

# Electrode and solid electrolyte thin films for secondary lithium-ion batteries

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## Abstract

Electrostatic spray deposition (ESD) was employed to prepare thin layers of  $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$  (nominal composition) and  $\text{BPO}_4:0.035\text{Li}_2\text{O}$  for all-solid-state thin film lithium-ion batteries. The relationships between layer morphologies and deposition conditions such as solvent composition of the precursor solutions and substrate temperature were investigated. It was found that a low substrate temperature and/or high boiling point of the solvent may lead to a relatively dense structure. Reticular porous structures are formed, if films were deposited at 250°C and a mixture of 85 vol.% butyl carbitol and 15 vol.% ethanol was used as the solvent. The  $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$  layers, formed in the 250–400°C temperature range, were amorphous or micro-crystalline. After annealing beyond 600 °C, they could be crystallized into a spinel-structured material. Glassy  $\text{BPO}_4:0.035\text{Li}_2\text{O}$  layers could fill the pores of porous  $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$  layers to form a dense intermediate electrolyte layer. Thin-film rocking-chair batteries,  $\text{Li}_{1-x}\text{Mn}_2\text{O}_4|\text{BPO}_4:0.035\text{Li}_2\text{O}|\text{Li}_{1-x}\text{Mn}_2\text{O}_4|\text{Al}$ , were prepared and revealed an open-circuit voltage of about 1.2 V after charging. © 1997 Elsevier Science S.A.

**Keywords.** Lithium manganese oxide; Lithium boron phosphate; Electrostatic spray deposition; Thin film lithium batteries

## 1. Introduction

Preparation of thin films for electrode materials and lithium-ion solid electrolyte thin film are important steps for the fabrication of rechargeable lithium-ion microbatteries. Recently, a thin film deposition technique, electrostatic spray deposition (ESD), has been developed in our laboratory. It has been employed successfully to deposit layers of cathode materials such as  $\text{LiMn}_2\text{O}_4$  [1] and  $\text{LiCoO}_2$  [2,3]. The crystal structure and lithium-ion transport properties of thin-film  $\text{LiCoO}_2$  cathodes have been reported in Ref. [4]. In this report, we report on the deposition of thin films of the electrode  $\text{Li}_x\text{Mn}_2\text{O}_4$  and the solid electrolyte  $\text{Li}_x\text{BPO}_4$ .

With regard to the electrochemical potential difference in the two ranges of lithium levels [5],  $0.3 < x < 1$  and  $1 < x < 2$ ,  $\text{Li}_x\text{Mn}_2\text{O}_4$  can be used simultaneously as the cathode as well as the anode in a 'rocking-chair'-type lithium battery generating an open-circuit voltage of ~1.2 V. On the other hand,  $\text{Li}_x\text{BPO}_4$  bulk material ( $0 < x < 0.6$ ) was found to be a lithium-ion electrolyte exhibiting  $2 \times 10^{-6}$  S/cm as the maximum lithium-ion conductivity at room temperature for  $x=0.07$  [6]. The ESD technique can also be applied for deposition of  $\text{Li}_x\text{BPO}_4$  thin layers. Therefore, a complete thin

film solid-state battery can be fabricated by alternating ESD steps of electrode and electrolyte layers. Such prototype microbatteries were manufactured and tested.

## 2. Experimental

All of the thin layers were deposited under ambient atmosphere on an ESD set-up with a vertical configuration. Details of the ESD set-up have been published in Ref. [3]. The following deposition parameters were used. The nozzle-to-substrate distance was 2 to 3 cm, and the applied high voltage varied between 8 and 12 kV. For  $\text{Li}_x\text{Mn}_2\text{O}_4$  (here  $x=1.2$ , nominal composition), a precursor solution was prepared using  $\text{Li}(\text{CH}_3\text{COO}) \cdot 2\text{H}_2\text{O}$  and  $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  as solutes, and absolute ethanol or a mixture of ethanol and butyl carbitol ( $\text{CH}_3(\text{CH}_2)_3\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$ ) as the solvent. For  $\text{Li}_x\text{BPO}_4$  ( $x=0.07$ ), in addition to lithium acetate,  $\text{H}_3\text{BO}_3$  and  $\text{P}_2\text{O}_5$  were also used as the precursors, and a mixture of 50 vol.% ethanol and 50 vol.% butyl carbitol as the solvent. Polished stainless-steel and aluminium were used as the substrates. Substrate temperatures were chosen in the 250–450 °C range. A typical concentration of precursor solutions was 0.005 M. The deposited layers were annealed in air at temperatures up to 800 °C in order to obtain crystallized

