

The influence of doping on the operation of lithium manganese oxide spinel

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Abstract

LiMn_2O_4 and $\text{LiMn}_{2-x}\text{Co}_x\text{O}_4$ ($0.1 \leq x \leq 0.4$) samples were prepared by a precipitation technique followed by an appropriate heat treatment in the 600–800 °C temperature range. The spinel materials were characterized by powder X-ray diffraction and electrochemical measurements. The differential capacity versus voltage plots indicate that the presence of cobalt strongly influences the order/disorder phase transition of the inserted lithium ions in the upper potential region of the spinel phase. This can be proven by X-ray diffraction measurements of delithiated spinels, showing two coexisting spinel phases in the undoped system whereas a single phase behavior in the cobalt-doped spinel system is observed. These materials show excellent capacity retention during extended cycling. © 1997 Published by Elsevier Science S.A.

Keywords: Lithium-ion batteries; Manganese oxide; Spinel

1. Introduction

Lithium manganese oxides with spinel structure are of great interest as insertion electrodes for use in 4 V lithium-ion rechargeable batteries because of cost, availability and environmental considerations. However, LiMn_2O_4 shows often low storage capability even at higher temperatures and a significant capacity loss during extended cycling. It is now well known [1–4] that the rechargeability of LiMn_2O_4 strongly depends on both the stoichiometry and the preparation conditions of the spinel. It has been recently reported that the capacity retention during cycling can be improved by adding a small excess of lithium to the stoichiometric LiMn_2O_4 spinel [3,5].

Earlier published results indicate the positive influence of cobalt and other metal dopants on cycling performance [6,7]. No particular attention has been denoted to the structural and electrochemical properties of these materials. This paper deals with the synthesis and the detailed structural and electrochemical characterization of cobalt-doped spinels.

2. Experimental

Samples of LiMn_2O_4 and $\text{LiMn}_{2-x}\text{Co}_x\text{O}_4$ ($0.1 \leq x \leq 0.4$) were prepared by a new precipitation technique followed by an appropriate heat treatment in the temperature range of 600–800 °C as described in Ref. [8].

The materials were characterized by X-ray diffraction (XRD) and chemical analysis. The lithium and cobalt contents were determined by atomic absorption spectroscopy (AAS); manganese was analyzed by photometrical methods. The structure of the compounds and changes in crystal structure at various states of charge were determined by powder XRD using a Siemens D5000 diffractometer (Cu K α radiation, secondary monochromator). Scans were performed from 10° to 120° in scattering angle.

All electrochemical measurements were performed in a glove box under argon atmosphere. Test electrodes were prepared by mixing spinel powders, 45 wt.% carbon and polytetrafluoroethylene (PTFE) binder. 20 mg of this mixture was pressed onto an aluminum grid. Prior to use the electrodes were dried at 120 °C in a vacuum furnace for a period of

