

## Electrostatic spray deposition of thin layers of cathode materials for lithium battery

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### Abstract

A novel fabrication technique, namely electrostatic spray deposition (ESD), has been developed in order to prepare thin layers of solid electrolytes and cathode materials for lithium batteries. In this study, the 4-volt cathode material  $\text{LiCoO}_2$  was chosen, and prepared by spraying alcohol solutions of nitrates and acetates of cobalt. ESD set-ups, with either horizontal or vertical configurations, were used. Depending on the precursor and process deposition conditions, the morphology of the layers can be relatively dense, fractal-like porous, or unique 3-D cross-linked porous structures with a high porosity and a narrow pore size distribution. For low deposition temperatures,  $\text{LiCoO}_2$  layers are XRD amorphous. Upon annealing, crystallized layers are obtained. The lithium chemical diffusion coefficient of the  $\text{LiCoO}_2$  layers has been measured with Galvanostatic Intermittent Titration Technique (GITT), values range from  $10^{-14}$  to  $10^{-12}$   $\text{cm}^2/\text{s}$ , depending on the lithium content and the annealing temperatures. Cyclic voltammograms of a test cell reveal that both lithium insertion and extraction are one-step processes.

*Keywords:* Electrostatic spray deposition; Lithium battery; Thin films

### 1. Introduction

Fabrication of all-solid-state microbatteries has received wide spread attention. Among these batteries, thin film lithium batteries are of enormous interest, which makes the preparation of thin films of lithium electrolytes and cathode materials crucial in this subject. It is noted that several cathode materials have been explored for use as anode materials using the concept of rocking chair batteries. Examples of such materials are  $\text{TiS}_2$  and  $\text{Li}_x\text{Mn}_2\text{O}_4$ .

Deposition techniques, such as chemical vapor deposition and sputtering, have been used to fabri-

cate thin films of various lithium battery components. However, in the past few years, a novel fabrication technique for oxidic thin layers, electrostatic spray deposition (ESD), which is also referred to as electrostatic spray pyrolysis (ESP), has been developed in this laboratory to prepare thin layers of solid electrolytes and cathode materials for lithium batteries [1-4]. It has shown many advantages over some conventional deposition techniques, such as a simple set-up, inexpensive and non-toxic precursors, high deposition efficiency and easy control of the surface morphology of the deposited layers. The aspect of morphology control is especially remarkable because, besides crystallinity, it provides an extra possibility to optimize the battery performance. In this study, the 4-volt cathode material ( $\text{LiCoO}_2$ )

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was chosen to be prepared by this technique and characterized.

## 2. Electrostatic spray deposition

Electrostatic spray deposition is a spray deposition technique, in which, unlike other spray techniques, the spray of a precursor solution is generated by an electrohydrodynamic (EHD) force. The schematic of the set-up used in this study is shown in Fig. 1. A DC voltage (in the range 0–20 kV) is applied between an electrically conductive substrate such as a metal or ITO glass and a metal capillary nozzle, which is connected to a precursor solution. Under a hydrodynamic pressure and/or an applied gas pressure, a certain flow rate of the precursor solution can be achieved at the nozzle. When the DC voltage is increased to a certain onset value (usually above 5 kV) the solution is atomized at the orifice of the nozzle, hence, a spray is generated. The onset DC voltage mainly depends on the nozzle–substrate distance and the physical properties of the precursor solution, especially its electrical conductivity, due to EHD force. The spray moves towards the heated substrate under the electrostatic force and, due to pyrolysis of the precursors, a thin layer is deposited on the substrate surface. It is common practice to use alcohols as solvent for adequate solubility of many

inorganic salts to be used as precursors. The deposition kinetics and thus the layer morphology are influenced by many factors, including substrate temperature, flow rate and physical properties of the precursor solution, as well as the evaporation of the solvent before the spray of droplets reach the substrate temperature. A detailed study concerning the influence of these factors has been presented elsewhere [4].

