Ag/$LiMn_{1.5}Ni_{0.5}O_4$ Thin Film Lithium Ion Microbattery

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The development of 5V cathode materials for lithium ion batteries has brought the hope of a new generation of high energy/high power devices [1]. However, the main problem with these systems is either to find an electrolyte which electrochemical window will go up to 5V vs lithium, or to increase the charge and discharge times so that usual aprotic electrolytes will not have time to be oxidized during the use of the battery.

A good way to overcome this problem is to design thin film electrodes which can be usually cycled at faster rates compared to standard composite electrodes. Up to now, only little work has been done on the deposition of thin layer of 5V cathodes such as $LiMn_{1.5}Ni_{0.5}O_4$ [2]. Additionally, the design of a complete battery will required the use of a low potential anode to keep a high average working voltage.

In this paper, we present the first results on a microbattery device built with a $LiMn_{1.5}Ni_{0.5}O_4$ and a Ag anode separated by a standard aprotic electrolyte. Both electrodes were deposited by RF sputtering and are stable in air. The electrochemical properties of the positive and negative electrodes have been related to structural and microstructural characterizations.

As-deposited $Li_xNi_{0.50}Mn_{1.50}O_4$ cathode thin film exhibited poor specific capacity due to the poorly crystallized state. The annealing treatment as well as the lithium stoechiometry in the film have been carefully investigated. A good compromise between cycling ability and capacity of $Li_xNi_{0.50}Mn_{1.50}O_4$ thin film electrodes was determined for an annealing temperature of 600°C with x>1 (figure 1). In these conditions, the film crystallized in the expected spinel phase and the cell parameters are in good agreement with those published for bulk material. Such films reversibly exchange 0.4 lithium upon 2500 cycles at 16C rate (figure 2). Increasing the annealing temperature or decreasing the lithium content give rise to a second phase with a $NiMn_2O_4$ composition. Subsequently, the amount of nickel is decreased in the spinel structure and lower working voltages are observed.

Noble metal-based thin film anodes [3] and particularly silver layers were also investigated. Despite an irreversible capacity loss during the first cycle, the films exhibited a high reversible capacity according to the formation of different Li_xAg alloys at low potentials vs lithium. However, the cut-off voltages have to be carefully monitored in order to enhance the cycling ability of the films and to optimize the specific capacity.

Finally, both thin film electrodes were associated in a $LiPF_6$ EC:DEC electrolyte. The resulting device shows capacity of 25 $\mu Ah/cm^2$ over 1000 cycles at an average working potential of 4.65V (figure 3). Such devices open the way for the design of all solid microbatteries operating at high rates with high power density.

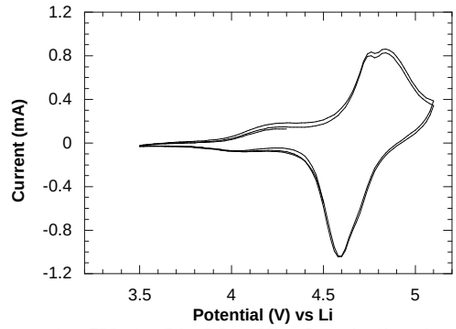

Figure 1 : CV of a $Li_{1.2}Mn_{1.5}Ni_{0.5}O_4$ thin film (annealed at 600°C) in $LiPF_6$ EC:DEC 1:2 electrolyte vs lithium.

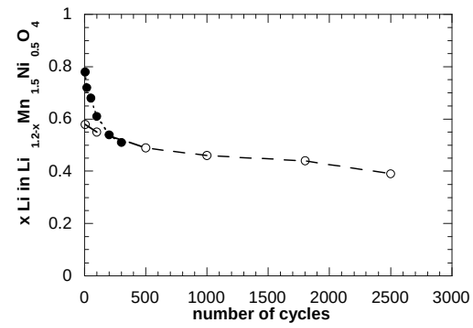

Figure 2 : Effect of the annealing treatment on the capacity of $Li_{1.2}Mn_{1.5}Ni_{0.5}O_4$ thin film in $LiPF_6$ EC:DEC 1:2 electrolyte vs metallic lithium electrode (16C between 4.4V and 5.1V).

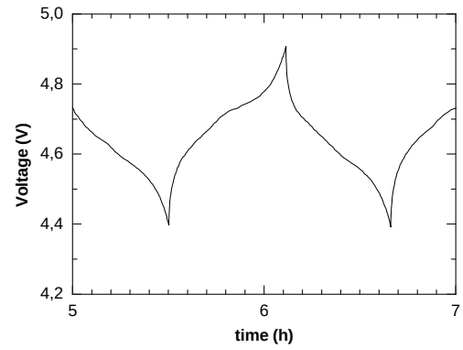

Figure 3 : Charge/discharge of an Ag thin film/ $LiPF_6$ EC:DEC 1:2/$Li_{1.2}Mn_{1.5}Ni_{0.5}O_4$ thin film microbattery. Current density 25 $\mu Ah/cm^2$.

References :

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2. K.A. Striebel, A. Rougier, C.R. Horne, R.P. Reade, E.J. Cairns, Journal of the Electrochemical Society, 146 (1999) 4339.
3. G. Taillades, N. Benjelloun, J. Sarradin and M. Ribes, Lithium Battery Discussions (LiBD), abstract #95, Arcachon, France (2001).