

Effects of Drying Temperature on the LiCoO₂ Thin Films Fabricated by Sol-gel Method

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ABSTRACT

LiCoO₂ thin films have received attention as cathodes of thin-film microbatteries in these days. In this study, LiCoO₂ thin films are fabricated by a sol-gel spin coating method followed by a post-annealing process. The thermal decomposition behaviour of precursor is investigated by TG/DTA analysis. The change of crystallinity, microstructure and electrochemical properties of final films as the drying temperature changes are also studied by XRD, SEM and galvanostatic charge/discharge cycling test. The relationship between the discharge capacity and the drying temperature are intensively investigated in this work.

Key words : LiCoO₂, Thin film, Microbattery, Sol-gel spin coating method, Drying

1. Introduction

In recent years, thin-film solid-state microbatteries have been studied for various applications. High-voltage cathode materials such as LiCoO₂, LiNiO₂ and LiMn₂O₄ are being developed for use in rechargeable lithium batteries.¹⁻³⁾ Especially fabrication of LiCoO₂ as thin-film cathode for application in all solid-state microbatteries has been an interesting field of research due to its excellent electrochemical properties and ease of manufacture.⁴⁻⁶⁾

To date, thin films of the cathode materials have been fabricated mostly by electron beam evaporation,⁷⁾ pulsed laser ablation,⁸⁾ sputtering⁴⁻⁶⁾ and electrostatic spray deposition.⁹⁾ But there have been few reports of the fabrication of LiCoO₂ thin films by the sol-gel method using a spin coater. The sol-gel method has some advantages such as easy doping, low cost and high deposition rate and good control over stoichiometry.

LiMn₂O₄ thin films fabricated by a sol-gel method showed excellent properties in recent study of our research group.¹⁰⁾ So we obtained LiCoO₂ thin films by means of annealing treatment (700°C for 10 min) after depositing them by the sol-gel method, using a spin coater. The effect of the drying temperature on the electrochemical properties, the crystallinity and the microstructure of the LiCoO₂ thin films have been investigated.

2. Experimental

We chose LiCH₃Co-CHCOCH₃ and Co(CH₃CO₂)₂·4H₂O as solutes and a mixture of 2-methoxyethanol and acetic acid

as solvent. The ratio of Li : Co was adjusted to 1 : 2. The precursor solution was stirred for 10 h with a magnetic stirrer in N₂ atmosphere. We made the precursor powder from the solution by an aging process at 80°C for 48 h and examined the thermal decomposition behaviour of the above powder by TG (Thermogravimetry)/DTA (Differential Thermal Analysis).

LiCoO₂ thin film was deposited on the Pt(111)/Ti/SiO₂/Si substrate by means of a spin coating technique. The solution was spin-coated on the substrate at 3000 rpm for 30s. After spin-coating process, the film was dried on the hot plate for 5 min. The purpose of the drying process is evaporating the solvents and the organic materials from the solutes. We repeated the above process for eight times and made the "as-deposited" films. We chose four different drying temperature such as 260, 300, 340 and 380°C to investigate the effect of the drying temperature on the electrochemical properties of final LiCoO₂ thin films. The thickness of "as-deposited" films are about 2800 Å as shown in Table 1. The "as-deposited" films were annealed at 700°C in O₂ atmosphere for 10 min to make crystalline LiCoO₂ phases. The final film thickness measured by α -step was about 2000 Å also as shown in Table 1. Large volume shrinkage (30% of first volume) occurs during annealing

Table 1. Comparison of the Thicknesses of LiCoO₂ Thin Films which were before and after Annealing Treatment

	260°C	300°C	340°C	380°C
Thickness of "as-deposited" thin film(Å)	2812	2795	2772	2723
Thickness of final thin film which was annealed at 700°C(Å)	1940	1957	1940	1933

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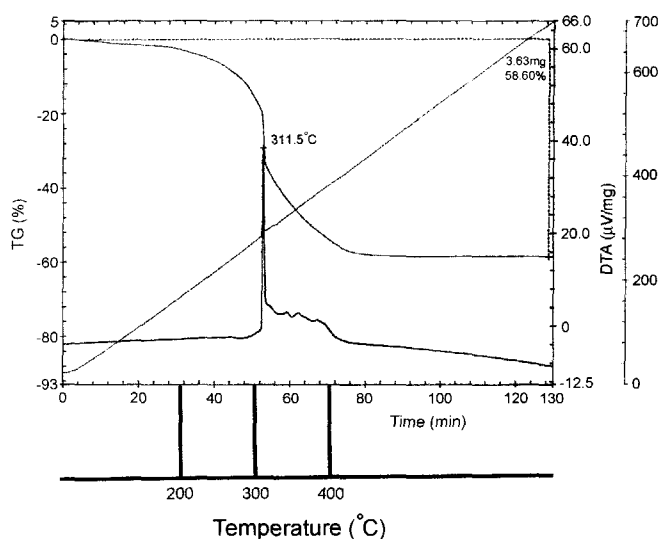