## 3. Experimental aspects

Unless otherwise stated, an absolute ethanol solution of lithium acetate ( $\text{LiAc} \cdot 2\text{H}_2\text{O}$ ) and cobalt nitrate ( $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) with a molar ratio Li:Co = 1:1 was used as the precursor solution (0.04M) for ESD. In addition, cobalt acetate ( $\text{CoAc}_2 \cdot 4\text{H}_2\text{O}$ ) dissolved in a mixture of ethanol (15 vol%) and butyl carbitol ( $\text{CH}_3(\text{CH}_2)_3\text{O}(\text{CH}_2)_2\text{O}(\text{CH}_2)_2\text{OH}$ ) (85 vol%) was also used. Stainless steel disks (1.4 cm in diameter) were used as substrates and weighed before and after the deposition, in order to calculate the weight of the deposit. The nozzle–substrate distance was varied between 2 and 6 cm, while the applied high voltage was about 10 kV. The deposition was done typically for 2 h at a substrate temperature between 240 and 450°C. In order to investigate the influence of

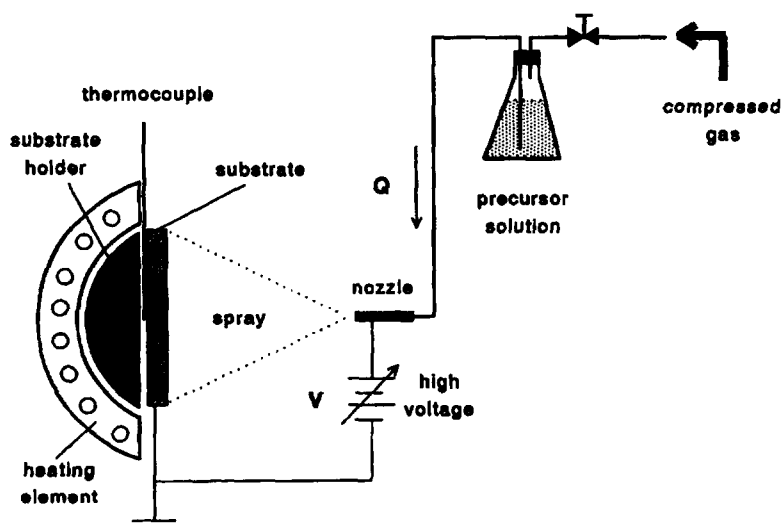


Fig. 1. Schematic of the ESD set-up used in the study.

temperature on the crystallinity, a few layers deposited at 340°C were annealed for 2 h at 400, 500, 600, 700, and 800°C, respectively.

The surface morphology of the deposited layers was studied using a scanning electron microscope (JEOL JSM-35), while the structure was analyzed using X-ray diffraction (Philips PW 1840 automated diffractometer).

Test cells were assembled using the un-annealed and annealed layers as cathodes, lithium metal as an anode, and a 0.7 M lithium perchlorate ( $\text{LiClO}_4$ ) propylene carbonate (PC) solution as the electrolyte. Galvanostatic Intermittent Titration Technique (GITT) [5] and cyclic voltammetry were used to measure the lithium chemical diffusion coefficient in  $\text{LiCoO}_2$  and the cyclic behaviour of the cells, respectively, with a EG & G PARC 273 potentiostat equipped with the 'Head Start creative electrochemistry' computer program. For the GITT measurement, the voltage  $E$  vs. time  $t$  relation was recorded in 100-second current pulses to derive  $dE/dt^{1/2}$  ( $100 \text{ s} < L^2/D$ ). The  $dE/dx$  values of  $\text{Li}_x\text{CoO}_2$  were calculated from the stationary data reported by Honders [6]. The contact surface area utilized in the calculation of the chemical diffusion coefficient was the geometrical area ( $0.785 \text{ cm}^2$ ). After the GITT measurement, cyclic voltammograms were measured at the cathode composition  $\text{Li}_{0.35}\text{CoO}_2$  with different potential sweep rates in the potential range between 4000 and 3000 mV.

