

## LiMn<sub>2-x</sub>Co<sub>x</sub>O<sub>4</sub> cathode with enhanced cycleability

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### Abstract

Lithium–manganese–cobalt oxides, LiMn<sub>2-x</sub>Co<sub>x</sub>O<sub>4</sub> with 0 < x < 0.2 were synthesized by a solid-state multi-step reaction, in air, from a mixed manganese–cobalt oxide with lithium hydroxide. The samples were characterized by X-ray diffraction and electrochemical tests. The crystal structure of the obtained compounds is spinel-related. The discharge capacity of an Li/LiMn<sub>2-x</sub>Co<sub>x</sub>O<sub>4</sub> cell with x = 0.1 was 114 mAh/g for the fifth discharge and stayed almost the same at the cycle no. 100 – 107 mAh/g – related to the cathode capacity. The demonstrated cycling stability for 100 cycles reaches 99.93%. The improvement in cycleability can be attributed to the stabilizing role of Co<sup>3+</sup> ions, substituting Mn<sup>3+</sup> in the initial structure. © 1997 Published by Elsevier Science S.A.

**Keywords:** Lithium; Manganese; Cobalt; Cycleability

### 1. Introduction

Numerous authors have investigated the possibility to optimize the synthesis conditions [1–4,7], or to modify the initial structure of LiNiO<sub>2</sub>, LiCoO<sub>2</sub> and LiMn<sub>2</sub>O<sub>4</sub> compounds by preparing a large variety of mixed oxides such as LiNi<sub>1-x</sub>Co<sub>x</sub>O<sub>2</sub> with 0 < x < 1, or by doping the lithiated manganese spinel LiMn<sub>2-x</sub>Me<sub>x</sub>O<sub>4</sub> with different metals such as V, Ni, Cr, Co, Mg, Zn, etc. [4–6]. The lithiated Ni and Co oxides practically de-insert reversibly up to a 0.5 equivalent of lithium which corresponds to a specific discharge value of 137 mAh/g. LiMn<sub>2</sub>O<sub>4</sub> has a theoretical capacity value of 148 mAh/g, but the practically obtained values are close to 105–115 mAh/g, e.g. 70% of the theoretical value. The latest reported data in Ref. [7] claim a reversible capacity at the fifth cycle of 135 mAh/g which corresponds to 90% of the theoretical value.

In this paper we consider the possibility to enhance the electrochemical performance of LiMn<sub>2</sub>O<sub>4</sub> with Co as a stabilizing agent.

### 2. Experimental

The spinel-related lithium–manganese–cobalt oxides LiMn<sub>1.9</sub>Co<sub>0.1</sub>O<sub>4</sub> was prepared by a solid-state reaction

between lithium hydroxide and manganese–cobalt oxides. The initial mixed oxide (Mn<sub>1.9</sub>Co<sub>0.1</sub>)<sub>2</sub>O<sub>4</sub> was obtained by thermal decomposition of co-precipitated manganese–cobalt oxalates at 800 °C for 12 h in air. The reaction between LiOH and the mixed oxide (Mn<sub>1.9</sub>Co<sub>0.1</sub>)<sub>2</sub>O<sub>4</sub> proceeded at three successive steps: (i) initial pretreatment at 400 °C for 24 h; (ii) second pretreatment at 600 °C for 24 h, and (iii) final synthesis temperature of 750 °C for 24 h. The synthesis conditions were chosen in such a way that a simultaneous stabilization of Co<sup>3+</sup> and Mn<sup>3+</sup> ions in LiMn<sub>1.9</sub>Co<sub>0.1</sub>O<sub>4</sub> was ensured, according to Refs. [2,4] and to our latest investigations for the optimum synthesis of pure LiMn<sub>2</sub>O<sub>4</sub> spinel [7]. The phase composition of the samples was determined by X-ray analysis using a Philips APD 15 powder diffractometer with Cu K $\alpha$  radiation, internal Si standard and computer data management [8].