Fig. 1. TG-DTA curve for LiCoO_2 precursor powder.

treatment. X-ray diffraction analysis using $\text{Cu K}\alpha$ radiation was performed on the final films to identify the crystalline phases. The morphology and surface roughness of the final films were observed with SEM (Scanning Electron Microscopy) and AFM (Atomic Force Microscopy) respectively. The electrochemical properties of LiCoO_2 thin films were investigated in a beaker-type cell made for a cathode, a reference electrode, an anode of Li foil (Cyprus Foote Mineral) and an electrolyte of 1 M LiClO_4 in PC (Propylene Carbonate) solution.

3. Results and Discussion

The TG curve shows the gradually increased weight loss associated with the removal of absorbed water and solvents at the start point to 260°C (Fig. 1). There is an abrupt large weight loss at 300°C due to the decomposition of the organic constituents of the precursor powder and this decomposition is continued to 400°C. The organic materials originated from the decomposition of precursors will be entirely removed if we employ high dry temperature such as 400°C. But in this study, we failed to adopt 400°C as dry temperature since a large stress is generated from the difference in the thermal expansion coefficient between the LiCoO_2 thin film and the substrate. This stress causes a failure to LiCoO_2 thin film. So we chose 260, 300, 340 and 380°C as the dry temperatures and continued experiment to investigate the relationship between the drying temperature and the discharge capacity of LiCoO_2 thin films.

As-deposited films (dried at 260, 300, 340 and 380°C) were annealed at 700 in O_2 flowing for 10 min. X-ray diffraction patterns for as-deposited and annealed film are given in Fig. 2. The peaks marked S are the peaks of substrate. (003) and (104) peaks of LiCoO_2 are observed in all films, which means that all films have a crystalline LiCoO_2

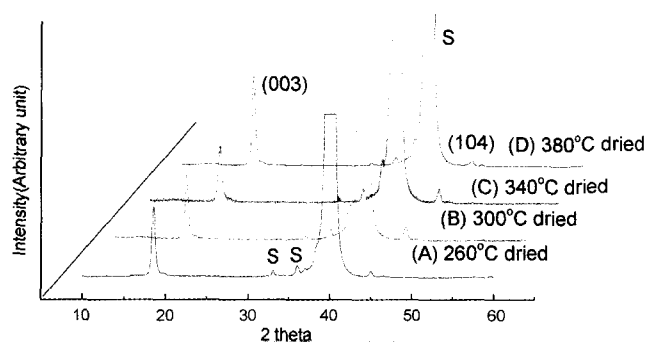


Fig. 2. XRD patterns of LiCoO_2 thin films dried at (A) 260, (B) 300, (C) 340 and (D) 380°C for 5 min. and annealed at 700°C for 10 min.

phase after annealing treatment. The peak heights of the films are almost same. This means that the crystallinities and the preference of orientation of the films are also almost same.

The surface morphologies of LiCoO_2 thin films annealed at 700°C after being dried at each drying temperature are given in Fig. 3. The surface morphologies of those films are almost same except 260°C dried thin film. For the film dried at 260°C, more pores are induced by abrupt evaporation of more amount of residual organic materials than other thin films. The existence of much oxygen defects of 260°C dried thin film as shown in RBS result of Table 2 can be also explained by the evaporation of residual organic materials. The average surface roughness results of thin films observed by Atomic Force Microscopy (AFM) are given in Fig. 4. The surface roughness decreases as the drying temperature increases. So the total surface area of thin film decreases as the drying temperature increases.

The electrochemical properties of LiCoO_2 thin films dried at various temperature were characterized by cycling test (100 cycles). The discharge curves of LiCoO_2/PC solution/Li cell operated between 4.3 and 3.3 V are given in Fig. 5. The initial discharge capacity, discharge capacity of 100th cycle and amount of capacity retention are shown in Table 3. The thin film dried at 260°C has a relatively smaller initial discharge capacity than other films. The initial discharge capacity increases as the drying temperature increases in our work.

