Electrochemical Behavior of $LiCo_yMn_{2-y}O_4$ ($0 \le y \le 1$) spinels synthesized from $Co_{3y/2}Mn_{3-3y/2}O_4$ precursor at different temperatures.

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INTRODUCTION

To improve cyclability at 4V doping of $LiMn_2O_4$ with iso- or aliovalent cations have been done (1). Among the dopant cations, the Co-doped spinels have shown the best electrochemical performance (2). We present the electrochemical properties in the 3.5-5.2V range in a lithium cell in which the positive active material is Co-doped spinels synthesized at several temperatures by using an original procedure designed by us (3).

EXPERIMENTAL

Co-doped $LiMn_2O_4$ spinels of general formula $LiCo_yMn_{2-y}O_4$ ($0 \le y \le 1$) have been synthesized by reacting $Co_{3y/2}Mn_{3-3y/2}O_4$ precursors with $LiOH.H_2O$ at 600º and 750ºC. The spinels are obtained as single-phases without the further annealing required by any solid-state reaction synthesis. High-temperature Co-doped spinels have been prepared by heating at 1100ºC the spinels previously synthesized. The samples have been characterized by X-ray powder diffraction, thermal analysis, transmission electron microscopy, electrical and electrochemical measurements.

RESULTS

Variation of lattice parameter vs. synthesis temperature for the $LiCo_yMn_{2-y}O_4$ ($0 \le y \le 1$) has been determined. The parameter increases on increasing the temperature, but decreases linearly with increasing the Co content Thermogravimetric analysis shows that the samples at $y>0.3$ undergo an irreversible weight loss on cooling from 1100ºC, that has been ascribed to oxygen removal. It gives way to the formation of oxygen-deficient spinels, in which a part of the Co and Mn ions are reduced. For the high-temperature spinels at $y>0.6$ a sharp increase in conductivity is observed. It has been associated with a change in the electron hoping mechanism from Mn^{3+}/Mn^{4+} ions to Co^{2+}/Co^{3+} ones.

The discharge curves for samples at $y=0.5$ obtained at 750º and 1100ºC are shown in Fig. 1. They show the 4V and 5V plateau, but the capacity drained in both stages is modified by the thermal treatment of the samples. The cycling behaviour of the Co-doped spinels has been analyzed in the 4V region. We find for very low Cobalt content ($0.06<y<0.25$) a remarkable enhancement of the cyclability compared with $LiMn_2O_4$, the cycle efficiency being 99.7 %.

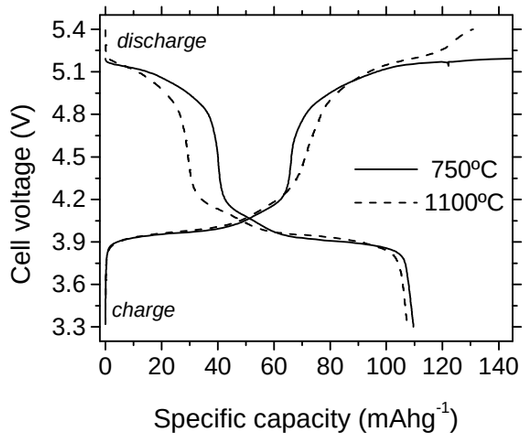

Figure 1.- Galvanostatic charge/discharge curves of the first cycle for the samples synthesized at 750º and 1100ºC.

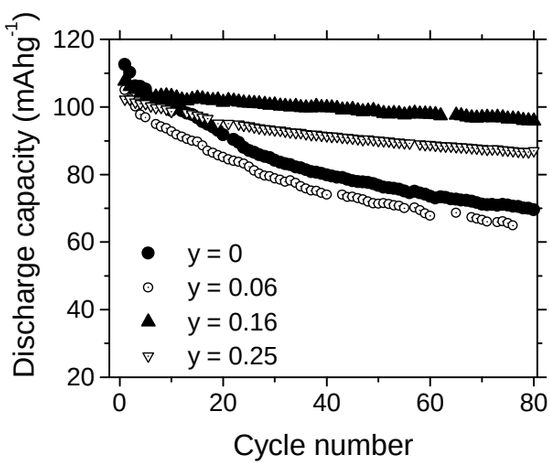

Figure 2.- Discharge capacity vs. cycle number for $LiCo_yMn_{2-y}O_4$ spinels. Potential range 3.3-4.5 V, j = 0.8 $mAcm^{-2}$ (C/5).

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REFERENCES

1.- G. Amatucci, J.M. Tarascon, J. Electrocehm. Soc. **149**, K31 (2002).
2.- L. Guohua, H. Ikuta, T. Uchida and M. Wakihara,, J. Electrochem. Soc., **143**, 178 (1996).
3.- J.M. Amarilla, J.L. Martín de Vidales, R.M. Rojas, Solid State Ionics **127**, 73 (2000).