

THE Li AND CO-SUBSTITUTED SPINEL Mn OXIDE, $(\text{Li})_{8a} [\text{Li}_{x/4} \text{Co}_{3x/4} \text{Mn}_{2-x}]_{16d} \text{O}_4$, AND ITS USE AS CATHODE MATERIAL IN FLAT AND FLEXIBLE LITHIUM BATTERY

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The partial substitution of manganese by lithium and cobalt ions in 16d octahedral sites enhances the electrochemical cyclability of LiMn_2O_4 upon cycling. The improvement in cycling performance is mainly attributed to the suppression of the Jahn–Teller distortion in the spinel structure. The as-doped spinel Mn oxide has been successfully used as cathode material in flat and flexible lithium battery.

Keywords: Flexible lithium batteries

1. INTRODUCTION

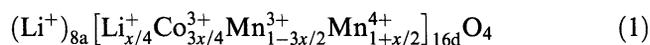
Spinel LiMn_2O_4 is a most attractive candidate as cathode material for rechargeable lithium batteries because it is less expensive and less toxic than other candidates such as cobalt oxides [1–16].

The crystal structure can be described as a closed-packed array of oxygen atoms (32e positions) with lithium atoms occupying tetrahedral 8a positions and manganese atoms 16d positions in the oxygen

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framework (Fig. 1). The arrangement of manganese and oxygen atoms can be seen as a three-dimensional framework for an interlinked network of tetrahedral (8a) and octahedral (16c) interstices, which can serve as pathways for the transport of lithium ions. The manganese/oxygen framework remains essentially the same for lithium insertion/extraction processes in the composition range $\text{Li}_x\text{Mn}_2\text{O}_4$, $0 \leq x \leq 2$. Indeed, lithium ions can be extracted from LiMn_2O_4 to form the $\lambda\text{-MnO}_2$ phase, while still maintaining cubic symmetry. Lithium-ion insertion into $\lambda\text{-MnO}_2$ causes the cell to expand isotropically up to the composition $\text{Li}_{1.08}\text{Mn}_2\text{O}_4$ [17–19].

Recently, some of us have successfully prepared cubic LiMn_2O_4 spinel simultaneously doped by lithium and cobalt [20]. According to Rietveld refinements of X-ray diffraction data, the lithium and cobalt are simultaneously substituted for manganese ions selectively in the 16d sites. Therefore, the following new formula:



could be proposed for the cubic spinel [20], in agreement with XPS data [21].

Consequently, the inclusion of lithium and cobalt ions enhances the $\text{Mn}^{4+}/\text{Mn}^{3+}$ ratio above 1 value ($\text{Mn}^{4+}/\text{Mn}^{3+} = 1$ in LiMn_2O_4) and, thereby, stabilises the cubic spinel structure due to the reduction of the Jahn–Teller distortion. That should enhance the electrochemical

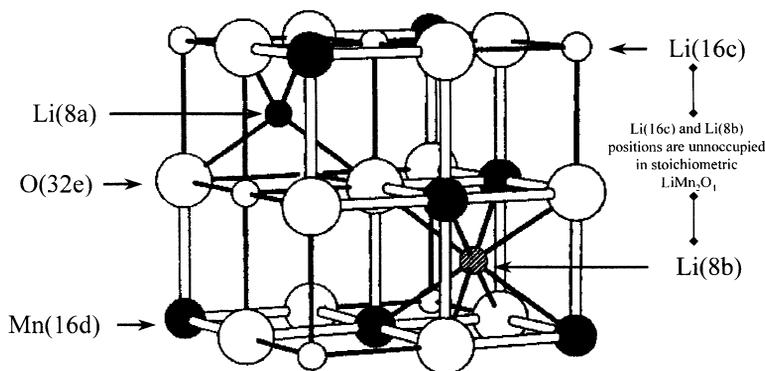


FIGURE 1 A part of the cubic LiMn_2O_4 spinel structure.

stability of the corresponding electrode material in the 3–4 V domain, according to our previously reported “electrochemical model” [22].

