

Electrochemical-Hydrothermal Synthesis of Co-doped Manganese Dioxides and Study of their Electrochemical Properties.

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A prospective search is in place in some laboratories in order to develop positive electrode materials for Li-metal primary and secondary batteries, having lower toxicity, lower cost, and higher average voltage than vanadium-based oxides. It seems that manganese oxides are good candidates, especially γ - MnO_2 . These materials can be described as a random intergrowth of two types of structural units: pyrolusite (1x1 channels) and ramsdellite (2x1 channels), these channels allowing reversible lithium insertion. This structure shows another type of defect, microtwinning. Therefore, γ - MnO_2 materials are characterized by the amount of pyrolusite intergrowth denoted P_r (in percent) and by the amount of microtwinning defects denoted M_t (in percent).^{1,2}

According to the literature, the reversible lithium insertion capacity of γ - MnO_2 materials should increase when the amounts of pyrolusite and microtwinning defects are the lowest. With this goal in mind, we have chosen to explore the electrochemical-hydrothermal method for the synthesis of MnO_2 materials approaching the ramsdellite limit.^{3,4,5,6}

The doping of manganese oxides with different transition metals, such as cobalt, has been shown to improve their electrochemical properties. In the case of LiMn_2O_4 , the Co-doping leads to the suppression of the Jahn-Teller distortion during reversible lithium insertion (at 3V).⁷ During the reversible lithium extraction (at 4V), the Co-doping in LiMn_2O_4 limits the dissolution phenomena and reduces the variation of the lattice volume.⁸ Another example is the doping of δ - MnO_2 (Birnessite) by different transition metals (such as Al, Fe, Co). According to this study,⁹ cobalt is the best dopant. In fact, during the lithium insertion, one can observe an increase of the capacity and a better cyclability compared to non-doped materials.

Given these results, the purpose of this study is to synthesize Co-doped γ - MnO_2 by the electrochemical-hydrothermal method, to study their physico-chemical and structural properties and to determine the effect of Co-doping on the electrochemical properties by comparison with non-doped MnO_2 .

Co-doped MnO_2 have been prepared by oxidation of an aqueous $\text{MnSO}_4/\text{CoSO}_4$ solution. In some preparations, Li_2SO_4 was also added to the initial solution to probe the effect of Li^+ on the synthesis. To determine the effect of synthesis conditions on the structure, we have varied the temperature, the applied current and the pH of the solution.

Chemical compositions and water contents were determined with atomic absorption spectroscopy by inductively coupled plasma (AAS/ICP analysis) and with thermogravimetric analysis (TGA), respectively. The average Mn oxidation state was determined by redox titration. Surface area measurements were carried out with the BET method. The morphology of samples was studied using scanning electron microscopy. The average Co

oxidation state was determined with X-Ray Absorption Near Edge Spectroscopy (XANES).

The chemical and structural characterizations indicate the cobalt is present (3% mol.) in the compound (for a $\text{pH} \geq 4$) and limits the formation of the pure pyrolusite phase, which is a positive point as the β - MnO_2 phase is inactive towards the lithium insertion (see Figures 1 and 2).

Further details of the structural and physico-chemical characterizations, as well as the effect of the cobalt presence in the composition on the morphology and on the electrochemical properties will be discussed.

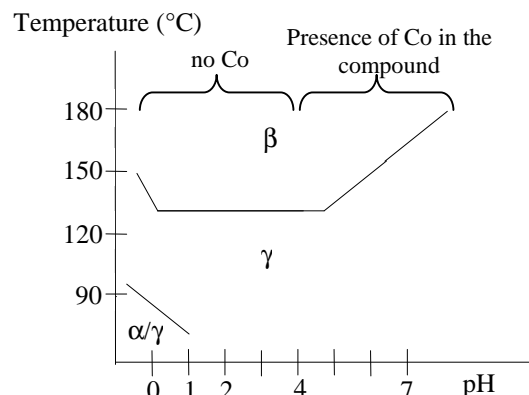


Figure 1 : Phase diagram, in the temperature-pH plane, of compounds synthesized from a solution containing MnSO_4 and CoSO_4 and an applied current density $J = 0.36 \text{ mA/cm}^2$.