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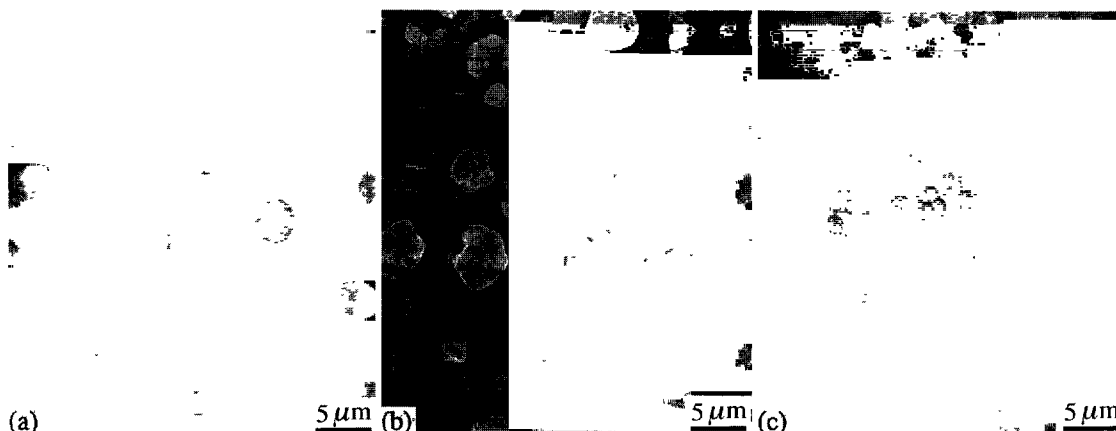


Fig. 1. SEM of  $\text{Li}_{1.2}\text{Mn}_2\text{O}_4$  layers deposited for 1 h at (a) 250 °C; (b) 300 °C, and (c) 400 °C. The solvent of the precursor solution was pure ethanol

layers. The surface morphology and crystal structure of deposited thin layers were examined using an scanning electron microscope (SEM) (JEOL JSM-35) and an X-ray diffractometer (XRD) (Philips PW 1840).

Microbatteries at discharge state were obtained by depositing two  $\text{Li}_{1.2}\text{Mn}_2\text{O}_4$  layers as the electrodes and an intermediate  $\text{BPO}_4 \cdot 0.035\text{Li}_2\text{O}$  layer as the electrolyte on an aluminium substrate with a symmetrical configuration:  $\text{Li}_{1.2}\text{Mn}_2\text{O}_4 | \text{BPO}_4 \cdot 0.035\text{Li}_2\text{O} | \text{Li}_{1.2}\text{Mn}_2\text{O}_4 | \text{Al}$ . Gold was sputtered in air on top of the  $\text{Li}_{1.2}\text{Mn}_2\text{O}_4$  layer for the electrical contact. They were annealed at 600 °C, and then charged by a 10 V d.c. voltage at room temperature. The discharge behaviour of the charged batteries was tested.

### 3. Results and discussions

As shown in Fig. 1, most of the  $\text{Li}_{1.2}\text{Mn}_2\text{O}_4$  layers exhibit a granular morphology, especially when pure ethanol is used as the solvent or at relatively high substrate temperatures. At substrate temperatures below 300 °C the layers are dense. The porosity of a layer increases with the deposition temperature. Increased density is ascribed to the smoothing-out effect of spray droplets of which the evaporation of solvent is far from complete when reaching the substrate surface. If butyl carbitol (with a boiling point 230 °C) is mixed with ethanol, evaporation of solvent becomes slower, and hence the deposited layers are denser in comparison with those deposited using pure ethanol solvent. However, further increase of the fraction of butyl carbitol to 85 vol.% gives rise to a unique reticulate structure at 250 °C (Fig. 2), as also obtained for  $\text{LiCoO}_2$  layers [3]. The structure is believed to be favourable for electrodes owing to the concomitant high surface area. A possible mechanism for the formation of such a structure was proposed in the previous report [3]. However, to be used as lithium battery electrode, the substrate temperature should not be too high, e.g. above 400 °C, because these highly porous but not reticulate layers deposited at high temperatures, such as the one shown in Fig. 1(c), adhere poorly to the substrate. It was also found that acidifying the precursor

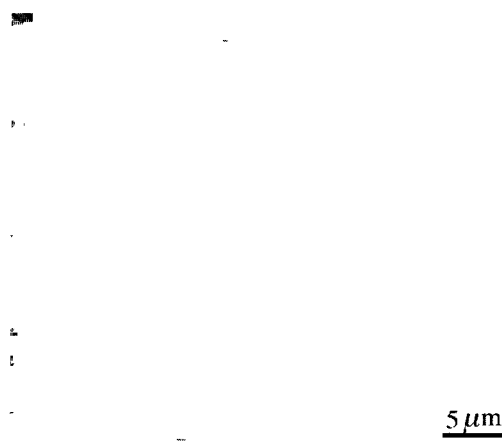


Fig. 2. SEM of an  $\text{Li}_{1.2}\text{Mn}_2\text{O}_4$  layer deposited at 250 °C for 1 h. The solvent of the precursor solution was 85 vol.% butyl carbitol and 15 vol.% ethanol

solutions with small amounts of nitric acid usually results in a denser morphology of the layers. This may be attributed to the higher electrical conductivity of the precursor solutions and hence smaller spray droplet sizes as a result of acidification.