Our objective, here, is to investigate such effect with the following flat and flexible lithium batteries:

Li/Li⁺ polymer electrolyte membrane/(Li) [Li_{*x*/4} Co_{3*x*/4} Mn_{2–*x*}]O₄ and for the nominal compositions $x = 0$ and $x = 0.064$.

2. EXPERIMENTAL

2.1. Sample Preparation

(Li) [Li_{*x*/4} Co_{3*x*/4} Mn_{2–*x*}]O₄ samples ($x = 0$ and $x = 0.064$) were synthesised by combining conventional solid-state and sol–gel reactions [20]. Stoichiometric LiMn₂O₄ starting material was first prepared by intimately mixing the right amounts of Li₂CO₃ and MnO₂, followed by a heating at 750°C for 12 h in air. For the (Li) [Li_{*x*/4} Co_{3*x*/4} Mn_{2–*x*}]O₄ sample, the stoichiometric amounts of lithium acetate, cobalt acetate, and LiMn₂O₄ powder were mixed in water with a small amount of citric acid as a chelating agent. According to the solubility diagram of Li-Co-citric acid, the pH of the mixture was adjusted up to 6.5 by adding aqueous NH₄OH solution. The dried sample mixed with lithium- and cobalt-citrate gel was obtained by evaporating water from the solution at 70°C on a hot plate while it was mechanically stirred. The mixture was first heated at 300°C for 1 hr and finally at 700°C for 5 hrs in air. The lithium, cobalt, and manganese contents of the resulting samples were determined by atomic absorption analysis. The average oxidation state of metal ions in the samples was determined by the following procedure. About 50 mg of sample was dissolved in 10 ml of 0.1 M Na₂C₂O₄ in 1 M H₂SO₄ under continuous stirring until complete dissolution was achieved, and which was titrated with standard 0.02 M KMnO₄ solution. The titration was assigned to the excess of C₂O₄^{2–} ions in the sample dissolution [20].

2.2. Preparation of the Flat and Flexible Lithium Battery

The device (Fig. 2) is formed by hot-rolling (70°C) in a dry box a lithium metal strip (~ 80 μm thick), a polymeric electrolyte membrane and a composite cathode membrane (~ 50 μm thick).

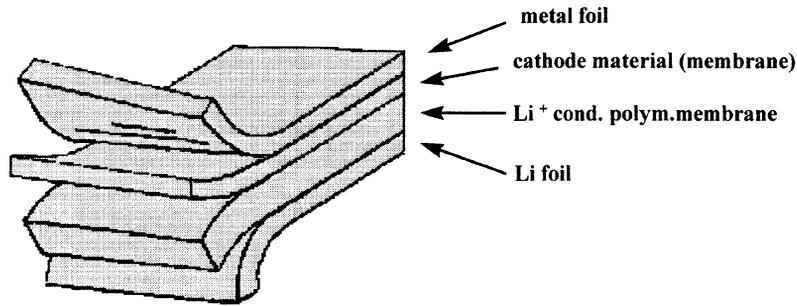
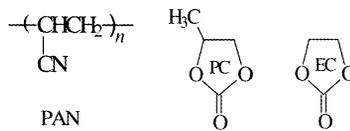


FIGURE 2 The flat and flexible lithium battery.

