

Characterization of sprayed and sputter deposited LiCoO_2 thin films for rechargeable microbatteries

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Abstract

Thin films of LiCoO_2 have been prepared by both spray pyrolysis and r.f. sputtering. Structural properties of the films have been investigated by X-ray powder diffraction and scanning electron microscopy. The LiCoO_2 hexagonal high-temperature phase was obtained on the samples after post-deposition annealing treatments at 600°C in air. Films as thin as 75 nm have been deposited on large aluminium and aluminium/gold substrates. Sputter deposition improved the density and homogeneity of thin films compared with the spray pyrolysis method. Cells with sprayed and sputtered LiCoO_2 compounds versus lithium using LiClO_4 in propylene carbonate as the liquid electrolyte have been tested, the importance of annealing the thin films before cycling discussed, and the importance of the substrate in the cycling behaviour is evidenced. The cyclic voltammograms demonstrate that the LiCoO_2 cathodes prepared by both methods are electrochemically active, showing promising cycling behaviour.

Keywords: Rechargeable microbatteries; Lithium cobalt oxide; Thin films

1. Introduction

Lithium cobalt oxide in powder form is commonly used as a cathode material for commercial lithium-ion batteries. This lithiated oxide shows good cycleability and a relatively high energy density relative to other lithiated oxides. Perhaps the greatest single advantage of this compound relative to other lithiated oxides is the simplicity of the lithium/cobalt oxide phase diagram and the relative ease of preparing the desired phase. Considering the cost of cobalt and its relative scarcity on the planet, this ease of synthesis undoubtedly accounts for its use on a relatively large scale. Since this material is already successfully used as a cathode in commercial batteries, we felt that this material would serve as a useful cathode in thin-film lithium-ion microbatteries [1], thus eliminating the need to use a lithium metal anode. We have already reported successful attempts to prepare this material with a non-aqueous sol method, i.e. spray pyrolysis [2–4]. This method leads to the easy preparation of large surface films; however, the films are usually thicker than $1\ \mu\text{m}$. In addition, the films prepared by spray pyrolysis have high porosity leading to decreased conductivity. Since only a few attempts have been made to prepare dense LiCoO_2 thin films with physical vapour deposition (PVD) methods [5–7], we have chosen to use an r.f.

sputtering method to achieve thin films of this material [8] and compare the results of the two different preparation techniques. We felt that electrochemical measurements would allow us to compare the relative advantage of a more porous film, i.e. higher surface area, with the advantage of higher electrical conductivity.

2. Experimental

2.1. Sprayed thin films

The general route was to react anhydrous lithium nitrate and hydrated cobalt nitrate with propylene glycol. The salts were added in stoichiometric proportions to propylene glycol and subsequently heated at 180°C for 2 h. Sols of different concentrations (0.04 M and 0.17 M) were prepared. The sols were then kept at room temperature until they were sprayed with an air brush assembly (Olympus Medea) onto heated aluminium, aluminium/gold and glass substrates (temperature close to 600°C). The sols were air stable and no precautions were taken to avoid contact with humid air. The substrates were kept at temperature using a halogen hot plate. After deposition, the films deposited on aluminium and aluminium/gold were annealed 1 h at 600°C , while the films on glass substrates were annealed at 500°C . Aluminium/

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gold substrates are prepared by gold evaporation at room temperature on aluminium foil before the spray pyrolysis.

2.2. Sputtered thin films

LiCoO₂ was obtained by spraying an LiCoO₂ sol (as indicated above) onto an aluminium support (3 mm thick, 160 mm diameter). The film showed good adhesion to the aluminium substrate. The target was then connected to the aluminium target holder of an r.f. sputtering apparatus (Alcatel SCM 400). Aluminium, aluminium/gold and glass substrates were located at 45 mm under the target. The substrate temperature was not controlled inside the chamber. The residual pressure in the chamber was 10⁻³ Pa before being filled with pure argon at a pressure of 8 Pa. An r.f. power of 350 W at 13.6 MHz was applied and different deposition times were tested. Film thickness was measured using a DEKTAK 3 ST profilometer after etching the LiCoO₂ layer with a HCl/HNO₃ mixture. A deposition time of 20 min resulted in a film thickness of 75 nm while increasing to a 1 h run led to a 240 nm thick film, i.e. a deposition rate of 4 nm/min. Films as large as 80 mm × 80 mm could be deposited in this way. All the films showed strong adhesion to the aluminium, aluminium/gold and glass substrates. Since the XRD patterns of as-deposited films showed no Bragg diffraction peaks, an indication of crystallinity, the samples on glass substrates were annealed for 1 h at 500 °C and those on aluminium and aluminium/gold substrates for 1 h at 600 °C.