All  $\text{Li}_{1.2}\text{Mn}_2\text{O}_4$  layers deposited in the 250–400 °C temperature range have X-ray amorphous or microcrystalline structures. Upon annealing in air at up to 800 °C, the layers crystallize into the spinel phase (Fig. 3). Traces of  $\text{Mn}_2\text{O}_3$  or  $\text{Mn}_3\text{O}_4$  can also be detected. The mechanism of this segregation is not known.

$\text{BPO}_4 \cdot 0.035\text{Li}_2\text{O}$  layers deposited by ESD also revealed various morphologies, depending on the deposition temperature and type of substrate. A similar reticulate structure as shown in Fig. 2 can be obtained on an aluminium substrate. However, only a dense structure can be formed on top of the  $\text{Li}_{1.2}\text{Mn}_2\text{O}_4$  layers. Even on porous  $\text{Li}_{1.2}\text{Mn}_2\text{O}_4$  layers,  $\text{BPO}_4 \cdot 0.035\text{Li}_2\text{O}$  fills pores to obtain dense structures (Fig. 4), which are favourable for battery operation. This might be caused by the glassy nature of  $\text{BPO}_4 \cdot 0.035\text{Li}_2\text{O}$  at low temperatures (e.g. below 400 °C). Above 500 °C,  $\text{BPO}_4 \cdot 0.035\text{Li}_2\text{O}$  crystallizes [6].

Thin-film prototype 'rocking-chair' batteries  $\text{Li}_{1.2}\text{Mn}_2\text{O}_4 | \text{BPO}_4 \cdot 0.035\text{Li}_2\text{O} | \text{Li}_{1.2}\text{Mn}_2\text{O}_4 | \text{Al}$  revealed, after apply-

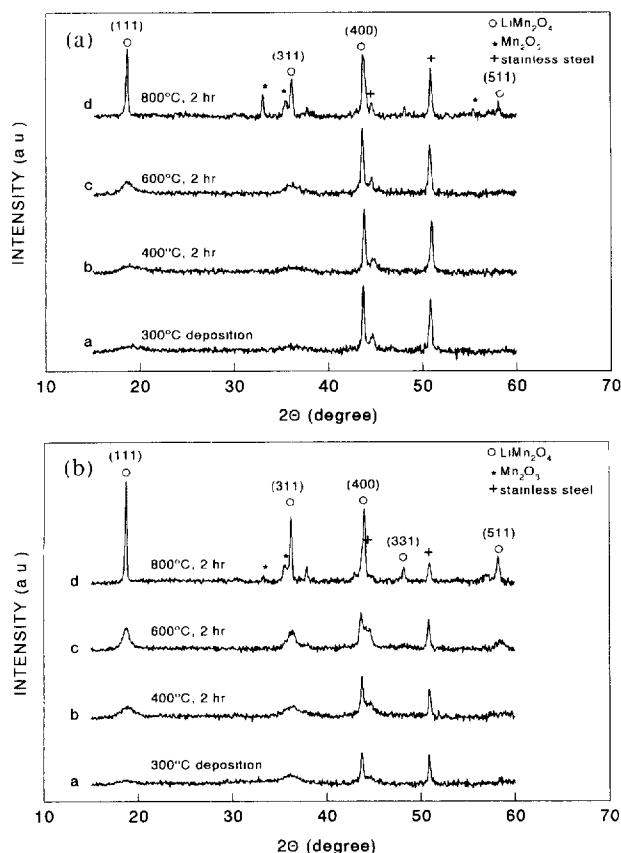


Fig. 3 XRD patterns of  $\text{Li}_{1.2}\text{Mn}_2\text{O}_4$  layers as-deposited at 300 °C and heat-treated at several temperatures. The solvents used were (a) pure ethanol and (b) 85 vol.% butyl carbitol and 15 vol.% ethanol

ing a charging voltage of 10 V d.c. voltage for about 10 h, an OCV of about 1.2 V. The discharge curve of a thin-film battery is shown in Fig. 5. These thin-film batteries have high internal resistances (about 1 MΩ or higher) and short shelf life. The high resistance is related to the amorphous structure of as-deposited  $\text{BPO}_4 \cdot 0.035\text{Li}_2\text{O}$  layers. Current research is directed towards improvement of the battery performance.