The electrochemical characteristics were performed in a three-electrode glass cell with a lithium reference electrode in excess of the electrolyte, and with a floating test electrode (described in Refs. [9,10]). The electrolyte was a solution of 1 M LiClO<sub>4</sub> in EC:DMC (ethylene carbonate:dimethyl carbonate) 1:1 ratio by volume mixture. The composite test electrode material was composed of a mixture of the compounds studied with Teflonized acetylene black (TAB-2) [11] at a 8:2 ratio by weight, pressed on an expanded aluminum grid (diameter: 15 mm), both sides covered, see Refs. [9,10]). The weight of the electrodes were 50 mg, without

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the aluminum grid. A 0.3 C charge/discharge current was applied in the electrochemical tests.

### 3. Results and discussion

Fig. 1 represents the X-ray diffraction (XRD) patterns of the sample pretreated at 400 °C. The temperature is rather low in order to obtain a well-crystallized product but, nevertheless, the spectrum is very close to the XRD pattern of a pure  $\text{LiMn}_2\text{O}_4$  spinel pretreated at the same temperature range [2]. Impurities such as  $\text{Mn}_2\text{O}_3$  are not detected in the XRD pattern of the Co-doped spinel. In contrast, the spectrum of the undoped spinel  $\text{LiMn}_2\text{O}_4$  pretreated at this temperature contains a perceptible quantity of  $\text{Mn}_2\text{O}_3$  and  $\text{Li}_2\text{MnO}_3$  impurities.

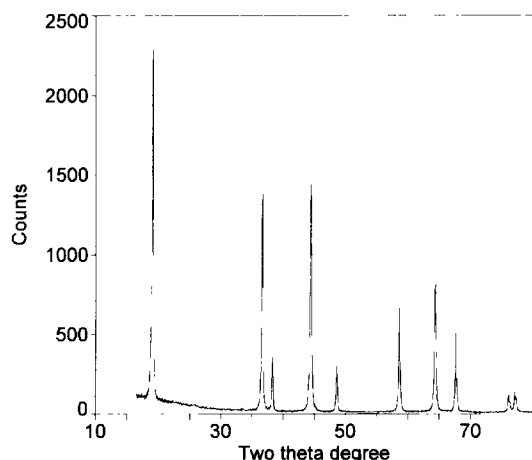


Fig. 1. XRD diagram of  $\text{LiMn}_{1.9}\text{Co}_{0.1}\text{O}_4$  sample pretreated at 400 °C.

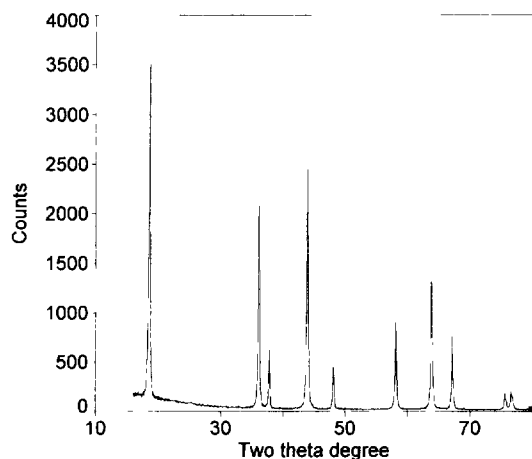


Fig. 2. XRD diagram of  $\text{LiMn}_{1.9}\text{Co}_{0.1}\text{O}_4$  sample treated at 600 °C.

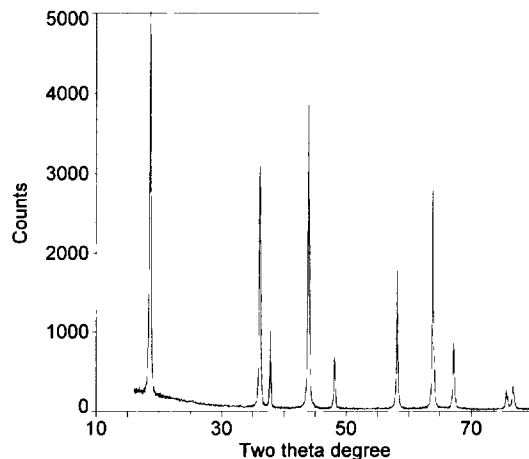


Fig. 3. XRD diagram of  $\text{LiMn}_{1.9}\text{Co}_{0.1}\text{O}_4$  sample synthesized at 750 °C.

