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# Fabrication of $LiCoO_2$ thin film cathodes for rechargeable lithium battery by electrostatic spray pyrolysis

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**Abstract**

$LiCoO_2$ thin films for cathodes in rechargeable lithium batteries were prepared by the electrostatic spray pyrolysis technique. The surface morphology may be either dense or porous, depending on the process conditions. Low temperature (280°C) results in amorphous films. Deposition at a temperature higher than 340°C results in the hexagonal phase of $LiCoO_2$. The lithium chemical diffusion coefficients of these films range between $10^{-13}$ and $10^{-12}$ $cm^2/s$.

*Keywords:* Electrostatic spray pyrolysis; Intercalation; Lithium cobalt oxide

## 1. Introduction

In the past few years a novel preparation technique for thin films of metal oxides, electrostatic spray pyrolysis (ESP), has been developed in our laboratory. Although the detailed processes, physical as well as chemical, and kinetics involved are not completely clear at this moment, it has shown many interesting features such as a simple and low-cost set-up, low-temperature synthesis, wide range of precursor selection. We have reported several results on the production of $LiMn_2O_4$ [1], YSZ and $BaCeO_3$ [2]. This study is a continuation of applying such technique to prepare cathode materials for rechargeable lithium batteries, and here new results on $LiCoO_2$ are presented. The full paper on $LiCoO_2$, and the results on other 4 V-cathode materials, such as $LiMn_2O_4$ and $LiNiO_2$ will be reported in the near future.

## 2. Experimental

Ethanol (100%) solutions of $LiAc \cdot 2H_2O$ and $Co(NO_3)_2 \cdot 6H_2O$ were prepared separately. The solutions were mixed in order to get a molar ratio Li : Co = 1 : 1, which was used as the precursor solution. A horizontal ESP set-up with capillary – plate configuration was used (Fig. 1). Round stainless steel disks (1.4 cm in diameter) were chosen as the substrate and acted as the "plate". A heating element was used to control the substrate temperature. A positive high voltage up to +12.5 kV was applied to the nozzle (a hollow needle or "capillary") through which the precursor solution is forced to flow, and from which a positively charged spray was generated. Under mainly the electrostatic force (other forces like, for instance, electric wind play a minor role) the droplets of the spray tended to move to the hot substrate, where pyrolysis took place at or near


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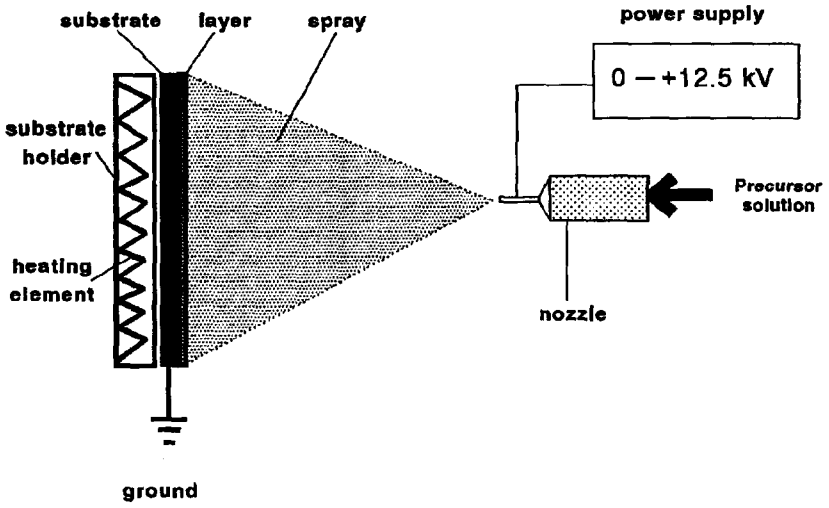


Fig. 1. A schematic figure of the ESP set-up.

the surface of the substrate. The nozzle-to-substrate distance was 6 cm.