3. Results and discussion

3.1. Li/Co ratio

In samples of sprayed LiCoO₂, the lithium and cobalt concentrations were determined using inductively coupled plasma (ICP). Table 1 summarizes the Li/Co ratio in the different films. It can be pointed out that the sprayed samples are more similar to LiCoO₂ than the sputtered ones.

Table 1

Li/Co ratios determined by means of inductively coupled plasma (ICP) for sprayed and sputtered LiCoO₂ thin films on aluminium substrates, annealed 1 h at 600 °C

Deposition method	Li/Co molar ratio	Chemical formula
Spray/pyrolysis	1.03	Li _{1.03} CoO ₂
R.f. sputtering	0.88	Li _{0.88} CoO ₂

3.2. X-ray diffraction patterns

Typical XRD patterns of sprayed LiCoO₂ thin films (> 1 μm thick) show all the peaks of the high-temperature form (see Fig. 1) in good agreement with the calculated relative intensity of the LiCoO₂ XRD reference pattern [9]. Decreasing the thickness of the sprayed thin films resulted in the loss of minor peaks, so that only the (003) reflection could be observed. Fig. 2 shows XRD patterns obtained from LiCoO₂ thin films by means of both spray pyrolysis and sputtering. Before annealing the sputter-deposited thin films shows no peaks except those due to the substrate and the spray pyrolysis films show only a very weak, broad (003) reflection. After annealing it is possible to identify the major crystalline peaks of both the sputtered and the sprayed samples even when the films had a thickness of only 0.2 μm. Our aluminium substrate is a standard cooking foil so unidentified peaks appeared more or less depending on the sample of substrate used. For the samples with an Al/Au substrate (sprayed, annealed sample shown in Fig. 2), we observe the formation of Al₂Alu alloy after annealing. The poor adhesion of LiCoO₂ onto gold is substantially reduced after the formation of this alloy. Using the Scherrer formula [10] the average crystalline size determined with the full width at half-maximum height (FWHM) of the (003) reflection for both kinds of films have been reported in Table 2. The films prepared by r.f. sputtering show a smaller grain size than those prepared by spray pyrolysis. Although the annealing treatment is the same for both samples (1 h at 600 °C).

Micrographs of sprayed and sputter-deposited LiCoO₂ thin films are shown in Fig. 3. At low magnification, the sprayed samples appeared less homogeneous and more porous than

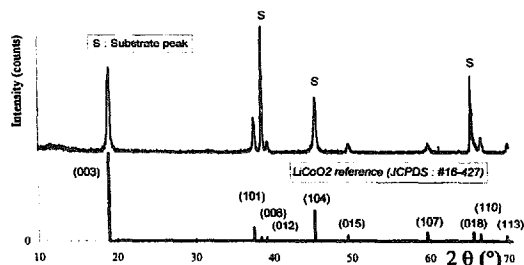


Fig. 1. XRD patterns of sprayed LiCoO₂ thin films on an aluminium substrate annealed for 1 h at 600 °C, compared with a LiCoO₂ reference.

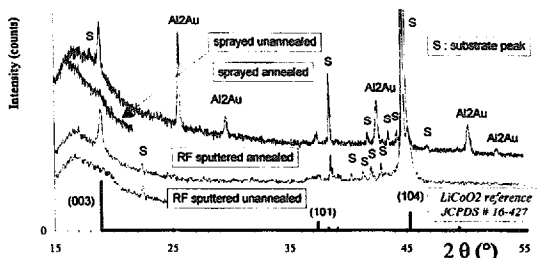


Fig. 2. XRD patterns of sprayed LiCoO_2 thin films (deposited by r.f. sputtering and spray pyrolysis) both before and after annealing for 1 h at 600°C , compared with an LiCoO_2 reference.

Table 2

Average crystallite size for sprayed and sputtered LiCoO_2 thin films on aluminium substrates.

