

## STRUCTURAL CHARACTERIZATION AND ELECTROCHEMICAL BEHAVIOR OF TRANSITION METAL CARBONATES.

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As a result of the studies done to replace graphite as a conventional anode material, recently a large number of compounds have shown reversible reactions with lithium. Particularly, transition metal oxides<sup>18</sup> and fluorides<sup>19, 20</sup> have shown to participate in conversion reaction with lithium, showing a reduction of the metal ions to the metallic state together with the formation of lithium oxide or lithium fluoride, respectively. Recently, this process was extended to submicronic particles of manganese carbonate<sup>21</sup>. In this work, we were able to extend this process to nanostructured particles of manganese cobalt carbonate ( $Mn_{1-x}Co_xCO_3$ ).

The synthesis of nanostructured Mn /Co carbonates ( $Mn_{1-x}Co_xCO_3$ ,  $x = 0-0.5$ ) was done with reverse micelle method. Two water-in-isooctane microemulsions, one containing  $Mn(NO_3)_2 \cdot 4H_2O$  and  $Co(NO_3)_2 \cdot 6H_2O$  and the other one containing  $NaHCO_3$  as aqueous phase and stabilized with CTAB (surfactant) and hexanol (co-surfactant) were mixed in order to obtain  $Mn_{1-x}Co_xCO_3$  nanostructured particles.

The x-ray patterns of for all the samples were in agreement with a Calcite structure and the variation of unit cell parameters, a and c, with Co content was linear and in agreement with Vegard's law.

According to the TEM images, submicronic monodispersed regular shaped particles in the samples with  $x = 0, 0.1$  and  $0.2$  per formula, submicronic monodispersed distorted particles for  $Mn_{0.7}Co_{0.3}CO_3$ , a mixture of distorted particles and agglomerates for  $Mn_{0.6}Co_{0.4}CO_3$  and only agglomerates for  $Mn_{0.5}Co_{0.5}CO_3$  were observed. This was also confirmed by Williamson-Hall method calculations.

In relation to galvanostatic characterizations, all the samples showed similar initial capacity (ca.  $1500 \text{ mAhg}^{-1}$ ) and a considerable irreversible capacity of  $500 \text{ mAhg}^{-1}$  that decreased significantly upon cycling. The capacity fading was significant for all the samples, while  $Mn_{0.7}Co_{0.3}CO_3$  and  $Mn_{0.6}Co_{0.4}CO_3$  showed the highest capacity retention. The potentiostatic discharge/charge cycles for all the samples showed a reduction peak in the range  $0.5$  to  $0.0 \text{ V}$  related to  $Mn^{2+}$  and  $Co^{2+}$  cation reduction. This peak shifted to lower voltages by increasing the voltage sweep rate and by decreasing the cobalt content. The main contribution to capacity at low discharge sweep rates and higher cobalt contents was faradic, while capacitive contribution became important in high rates of discharge and lower amounts of cobalt.

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