□ Starting materials

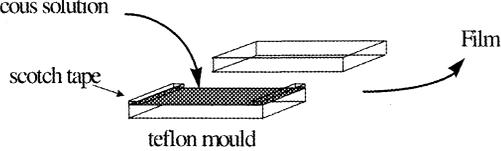
- polyacrylonitrile PAN
($M_w=1.5 \cdot 10^5 \text{g} \cdot \text{mol}^{-1}$)
- organic liquid : EC / PC
- salt : LiPF_6

□ Structures of PAN, PC, EC



□ Manufacturing process

- ① dissolution of $\text{LiPF}_6 + \text{EC} + \text{PC}$ at 25°C ; drying PAN at 60°C (48 hr.) under vacuum
- ② $\text{LiPF}_6 + \text{EC} + \text{PC} + \text{PAN} \xrightarrow{110^\circ\text{C} (20')}$ ③ dissolution of $\text{LiPF}_6 + \text{EC} + \text{PC} + \text{PAN}$ *
- ④ «casting» of the viscous solution



* 1) The optimized composition is (molar %) : 20 PAN // 5 LiPF_6 / 40 EC / 35 PC, [21].

2) Addition of finely dispersed inorganic powder was found to :

- enhance the mechanical stability of the membrane \Rightarrow the battery can be heated up to 150°C without damage.
- enhance the electrolyte retention.
- prevent short-circuit formation during the charge, [21].

FIGURE 3 Manufacturing process of the polymeric electrolyte membrane.

The manufacturing process of the polymeric electrolyte membrane is illustrated on Figure 3: the reagents were first mixed at the required mass ratio in the inert atmosphere of a dry box and, then, heated at 110°C in order to get a solution of appropriate viscosity which can be easily cast onto a substrate. Membranes having a translucent elastomeric appearance were finally obtained after cooling at room temperature.

The composite cathode membrane is constituted of a mixture, compacted at 1 t/cm², of 75 (weight) % of active material, 25% of Ketjenblack and 5% of PVDF. Before assembling, it is dried at 90°C, under vacuum for 1 h.

3. ELECTROCHEMICAL PROPERTY

Figure 4 gives the variation of charge/discharge capacity upon cycling (between 4.2 V and 3.2 V at C/5) for the Li//Li[Mn₂]O₄ and Li//Li[Li_{x/4}Co_{3x/4}Mn_{2-x}]O₄ ($x=0.064$) flexible batteries.

The figure shows the enhanced cycling performance of Li⁺/Co³⁺ co-doped spinel. This result can be explained by considering that the Li⁺/Co³⁺ co-doping suppresses the Jahn–Teller distortion in the spinel electrode at the end of discharge. In addition, comparing

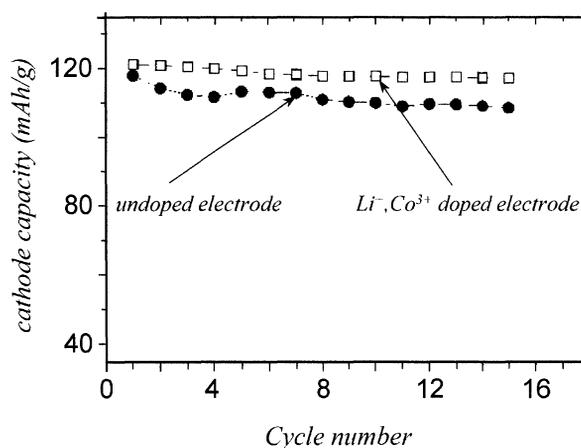


FIGURE 4 Variation of charge/discharge capacity (between 4.2 V and 3.2 V at C/5) for the Li/(Li)[Mn₂]O₄ Li/(Li)[Li_{x/4}Co_{3x/4}Mn_{2-x}]O₄ ($x=0.064$) flexible batteries.

the binding energy of MnO_2 (946 kJ/mol) and CoO_2 (1067 kJ/mol), it would be reasonable to think that the Co—O bond is stronger than the Mn—O bond, resulting in an enhancement of the stability of the spinel structure.

4. CONCLUDING REMARK

The flat and flexible battery based on the electrolyte membrane of composition (molar %): 20 PAN//5LiPF₆/40 EC/35 PC (Fig. 3), and sandwiched between a lithium foil and the composite cathode based on the $\text{Li}^+/\text{Co}^{3+}$ co-doped spinel, appears to be attractive for industrial application, although further investigation is needed.

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