**Synthesis and Deposition of Nanostructured Lithium Nickel Manganese Film as material for 3D micro-batteries**

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## Introduction

The main request of the smart systems developers is to get relevant micro batteries to enable further miniaturization of their devices [1]. Increase in miniaturization, integration and energy autonomous performance is today limited by the low energy density of batteries. To circunvent this problem, batteries with higher capacities and/or higher voltages are needed. Thin films Li Ion batteries are the most suitable for small scale applications due to the fast ion transport over short distances. However, the capacity is restricted by the dimensions. In this respect, 3D microbatteries (MB) have the advantage of higher surface area, increasing battery capacity (fig 1). On the other hand, lithium nickel manganese spinel has been studied extensively and is an attractive candidate due to its high operating voltage [2, 3].

In this work, nanostructured $LiNi_{0.5}Mn_{1.5}O_4$ film has been synthesized by Electrostatic Spray Deposition (ESD) on 3D and flat substrates.

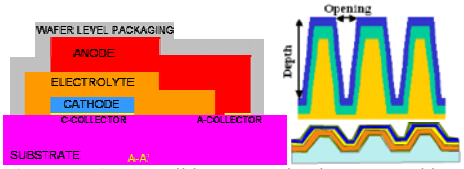


**Fig 1** E-Stars solid state microbattery architecture deposited on moderate aspect ratio (MAR) and high aspect ratio (HAR) substrates, from ref [1].

## Experimental

Nickel nitrate hexahydrate, Lithium nitrate anhydrous, and Manganese nitrate tetrahydrate, where dissolved in 2-propanol with a concentration of 0.1 M, following the spinel stochiometry. The films were prepared using the ESD method and further pyrolisis, a promising method for the production of cathode thin films for MBs [5]. Similar experimental procedures have been thoroughly discussed and described elsewhere [4-6]. The morphology and thickness of the as-deposited films have been tuned using different pyrolysis temperatures (450 or 500°C) and spraying times (5, 10 or 20 min). The flow rate and applied voltage were fixed at 0.7 ml/h and 10.5 kV, respectively. Textured silicon (provided by ST Microelectronics) with MAR, 2:1, and HAR, 10:1, were used as 3D substrates. CR2320 coin cell caps were used as flat substrates. SEM was used to determine morphology, size and thickness of the films. TEM and XRD were performed in order to study the morphology, structure and composition. The electrochemical performance of the $LiNi_{0.5}Mn_{1.5}O_4$ film was studied by galvanostatic measurements using metallic Li as reference and counter electrode in presence of 1M LiPF6 in EC:DMC (2:1 by wt.) as electrolyte.

## Results and Discussion

XRD measurements (not shown) suggest the crystalline behavior of the as-deposited film. The material exhibits nanostructure particles of 4-8 nm (fig 2a) and confirm the presence of crystalline domains.

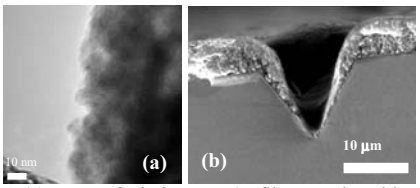


**Fig 2** (a) TEM of $LiNi_{0.5}Mn_{1.5}O_4$ films produced by ESD at 450°C. (b) SEM cross-section on MAR substrate.

SEM micrograph in fig. 2b shows (MAR) cross section analysis of layers corresponding to a 10 min spraying time. Controlled thicknesses on MAR substrates of about 2, 3.5 and 4.5 µm can be achieved with spraying times of 5, 10 and 20 min, respectively. Fig 3 shows a SEM (HAR) cross section image for a 10 min deposition layer with a thickness of about 500 nm across the channel.

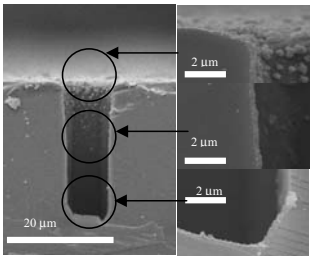


**Fig 3** SEM of the film cross-section on HAR substrate

Fig 4 shows the voltage discharge profile of the 1st, 2nd and 50th cycle for the $LiNi_{0.5}Mn_{1.5}O_4$ electrode, while fig 4b depicts the cycle performance showing reversibility during lithium insertion and extraction for 50 cycles.

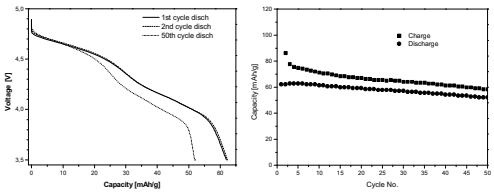


**Fig 4** Voltage profiles for the flat surface electrodes (a) and cycle performance (b).

ESD is suitable for thin film deposition on 3D architectures. Moreover the electrochemical performance of the material is encouraging for application as positive electrode for Li-Ion MBs.

## Acknowledgements

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