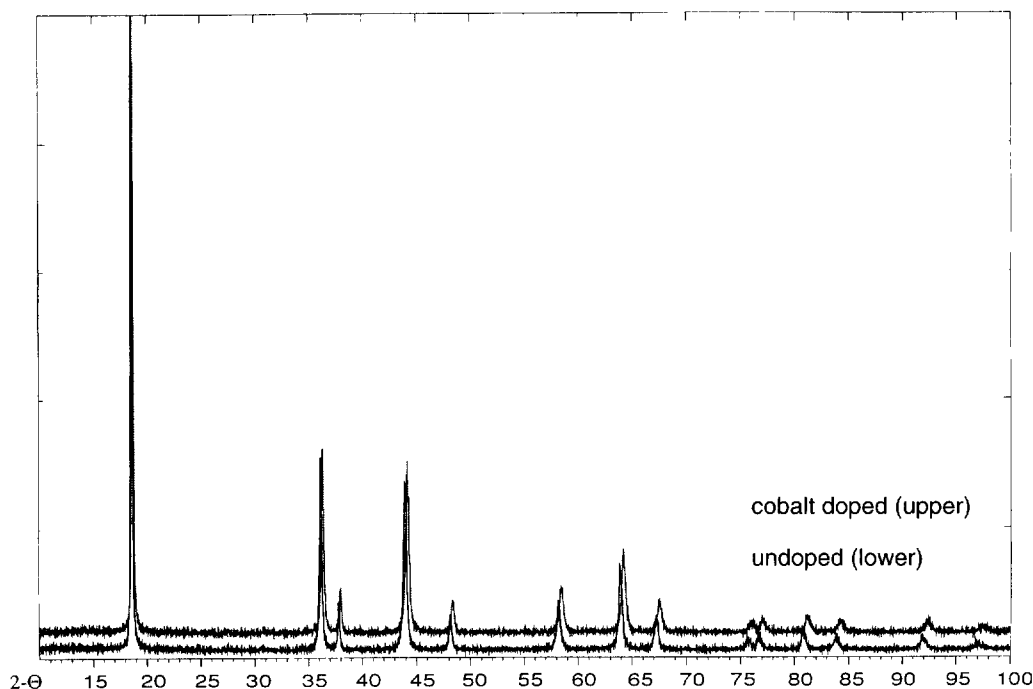


Fig. 1. Powder XRD pattern of undoped and 10 mol% cobalt-doped lithium manganese spinel.

12 h. Lithium foil was used as the counter and reference electrodes. The electrolyte used was 1 M LiPF₆ dissolved in a (1:1) mixture of ethylene carbonate (EC) and diethyl carbonate (DEC). For long-term cycling experiments the cells were charged to 4.3 V versus Li/Li⁺ and discharged to 3.3 V versus Li/Li⁺ using constant discharge and charge currents.

3. Results and discussion

3.1. Crystal structure

XRD patterns of cobalt-doped lithium manganese oxides indicate the presence of pure spinel phases up to a cobalt content of 20%. No impurities can be detected. Fig. 1 gives the powder XRD patterns of LiMn_{1.8}Co_{0.2}O₄ and LiMn₂O₄.

Table 1 shows the lattice constants *a* of LiMn₂O₄ and of four cobalt-doped samples with *x* = 0.1, 0.2, 0.3 and 0.4. A linear decrease in lattice constant *a* is observed with an increasing cobalt content.

Table 1
Lattice constant *a* of spinels versus cobalt content

Spinel	Lattice constant <i>a</i> (Å)
LiMn ₂ O ₄	8.242(5)
LiMn _{1.9} Co _{0.1} O ₄	8.234(5)
LiMn _{1.8} Co _{0.2} O ₄	8.212(5)
LiMn _{1.7} Co _{0.3} O ₄	8.187(5)
LiMn _{1.6} Co _{0.4} O ₄	8.163(5)

3.2. Electrochemical measurements

Fig. 2 gives the potential/capacity plots of LiMn_{1.9}Co_{0.1}O₄ and LiMn_{1.6}Co_{0.4}O₄ samples compared with stoichiometric LiMn₂O₄. The corresponding d*Q*/d*E* versus potential curves are shown in Fig. 3.

As expected a decrease in specific capacity with increasing cobalt content is observed, due to a decrease in the amount of extractable lithium. The removal of lithium from the spinel is accompanied by an oxidation of Mn³⁺ to Mn⁴⁺. Taking into account that the Co³⁺ ions cannot be oxidized in this potential range the amount of removable lithium is determined by the Mn³⁺ content. Thus only (1−*x*)Li can be extracted from LiMn_{2−*x*}Co_{*x*}O₄. This has been confirmed by chemical analysis of the lithium content in charged spinels.

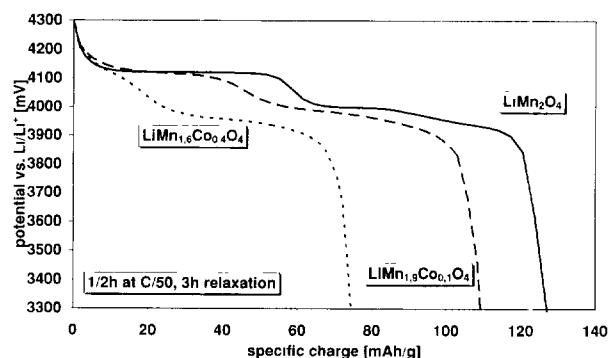


Fig. 2. Equilibrium curves of undoped, 5 and 20 mol% cobalt-doped lithium manganese spinel. Electrodes were charged potentiostatically up to 4300 mV vs. Li/Li⁺ and intermittently discharged at a C/50 rate. Open-circuit voltages every 3 h after current was switched off are plotted.