#### 4. Results and discussion

The morphology of the layers is found to be controlled mainly by the deposition temperature and the used solvent [4]. Three layers of different morphologies are shown in Fig. 2. It can be seen that using pure ethanol as solvent and at low substrate temperature, the deposited layer reveals to comprise a relatively dense matrix with scattered particles incorporated in it (Fig. 2a). By increasing the deposition temperature, a fractal-like, highly porous layer is obtained (Fig. 2b). The morphology difference is due to the different state of the spray droplets arriving at the substrate surface. At low substrate temperature, solvent evaporation is incomplete during the flight of the droplets from the nozzle to the substrate. Therefore, the particles arriving at the

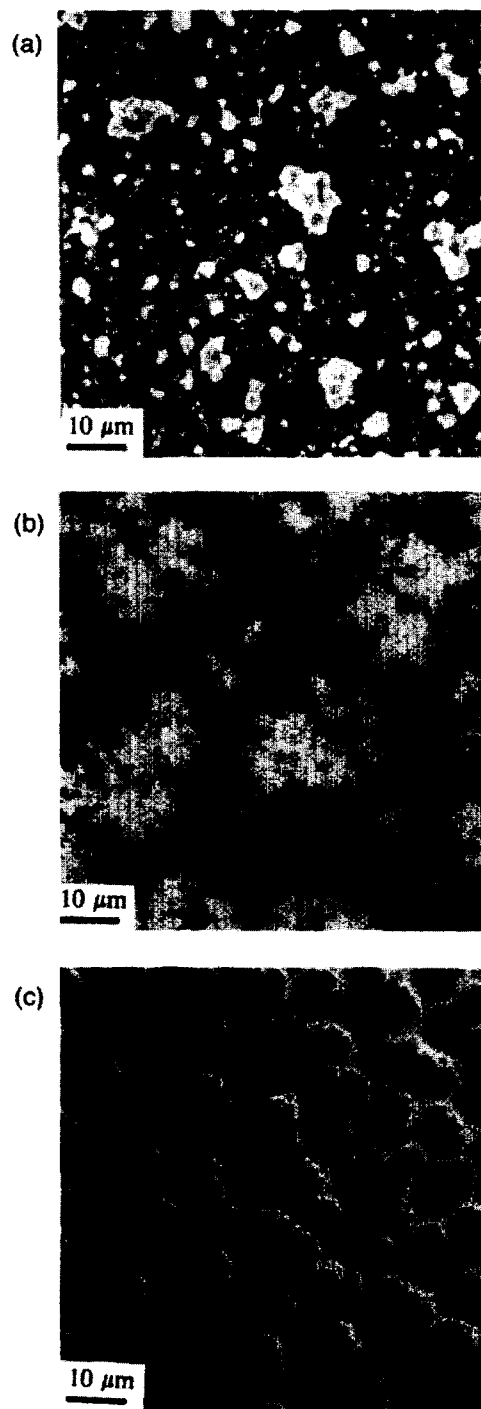


Fig. 2. SEM micrographs of  $\text{LiClO}_2$  layers deposited at 340°C using ethanol based precursor solution (0.04 M) (a), deposited at 450°C using the same precursor solution (b), and deposited at 240°C using 85 vol% butyl carbitol–15 vol% ethanol solution (0.005 M) as precursor (c).

substrate are still wet. They hit the substrate surface and spread out, forming relatively dense morphologies, as shown in Fig. 2a. On the contrary, at high deposition temperatures, the solvent evaporation is almost or even completed. Consequently, the nearly dry particles are collected at the substrate, forming a highly porous layer. It is believed that a preferential coulombic force also plays a role in the formation of such a fractal-like morphology. A detailed discussion on the mechanism, however, is beyond the scope of this paper. This fractal-like porous layer is found to be unsuitable as a cathode layer because of its poor mechanical properties and its high electrical resistance. This obviously is due to the poor connection between the deposited particles. The layer shown in Fig. 2c, which was prepared at 240°C with cobalt acetate as the cobalt precursor and the mixture of ethanol (15 vol%) and butyl carbitol (85 vol%) as solvent, shows a quite unique morphology. It is a 3-D cross-linked porous structure with a high porosity and a narrow pore size distribution. It is found to be mechanically strong, and thermally as well as chemically stable. With these characteristics and in particular its open structure, layers of this morphology are expected to be favourably used as cathodes of lithium batteries. The study on this unique morphology is part of our ongoing research.