The weights of the films were obtained by weighing the substrate before and after deposition. The deposited thin films were analyzed by X-ray diffraction (XRD) and scanning electron microscope (SEM). Electrochemical cells:

$$\mathrm{Li} \mid \mathrm{LiClO_4}\ (0.7\ \mathrm{M})\ \text{in propylene carbonate (PC)} \mid \mathrm{LiCoO_2} \mid \text{stainless steel} \quad (1)$$

were prepared. Charge curves and lithium ion chemical diffusion coefficients were measured by the Galvanostatic Intermittent Titration Technique (GITT) [3] using a computer-controlled potentiostat.

### 3. Results and discussion

The surface morphology of a $LiCoO_2$ thin film resulting from two hours of deposition is shown in Fig. 2 (the deposition parameters are given in the caption). It can be seen that the film is quite dense. The lines appearing at the micrograph are caused by the surface roughness of the substrate, which also indicates that the layer is thin and relatively smooth. However, the morphology tends to become more porous with increasing layer thickness. Comparing this result with parallel experiments on other materials, this seems to be a general trend in the deposition of oxide layers by this technique. It could be related

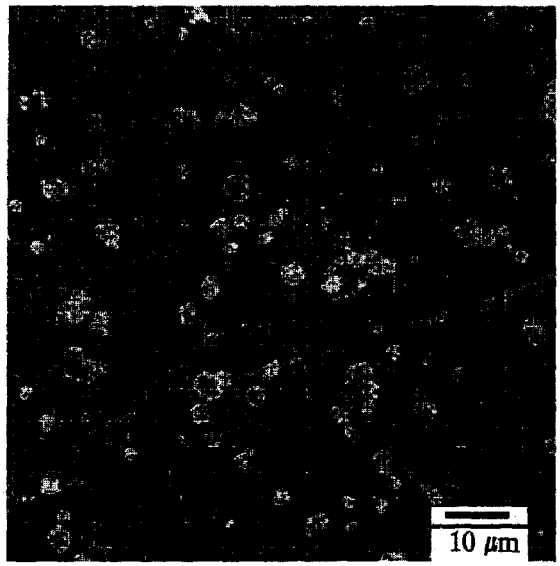


Fig. 2. A SEM micrograph of a $LiCoO_2$ layer deposited at 340°C for two hours. The applied high voltage is 11 kV; and the concentrations of Li and Co in the precursor solution are 0.04142 M.

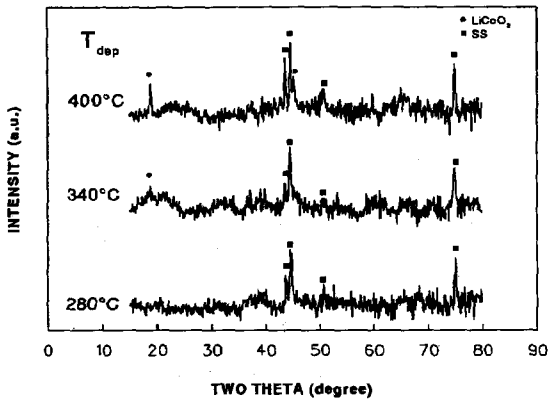


Fig. 3. XRD patterns of $LiCoO_2$ layers deposited at three different temperatures. The substrate is stainless steel (SS).

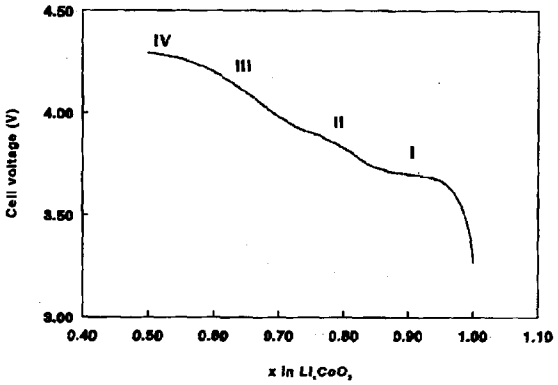


Fig. 5. A charge curve of the first cycle of cell (1) using a thin film of $LiCoO_2$ (about 350 nm thick, and a total area of 0.785 $cm^2$) as the cathode. The applied current density is 4 $\mu A/cm^2$. I, II, III and IV indicate different phases.

to oxides-metal interface reactions and high voltage charge or discharge effects. Fig. 3 shows the XRD patterns of three layers deposited at different temperatures. The layer deposited at 280°C is amorphous although the formation of cobalt oxide(s) can be proved by EDX (the light element Li is not detectable using our electron microscope). Above 340°C a $LiCoO_2$ phase with a hexagonal symmetry has been formed.

