. On the other hand, the structure may cause short-circuits in all-solid thin-film batteries using solid electrolyte and is therefore not desirable [11]. The film annealed at 600°C has an amorphous surface morphology similar to that of as-deposited film. The average surface roughness results of thin films observed by atomic force microscopy (AFM) are given in Fig. 5. The surface roughness increases as the annealing temperature increases. The thin film annealed at 750°C has the largest surface roughness due to abrupt increases in grain size.

The electrochemical properties of  $\text{LiCoO}_2$  thin films annealed at various temperatures were characterised by cycling tests (100 cycles). The discharge curves of a  $\text{LiCoO}_2/\text{PC}$

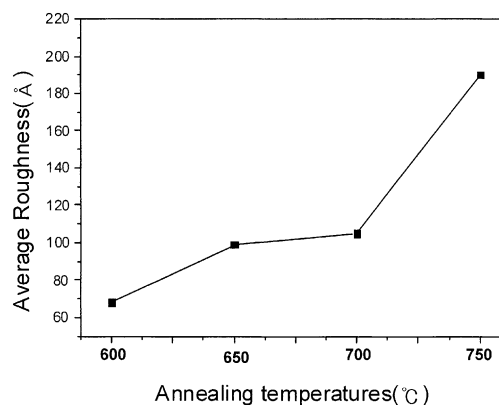


Fig. 5. Surface roughness of  $\text{LiCoO}_2$  films annealed at 600, 650, 700 and 750°C.

solution/Li cell operated between 4.3 and 3.3 V are given in Fig. 6. The typical 3.9 V plateau of  $\text{LiCoO}_2$  is observed under all conditions except for the film annealed at 600°C. The initial discharge capacity, the discharge capacity on the 100th cycle and amount of capacity retention are listed in Table 1. The electrochemical properties of the thin film varies markedly as the annealing temperature changes. The film annealed at 600°C has a relatively small initial capacity and poor rechargeability, this shows that the film does not