#### 4. Conclusions

Thin layers of the electrode material  $\text{Li}_{1.2}\text{Mn}_2\text{O}_4$  and electrolyte material  $\text{BPO}_4 \cdot 0.035\text{Li}_2\text{O}$  for secondary lithium-ion batteries may be prepared solely by the electrostatic spray deposition (ESD) technique under ambient atmosphere in the 250–400 °C temperature range. For  $\text{Li}_{1.2}\text{Mn}_2\text{O}_4$  layers, the lower the deposition temperature, the denser the morphology is. Using a high boiling point solvent opens the possibility to obtain denser morphologies. On the other hand, a unique reticulate structure can be obtained at 230 °C using 85 vol.% butyl carbitol and 15 vol.% ethanol as the solvent. A  $\text{BPO}_4 \cdot 0.035\text{Li}_2\text{O}$  layer deposited at low temperatures (below 400°C) onto an  $\text{Li}_{1.2}\text{Mn}_2\text{O}_4$  thin layer can fill the pores of the latter to form a dense structure. Preliminary tests of thin-film ‘rocking-chair’ batteries,  $\text{Li}_{1.2+x}\text{Mn}_2\text{O}_4$

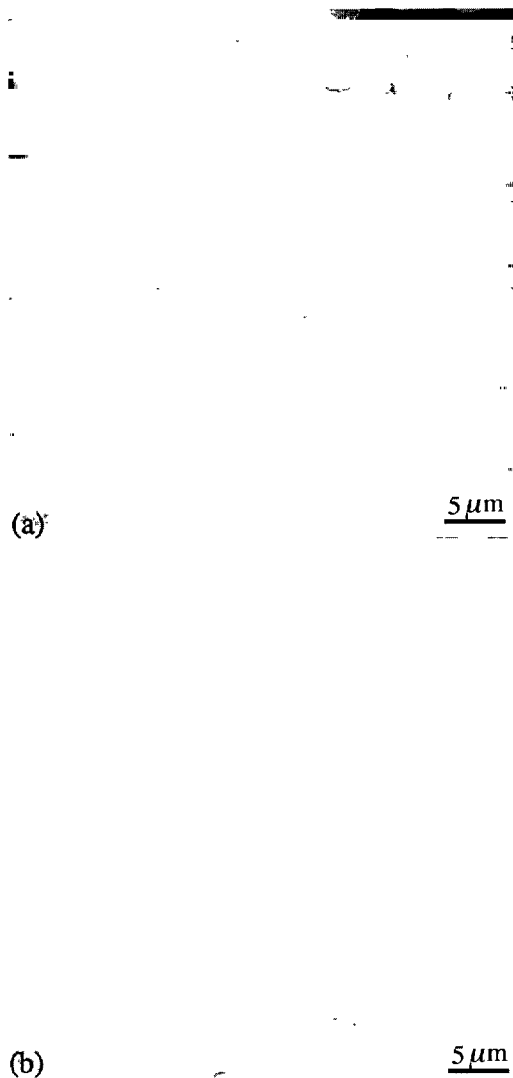


Fig. 4. SEM of thin layers of the battery components (a) an  $\text{Li}_{1.2}\text{Mn}_2\text{O}_4$  layer on an aluminium substrate, and (b) a  $\text{BPO}_4 \cdot 0.035\text{Li}_2\text{O}$  layer on top of an ESD-deposited  $\text{Li}_{1.2}\text{Mn}_2\text{O}_4$  layer.

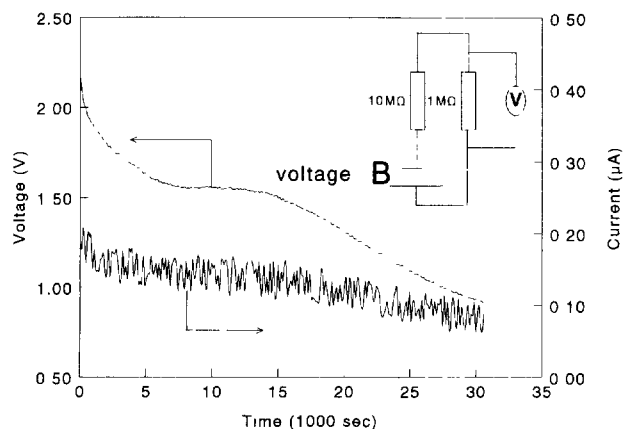


Fig. 5. Discharge curve of a thin-film battery  $\text{Li}_{1.2-x}\text{Mn}_2\text{O}_4|\text{BPO}_4 \cdot 0.035\text{Li}_2\text{O}|\text{Li}_{1.2+x}\text{Mn}_2\text{O}_4$

|BPO<sub>4</sub>:0.035Li<sub>2</sub>O|Li<sub>1-2-x</sub>Mn<sub>2</sub>O<sub>4</sub>|Al, exhibit the expected OCV. Further improvement in internal resistivity is required.

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