As shown in Fig. 4 a linear relation between the weight of the film and the deposition time was found. The weight growth rate is about 0.37 $mg/(cm^2 \cdot h)$ under the specific conditions as given in the caption. As the short-time-deposited films are dense, as mentioned above, the thickness growth rate may be calculated to be 0.78 $\mu m/h$ if assuming the films to be fully dense with the theoretical density 4.75 $g/cm^3$. This is rather comparable to the film growth rate by a chemical vapour deposition (CVD) process. In addition, the growth rate strongly depends on the concentration of the precursor solution, as was also observed in the case of deposition of YSZ and $BaCeO_3$ [2]. A more detailed study of the growth rate as a function of the concentration will be given in a forthcoming paper.

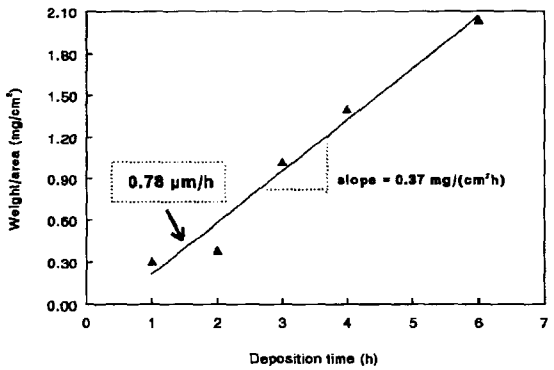


Fig. 4. The relation between the weight of $LiCoO_2$ films and the deposition time. Other conditions are the same as indicated in Fig. 2.

The cells represented by (1) reveal open circuit voltages between 3.1 and 3.6 V, varying with Li content $x$ and fabrication conditions. A charge curve (with $x$ changing from 1.0 to 0.5) is shown in Fig. 5. Four regions distinguished by different slopes occur in the curve, which may suggest three phase transitions. This agrees with the work of Reimers and Dahn [4]. Nonetheless, the compositions where the transitions occur are slightly different from their observation. This might be due to the difficulty in determining the stoichiometry of thin films. According to their analysis of in-situ X-ray diffraction, the transition from phase I to II is a first order one, while both transitions from II to III and from III to IV are order/disorder ones. Measurement with the GITT

method reveals the lithium chemical diffusion coefficients $\tilde{D}$ of the thin layers at room temperature to vary between $10^{-13}$ and $10^{-12}$ $cm^2/s$. It is observed that with increasing $x$, $\tilde{D}$ increases.

## 4. Conclusions

Thin films of $LiCoO_2$ can easily be prepared by the electrostatic spray pyrolysis technique. With the ESP-technique we are able to control the layer morphology, either dense or porous, by simply adjusting the deposition time. The $LiCoO_2$ layers used as cathodes in an actual lithium battery reveal a voltage of 3.1 to 3.6 V (versus Li). The lithium chemical diffusion coefficients are in the range between $10^{-13}$ to $10^{-12}$ $cm^2/s$.

## References

[1] A.A. van Zomeren, E.M. Kelder, J.C.M. Marijnissen and J. Schoonman, J. Aerosol Sci. 25 (1994) 1229.
[2] E.M. Kelder, O.C.J. Nijs, and J. Schoonman, Solid State Ionics 68 (1994) 5.
[3] W. Weppner and R.A. Huggins, J. Electrochem. Soc. 124 (1977) 1569.
[4] J.N. Reimers and J.R. Dahn, J. Electrochem. Soc. 139 (1992) 2091.