The crystalline phases of the deposited layers depend on the deposition temperature. We have reported that a deposition at 280°C resulted in an amorphous layer, while a deposition at 340°C resulted in a crystallized  $\text{LiCoO}_2$  layer with a hexagonal symmetry [3]. The crystallinity can be increased by annealing the layers at temperatures between 400 and 700°C, as shown in Fig. 3. However, annealing at 800°C,  $\text{LiCoO}_2$  starts to decompose since traces of  $\text{Co}_3\text{O}_4$  have been detected by XRD.

The lithium chemical diffusion coefficients,  $\bar{D}_{\text{Li}}$ , of  $\text{LiCoO}_2$  layers as-deposited at 340°C and two annealed at 500 and 700°C, respectively, are shown in Fig. 4. The  $\bar{D}_{\text{Li}}$  values are in the range between  $10^{-14}$  and  $10^{-12}$   $\text{cm}^2/\text{s}$ , depending on the lithium content in the layers of  $\text{LiCoO}_2$ , and the deposition temperature as well as the annealing temperature. For each layer, the  $\bar{D}_{\text{Li}}$  increases with increasing lithium content. It can also be seen that the  $\bar{D}_{\text{Li}}$  decreases after annealing at higher temperatures. This might be caused by an increase of the primary particle size and the crystallinity, and, hence, a decrease of the specific surface area of the layer. Therefore, annealing of the layers deposited at 340°C does not lead to an enhancement of the overall lithium diffusion.

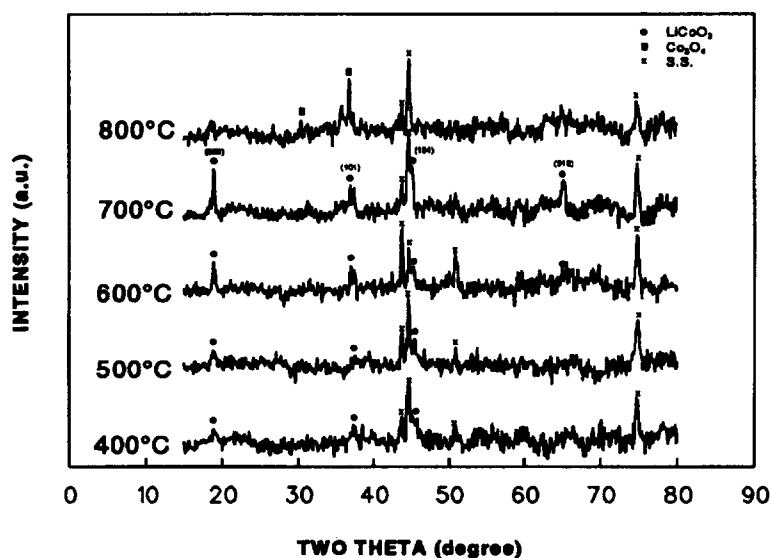


Fig. 3. XRD patterns of the annealed  $\text{LiCoO}_2$  layers deposited at 340°C. S.S. refers to stainless steel, i.e. the substrate material.

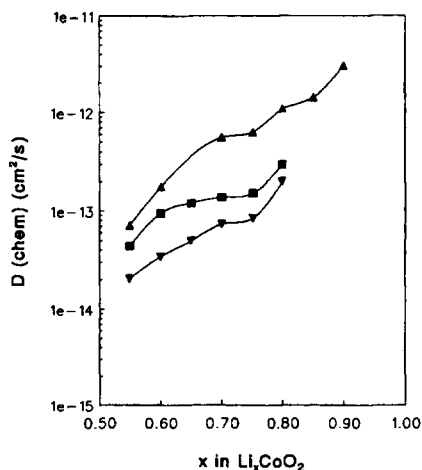


Fig. 4. Chemical diffusion coefficient of an un-annealed (▲), and two  $\text{LiCoO}_2$  layers annealed at  $500^\circ\text{C}$  (■) and  $700^\circ\text{C}$  (▼) obtained from GITT measurement.