Deposition method	Annealed (1 h at 600°C)	Average crystallite size deduced from the (003) reflection (\AA)
Spray/pyrolysis	No	25
Spray/pyrolysis	Yes	50
R.f. sputtering	Yes	35

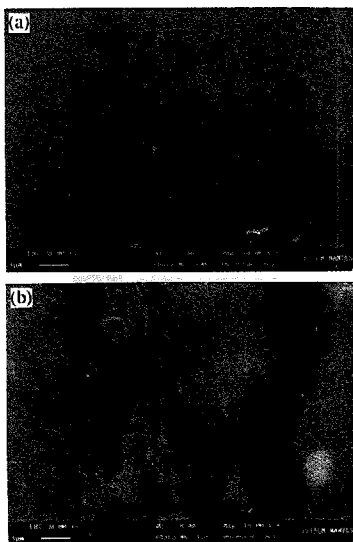


Fig. 3. (a) SEM micrographs of LiCoO_2 thin films deposited on aluminium substrates by spray pyrolysis and annealed 1 h at 600°C . (b) SEM micrographs of LiCoO_2 thin films deposited on aluminium substrates by r.f. sputtering and annealed 1 h at 600°C .

the films deposited by r.f. sputtering. Increasing the magnification to $\times 10\,000$ reveals that the grain shapes are also slightly different in both types of films. EDS analysis on

LiCoO_2 sputtered thin films deposited on glass substrate indicated the existence of aluminium, probably coming from the target holder.

3.3. Conductivity measurements

The conductivities of LiCoO_2 thin films prepared on glass substrate were determined using a standard 4 probe Van der Pauw method at room temperature. With the exception of the sputter-deposited samples before annealing, the conductivity of the samples ranged from 0.1 to 1.0 S cm^{-1} . Before annealing, the samples prepared with r.f. sputtering show a conductivity below our detection limit ($2 \times 10^{-4}\text{ S cm}^{-1}$).

3.4. Cyclic voltammetry

Figs. 4 and 5 show slow ($10\text{ mV}/10\text{ s}$) scan cyclic voltammograms of LiCoO_2 electrodes (both annealed and not-annealed) obtained by spray pyrolysis on Al/Au substrates. We have observed an important difference in the form of the

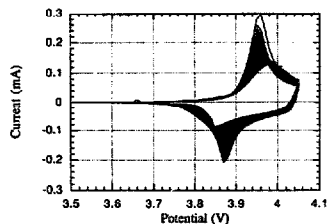


Fig. 4. Slow scan cyclic voltammograms ($10\text{ mV}/10\text{ s}$) of LiCoO_2 film deposited by spray pyrolysis onto an Al/Au substrate and annealed.

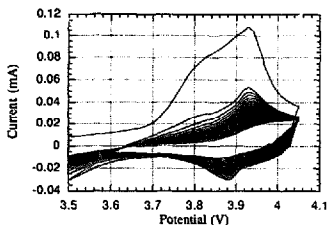


Fig. 5. Slow scan cyclic voltammograms (10 mV/10 s) of LiCoO₂ film deposited by spray pyrolysis onto an Al/Au substrate without annealing.

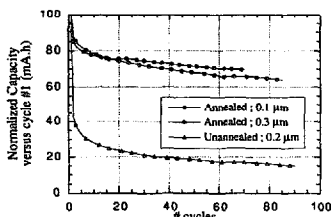


Fig. 6. Normalized capacity vs. cycle number for LiCoO₂ films deposited on Al/Au substrates by spray pyrolysis (annealed and non-annealed).

peaks (substantially broader for the non-annealed samples), and a much greater loss in capacity with cycle number for the non-annealed samples. This capacity loss is clearly shown in Fig. 6 which indicates the variation in capacity versus cycle number normalized to the first cycle. We have observed that the capacity variation is great during the first ten cycles (-25% for the annealed samples and -70% for the non-annealed samples), and thereafter the losses are similar. As previously indicated, samples prepared by spray pyrolysis showed less crystallinity before annealing (see Table 2 and Fig. 2), and therefore it appears that the amorphous or nanocrystalline material is more susceptible to failure during cycling than well-crystallized material. It should be noted that our non-annealed samples prepared by r.f. sputtering could not be cycled. This could be the result of very poor electrical conductivity or the amorphous nature of the film.

Figs. 4 and 7 show the cyclic voltammograms of LiCoO₂ obtained by spray pyrolysis on aluminium foil coated with gold and on a pure aluminium foil substrate, respectively. On aluminium foil substrates we observed a rapid loss in capacity (see Fig. 8), an increasing separation between the oxidation and reduction peaks and a broadening of the peaks during the first cycles. These modifications in the voltammogram are substantially decreased in the case of the Al/Au substrates. It seems possible that during the oxidation reaction the highly reactive de-intercalated cobalt compound is able to oxidize the aluminium substrate even though in theory there is a protective layer of Al₂O₃ preventing direct contact between the substrate and the highly oxidizing cobalt oxide. It is possible

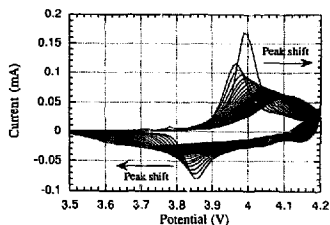


Fig. 7. Slow scan cyclic voltammograms (10 mV/10 s) of LiCoO₂ film deposited by spray pyrolysis onto an aluminium substrate and annealed.