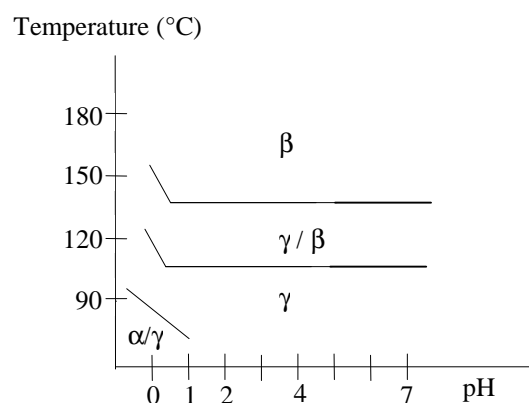


Figure 2 : Phase diagram, in the temperature-pH plane, of compounds synthesized from a solution containing MnSO_4 and an applied current density $J = 0.36 \text{ mA/cm}^2$, for comparison.

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Figure 11 : Diagramme de phase, dans le plan température- pH, des composés préparés à partir d'une solution de $MnSO_4$ et de $CoSO_4$ pour une densité de courant appliquée $J=0,36 \text{ mA/cm}^2$ (soit $I=10 \text{ mA}$) en présence d'ions Li^+

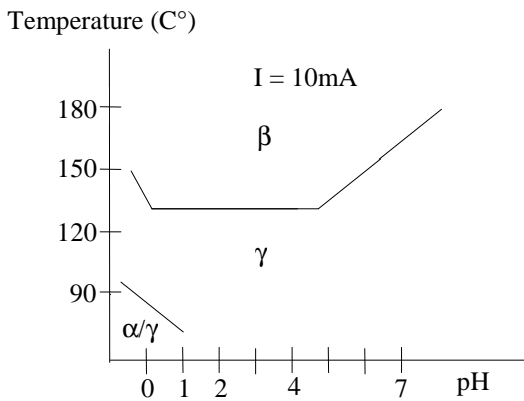
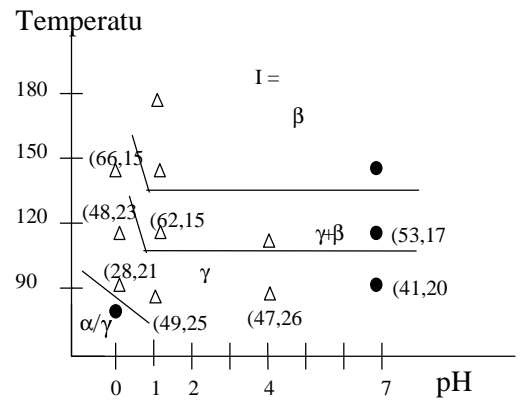
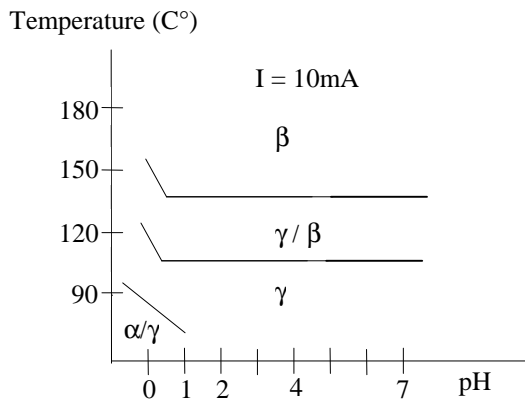


Figure 12 : Rappel du diagramme de phase dans le plan température- pH, des composés préparés à partir d'une solution de $MnSO_4$ pour une densité de courant appliquée $J=0,36 \text{ mA/cm}^2$ (soit $I=10 \text{ mA}$), en présence d'ions Li^+ (\circ) ou en absence de Li^+ (Δ) dans la solution. Il n'y a pas de cobalt dans la solution de synthèse.