The cyclic voltammograms of the test cell at the cathode composition of  $\text{Li}_{0.35}\text{CoO}_2$ , measured with different potential sweep rates, are shown in Fig. 5. It can be seen that the lithium insertion and extraction are both one-step processes. For slow sweep rate ( $0.125\text{ mV/sec}$ ), one anodic peak around  $3.6\text{--}3.7\text{ V}$

V during the extraction process, and one cathodic peak around  $3.35\text{--}3.45\text{ V}$  during the insertion process, were observed. According to the relation between peak current and potential scan rate [7],  $\tilde{D}_{\text{Li}}$  of  $\text{Li}_{0.35}\text{CoO}_2$  is estimated to be  $1.2 \times 10^{-14}\text{ cm}^2/\text{s}$ . This value is concordant with the value from Fig. 4 when the lithium content is extrapolated to 0.35.

## 5. Conclusions

ESD is a versatile technique to prepare thin layers of  $\text{LiCoO}_2$  with different morphologies. They can be relatively dense, fractal-like porous or uniquely porous. The crystallinity of the layers can be increased by annealing at temperatures below  $800^\circ\text{C}$ . At  $800^\circ\text{C}$  the layers decompose forming  $\text{Co}_3\text{O}_4$ . The lithium chemical diffusion coefficient  $\tilde{D}_{\text{Li}}$  ranges from  $10^{-14}$  to  $10^{-12}\text{ cm}^2/\text{s}$ .  $\tilde{D}_{\text{Li}}$  decreases after annealing due to crystallization of the layer. Therefore,  $\tilde{D}_{\text{Li}}$  decreases with increasing annealing temperature. For an unannealed layer of  $\text{LiCoO}_2$  deposited at  $340^\circ\text{C}$ , an anodic peak around  $3.6\text{--}3.7\text{ V}$  during lithium extraction, and a cathodic peak around  $3.35\text{--}3.45\text{ V}$  during lithium insertion exist in the cyclic voltammograms of the cell.

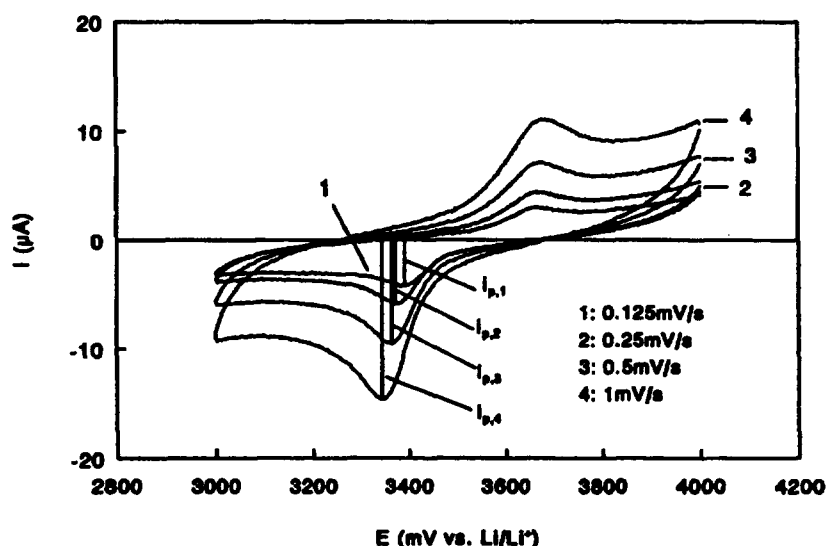


Fig. 5. Cyclic voltammograms with different potential sweep rates of the cell using a  $\text{LiCoO}_2$  layer deposited at  $340^\circ\text{C}$  as cathode.  $i_p$  represents the peak current during lithium insertion.

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