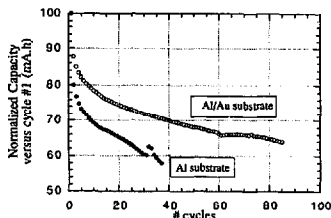
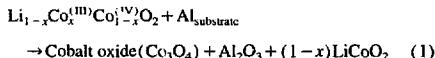


Fig. 8. Normalized capacity as a function of cycle number for LiCoO₂ films deposited on Al and Al/Au substrates and annealed.

to consider a chemical reaction modifying the electrode material present



Eq. (1) will generate the simultaneous loss of active cobalt oxide — Co₃O₄ is a non-active species — and increase the cell impedance due to the insulating Al₂O₃ formed at the interface. The loss in electrode capacity would correspond to the loss in active material present at the electrode, whereas the broadening observed in the oxidation and reduction peaks would correspond to the added resistance from the interfacial Al₂O₃ layer being formed between the active cobalt and the conducting aluminium contact.

In Figs. 4 and 9 are shown the cyclic voltammograms of LiCoO₂ samples deposited by either spray pyrolysis or r.f.

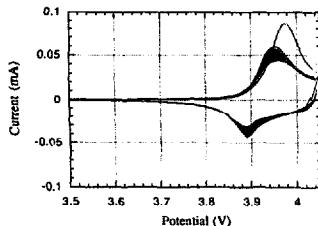


Fig. 9. Slow scan cyclic voltammograms (10 mV/10 s) of LiCoO₂ film deposited by r.f. sputtering onto Al/Au substrate and annealed

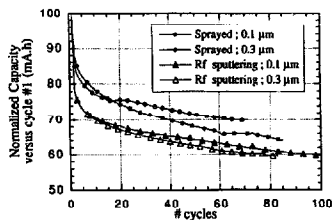


Fig. 10. Normalized capacity vs. cycle number for LiCoO_2 films deposited on Al/Au substrates by spray pyrolysis and r.f. sputtering (annealed).

sputtering (on similar gold-coated aluminium foil substrates) and then subsequently annealed. The oxidation and reduction peaks of the r.f. sputtered samples are broader than those observed in the samples prepared by spray pyrolysis. This peak broadening of r.f. sputtered samples occurs relative to spray pyrolysis samples at all film thickness studied, i.e. from 0.1 to 10 μm . It thus appears that the r.f. sputtered samples, even after annealing, are electrochemically slower and show more capacity loss (Fig. 10) than those prepared by spray pyrolysis.

4. Conclusions

Thin films of LiCoO_2 have been prepared using either spray pyrolysis or r.f. sputtering. Electrochemical tests have shown that these compounds are electrochemically active. We have shown that the electrochemical properties of the film cathodes can be considerably improved by annealing in air (80% loss in capacity after 40 cycles for non-annealed spray pyrolysis samples versus 30% loss in capacity after annealing for the same samples). In addition we have seen that the choice in substrate can modify the cycling behaviour of electrodes prepared by otherwise identical processes (40% loss in capacity for annealed spray pyrolysis films after 30 cycles on aluminium foil versus 25% loss in capacity for identical films prepared on an Al/Au substrate).

Prior to annealing, the r.f. sputtered films are amorphous in X-rays. These films show high resistivity and no activity in our cells. After annealing, the formation of a crystalline phase decreases the resistance and leads to electrochemical activity. Although these films appear far more dense than the material prepared by spray pyrolysis, their electrochemical behaviour never matches that of the films prepared by spray pyrolysis. The oxidation and reduction peaks are always broader and the current density is lower. Our conclusion is the more porous spray pyrolysis films allow for more permeation of the electrolyte and that are smaller diffusion distances within the active thin film electrode. This allows the films being created by spray pyrolysis to show faster kinetics when a liquid electrolyte is used. If a solid electrolyte is used, thus preventing the electrolyte from penetrating the electrode, the more dense r.f. sputtered films may have better a contact between the solid electrolyte and the electrode, as well as a better contact between the grains in the electrode. It is thus very difficult to compare electrodes if the electrolyte systems used are not the same, as is the case if one wishes to compare results from solid and liquid electrolytes. In addition, it appears that when LiCoO_2 thin films are used in a liquid electrolyte there is a problem associated with the aluminium foil substrate. This substrate is slowly attacked during cycling modifying the capacity and kinetics of the electrode.

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