At 600 °C, the thermal pretreatment leads to a pure monophase product with increased crystallinity, see Fig. 2. It was demonstrated in Ref. [7] that at temperatures around 600 °C the formation of a distorted nonstoichiometric spinel with a small excess of oxygen is observed.

When the final synthesis temperature of 750 °C is applied, a completely synthesized pure monophase and well-crystallized product was obtained, see Fig. 3. The XRD patterns coincide very well with the spectrum of a pure undoped spinel, with respect to the peak positions — which is not unexpected — because the  $\text{Co}^{3+}$  has a slightly low ionic radius and can replace  $\text{Mn}^{3+}$  in the crystal lattice. All XRD spectra differ from the XRD pattern of pure lithium–manganese dioxide spinel by the intensities of the peaks observed.

Table 1 gives the values of the parameter  $a_c$  of the crystal lattice during the thermal pretreatment. It can be seen that, when the final temperature synthesis step is applied, the parameter  $a_c$  of the crystal lattice of the Co-doped spinel became very close to the value of a pure spinel synthesized at 750 °C.

The discharge curves of electrodes composed of the compounds studied,  $\text{LiMn}_{1.9}\text{Co}_{0.1}\text{O}_4$  and with pure  $\text{LiMn}_2\text{O}_4$  spinel, are compared at  $C/3$  discharge rate, see Fig. 4. The pure spinel was especially chosen to yield the same specific capacity of 110–115 mAh/g as the Co-doped spinels. The first difference observed is the smooth profile of the Co-doped spinel discharge curve in contrast to the pure one with two well-defined plateaus at 4.10 and 3.95 V, respectively. The two discharge steps correspond to two different parameters  $a_c$  of the cubic lattice with values of 8.045 and 8.142 Å as demonstrated by Ohzuku et al. [1]. During cycling the crystal lattice of the pure spinel is subjected to volume changes with

Table 1  
Crystal lattice parameter,  $a_c$ , vs. temperature of the sample treatment

Synthesis temperature	400 °C	600 °C	750 °C
Parameter $a_c$ of Co-doped spinel $\text{LiMn}_{1.9}\text{Co}_{0.1}\text{O}_4$	8.182	8.207	8.216
Parameter $a_c$ of undoped pure spinel $\text{LiMn}_2\text{O}_4$	8.195	8.218	8.237

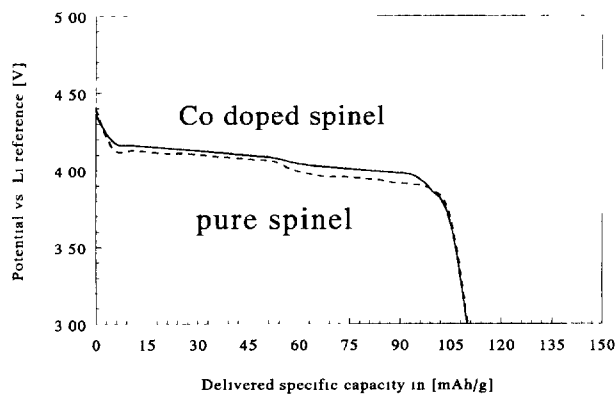


Fig. 4. Discharge profiles of  $\text{LiMn}_{1.9}\text{Co}_{0.1}\text{O}_4$  and the pure undoped spinel  $\text{LiMn}_2\text{O}_4$  at  $750^\circ\text{C}$ .