The change of the discharge capacity with the change of fabrication condition of thin film is explained by the change of the composition, crystallinity, preferred orientation and surface area amount.^{7,10,11} In this study, the change of crystallinity and orientation of film due to the change of drying temperature is not severe. Also the discharge capacity does not decrease in spite of the decrease of surface area induced by the increase of drying temperature. So the above three factors do not seem to affect so much the change of discharge capacity. The composition of thin film can be a candidate to explain the discharge capacity changing behaviour in this study. The more non-

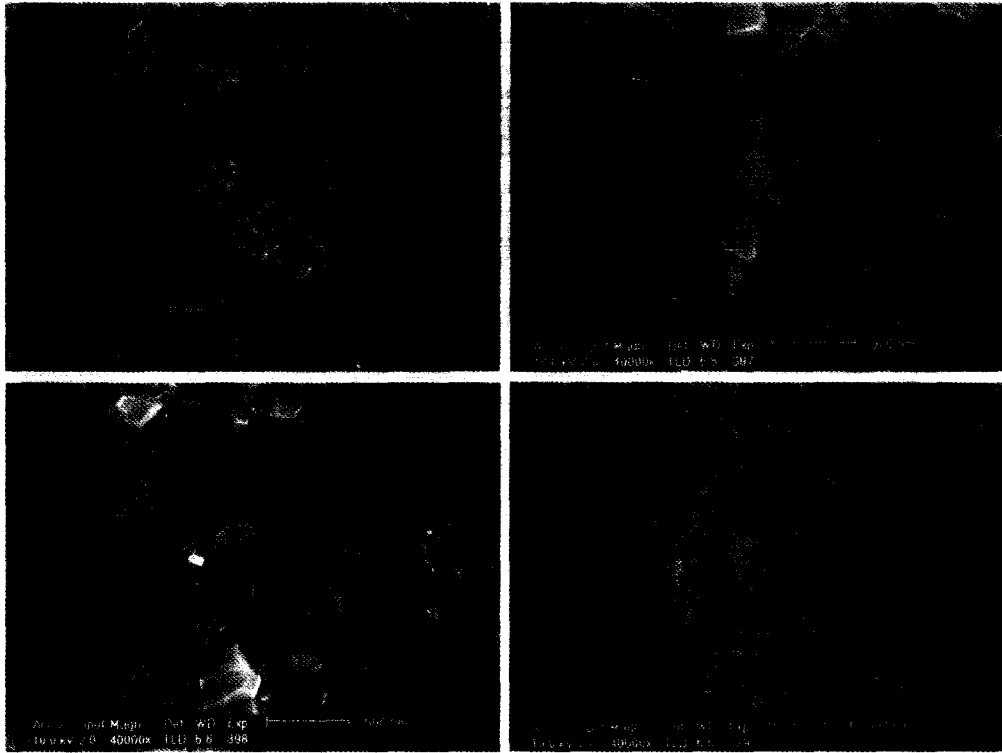


Fig. 3. SEM images (×40,000) of the films dried at (A) 260, (B) 300, (C) 340 and (D) 380°C for 5 min. and annealed at 700°C for 10 min.

Table 2. The Composition of LiCoO₂ Thin Films Dried at 260, 300, 340 and 380°C for 5 min. and Annealed at 700°C for 10 min.

Drying temp. (°C)	Composition
260	Li _{0.99} CoO _{1.73}
300	Li _{1.01} CoO _{1.84}
340	Li _{1.00} CoO _{1.86}
380	Li _{0.99} CoO _{1.88}

Table 3. Electrochemical Properties of Cell Li/1 M LiClO₄-PC Solution/ LiCoO₂ Films Dried at 260, 300, 340 and 380°C for 5 min. and Annealed at 700°C for 10 min.

	260°C	300°C	340°C	380°C
Discharge capacity of 1 st cycle (μAh/cm ² -μm)	28.3	40.5	39.2	43.2
Discharge capacity of 100 th cycle (μAh/cm ² -μm)	25.0	33.6	32.9	38.0
Capacity retention (%)	88.3	83.0	83.9	88.1

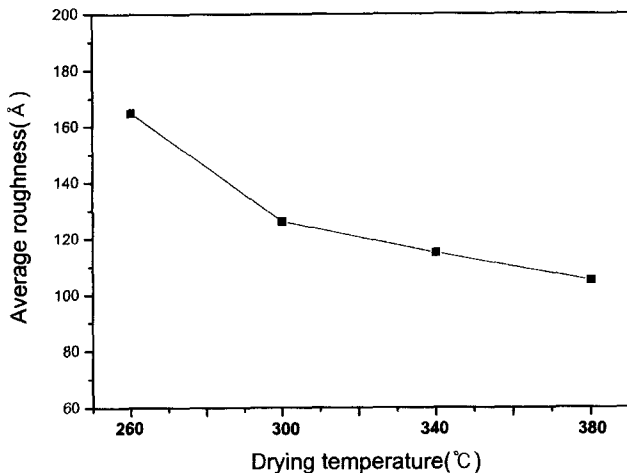


Fig. 4. Surface roughness of LiCoO₂ films dried at 260, 300, 340 and 380°C for 5 min and annealed at 700°C for 10 min.

stoichiometric thin film such as 260°C dried thin film is thought to have the smaller initial discharge capacity. When a LiCoO₂ thin film include oxygen defects, the valence of Co of that film increases. In this case the capability of accommodating Li ion decreases and the discharge capacity also decreases. So the composition is thought to be the most important factor to explain the initial discharge capacity changing behaviour in this study. Capacity retention improves as the drying temperature increases at 300 to 380°C. Thin film dried at 380°C experienced the least amount of evaporation of residual organic materials. It also has the most stoichiometric composition. These factors is thought to make thin film dried at 380°C have stronger LiCoO₂ framework and better capacity retention than other films. But the best capacity retention of 260°C dried thin films acquires more study.