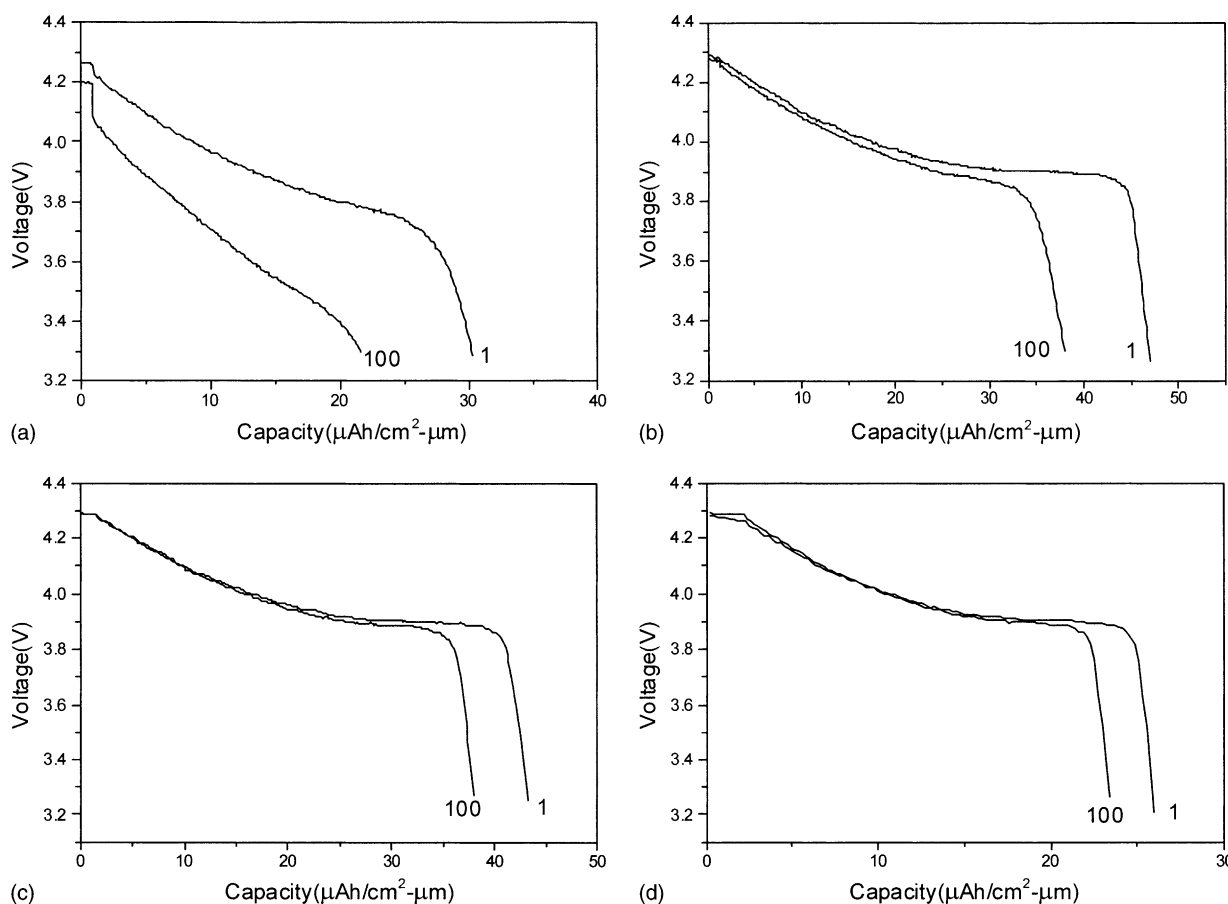


Fig. 6. Discharge curves (1st and 100th cycle) for cell  $\text{Li}/1 \text{ M LiClO}_4\text{-PC solution}/\text{LiCoO}_2$  films annealed at: (a) 600°C; (b) 650°C; (c) 700°C and (d) 750°C.

Table 1

Electrochemical properties of cell Li/1 M LiClO<sub>4</sub>-PC solution/LiCoO<sub>2</sub> films annealed at 600, 650, 700 and 750°C

	600°C	650°C	700°C	750°C
Discharge capacity of 1st cycle ( $\mu\text{Ah}/\text{cm}^2 \mu\text{m}$ )	30.3	47.0	43.2	26.0
Discharge capacity of 100th cycle ( $\mu\text{Ah}/\text{cm}^2 \mu\text{m}$ )	21.6	37.9	38.0	23.4
Capacity retention (%)	71.4	80.8	88.1	90.0

have sufficient crystallinity. This has been already indicated in the XRD pattern analysis. The poor electrochemical properties of the lithium transition metal cathode films of insufficient crystallinity have been reported in previous studies [4,11]. The discharge capacity decreases as the annealing temperature is increased from 650 to 750°C. This may be due to an increase in grain size [10–12]. Those researchers showed that the smaller the surface area, the smaller initial discharge capacity. In addition, it was reported that most of the lithium intercalation/deintercalation process takes place at the surface rather than at the core of the grains. Thus, a film which has large grain size and small surface area might have a small initial discharge capacity. The change in initial discharge capacity found in this study can be explained by a change in grain size. The smallest initial discharge capacity of the film annealed at 750°C ( $26 \mu\text{Ah}/\text{cm}^2 \mu\text{m}$ ) is due to the largest grain size.

Rechargeability is improved as the annealing temperature increases. It is considered that this is due to the improved crystallinity of the film which gives rise to a harder layered structure framework. There has been little discussion of the factors which affect the cycle life of lithium thin-film microbatteries and, therefore, more studies are required. The rechargeability of the LiCoO<sub>2</sub> thin film is moderate but not excellent. It is found that the film annealed at 700°C for 10 min has good properties such as large discharge capacity ( $43 \mu\text{Ah}/\text{cm}^2 \mu\text{m}$ ), a moderate rechargeability, and a relatively small grain size. Thus, it appears that films prepared by the sol–gel spin-coating method can be used as the cathode material for thin-film microbatteries.

#### 4. Conclusions

LiCoO<sub>2</sub> thin films have been fabricated by a sol–gel method using a spin coater and annealing process. The

decomposition of the LiCoO<sub>2</sub> precursor starts at 260°C and continues to 400°C. The crystallinity and the grain size of thin films increase as the annealing temperature increases. These features are considered to affect the electrochemical properties of the LiCoO<sub>2</sub> thin films. Films annealed at higher temperature have smaller discharge capacity and better rechargeability. The best electrochemical behaviour is obtained from a film annealed at 700°C which has moderate rechargeability and the largest discharge capacity at the 100th cycle. From these results, LiCoO<sub>2</sub> 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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