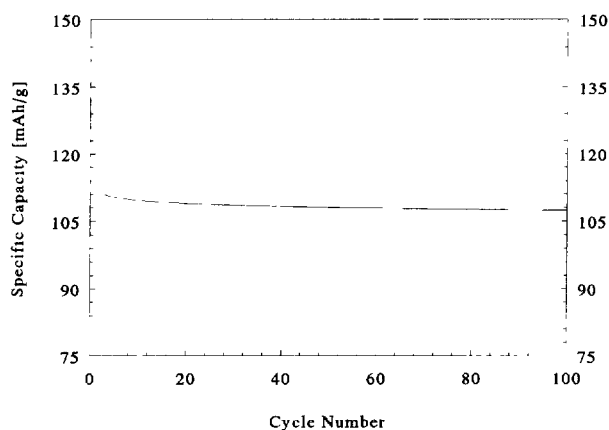


Fig. 5. Cycling behaviour of  $\text{LiMn}_{1.9}\text{Co}_{0.1}\text{O}_4$  at  $C/3$  discharge rate in a three-electrode glass cell in excess of electrolyte at  $750^\circ\text{C}$ .

a difference reaching 2.4% [1]. In the case of the Co-doped spinel the changes in the parameter  $a$ , during cycling proceeds smoothly and are reduced in amplitude.

The sample studied demonstrates the specific capacity versus cycle number, see Fig. 5. The initial specific capacity is 114 mAh/g, not so high, but decreases very slowly reaching 107 mAh/g after 100 cycles. It can be seen that the decay of the discharge capacity is very low regarding the cycle number. Yamaki and Tobishima [12] proposed an easy way to determine the cycling stability ( $CS$ ) of the cathode by the expression

$$(Q_d)_n = (Q_d)_m (CS)^{n-m}$$

under the assumption that  $CS$  is constant;  $m$  is the number of cycles during initial steep decay of the capacity when  $CS$  is decreasing (usually  $m=5$ ), and  $n$  is the number of the last cycle in the test. In our case the  $CS$  factor is 99.93%, which is a rather good value.

A direct comparison between pure and doped spinel is presented at Fig. 6. The three-electrode glass cell with a floating cathode allowed us to determine the real stability of active cathode material excluding factors such as pressure, construction of the cell and preparation of the test electrode. The

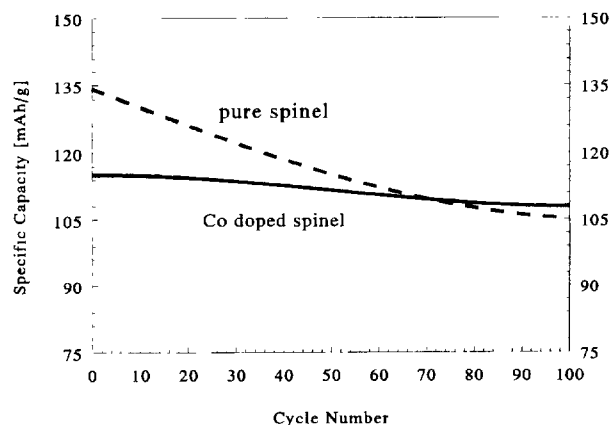


Fig. 6. Direct comparison of cycling stability of  $\text{LiMn}_{1.9}\text{Co}_{0.1}\text{O}_4$  and pure undoped spinel  $\text{LiMn}_2\text{O}_4$  for 100 cycles in a three-electrode glass cell in excess of electrolyte at  $750^\circ\text{C}$ .

difference between the initial capacity observed for the pure spinel (especially chosen to yield a specific capacity close to that of Co-doped one) and the doped one is only 18 mAh/g. The pure spinel starts with a specific discharge capacity of 128 mAh/g at the fifth cycle and declines to 102 mAh/g after 100 cycles, while the initial specific capacity of the cobalt-doped spinel is 114 mAh/g and decrease slowly to 107 mAh/g after 100 cycles.

#### 4. Conclusions

A small quantity of cobalt ( $x=0.1$ ) stabilizes the spinel structure of  $\text{LiMn}_{2-x}\text{Co}_x\text{O}_2$ , and, probably, reduces the variations in the crystal lattice parameter during cycling revealed by the smooth discharge curve in the 4.3–3.8 V discharge range, thus leading to an enhanced cycling stability of the active cathode material [13,14].

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