In these days, domestic researches are concentrated on the bulk type lithium secondary battery.¹²⁻¹⁴⁾ But there is a

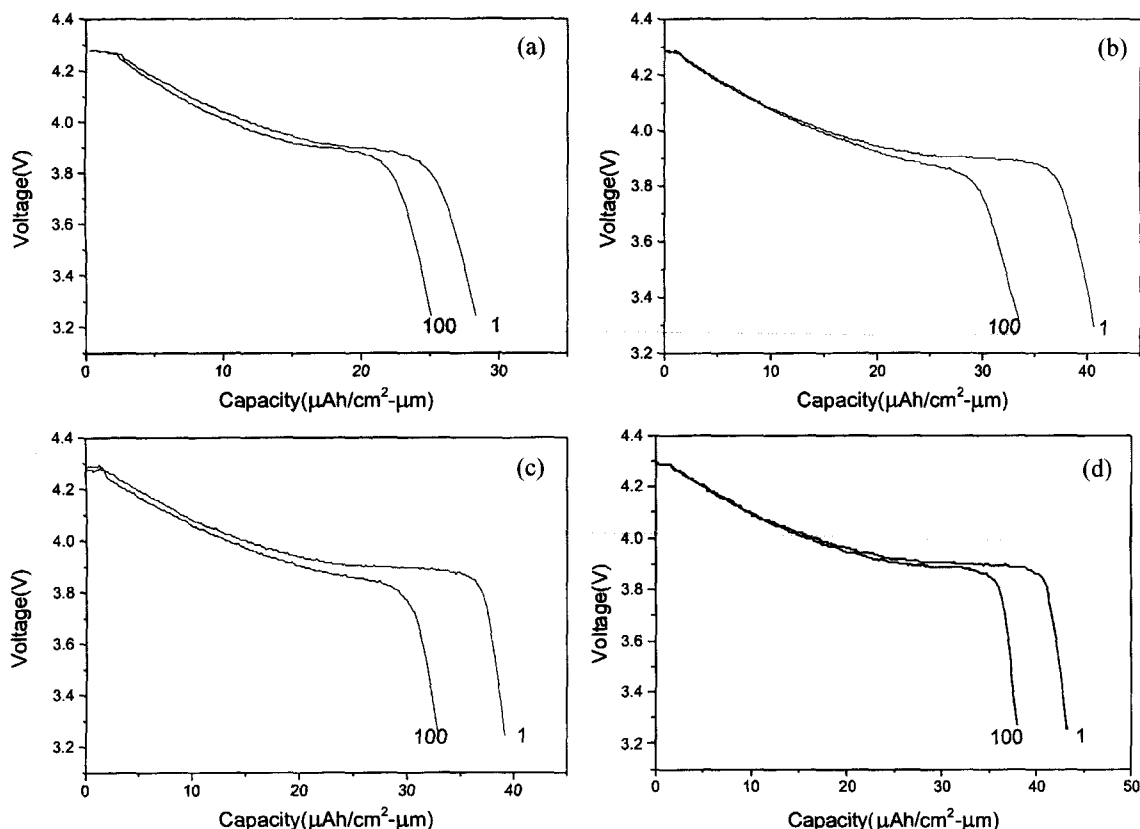


Fig. 5. Discharge curves(1st and 100th cycle) for cell Li/1 M LiClO₄-PC solution/LiCoO₂ films dried at (A) 260, (B) 300, (C) 340 and (D) 380°C for 5 min. and annealed at 700°C for 10 min.

need to concentrate efforts on the all solid-state thin-film battery.

4. Conclusion

LiCoO₂ thin films were fabricated by a sol-gel method using a spin-coater and annealing process. The decomposition of the LiCoO₂ precursor starts at 260°C and continues to 400°C. The films dried at lower temperature such as 260°C have smaller discharge capacity than other films. This can be explained by the existence of more oxygen defect at thin films dried at lower temperature. The nonstoichiometry of oxygen caused by evaporation of organic materials makes the discharge capacity decrease. So the composition is thought to be the most important factor to affect the initial discharge capacity in this study.

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