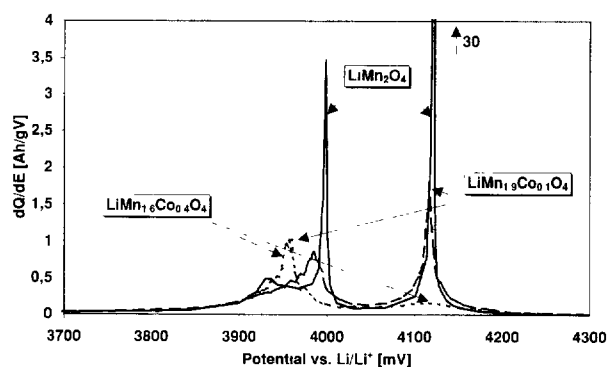


Fig. 3 Plots of differential capacity of undoped, 5 and 20 mol% cobalt-doped lithium manganese spinel. Data were taken from equilibrium measurements.

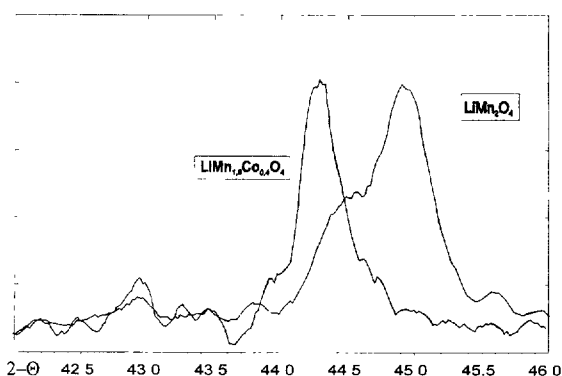


Fig. 4 (400) peak of undoped and 20 mol% cobalt-doped lithium manganese oxide spinel after electrochemical delithiation.

The amount of lithium in the delithiated state is proportional to the content of cobalt in the spinel.

As reported in the literature [9,2,3] the discharge curve of the undoped LiMn_2O_4 exhibits two potential plateaus at about 4.15 V versus Li/Li^+ and at about 4.0 V versus Li/Li^+ . The curves show a systematic trend of decreasing capacity only in the upper potential region with increasing cobalt content. This is better illustrated in the differential capacity versus potential plots shown in Fig. 3. The undoped spinel shows a very sharp peak at a potential about 4.15 V versus Li/Li^+ and one significant broader peak in the lower potential region, indicating a two-phase reaction at low lithium concentrations and a single-phase process at higher lithium contents. The most obvious interpretation of the phase relations observed is the formation of ordering of the inserted lithium ions over the available sites.

With increasing amount of cobalt the peak in the upper potential region diminishes. This means that the ordering of lithium ions is suppressed by the presence of cobalt ions. This can be proven by XRD measurements of the samples after electrochemical delithiation. Fig. 4 shows the (400) peak of an undoped and a 20 mol% cobalt-doped lithium manganese oxide spinel. Both samples were charged up to 4.1 V versus Li/Li^+ and then submitted to the XRD analysis. In the case of the pure lithium manganese oxide sample a splitting of the (400) peak occurs, indicating two coexisting cubic spinel

phases. Only one peak is observed for the cobalt-doped sample at full charge. This single-phase behavior leads obviously to a stabilization of the host structure during lithium insertion and extraction.

3.3. Cycling behavior

Fig. 5 shows the discharge capacity versus cycle number of LiMn_2O_4 and $\text{LiMn}_{1.8}\text{Co}_{0.2}\text{O}_4$ samples. The undoped material has a higher initial capacity but shows a significant loss of capacity during subsequent cycling. The cobalt-doped material shows very good cycling performance and retains more than 95% of initial capacity after 80 cycles. The loss of capacity of the undoped sample occurs mainly in the upper potential region. The changes of the dQ/dV versus potential

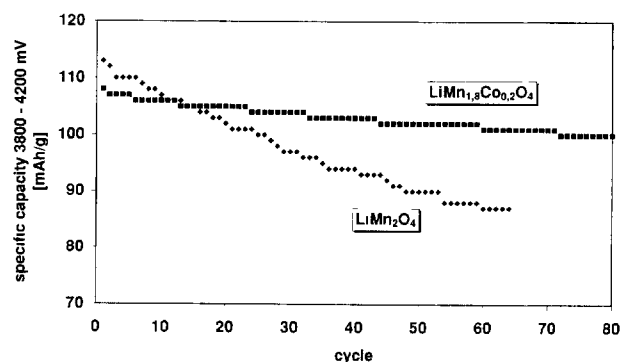


Fig. 5. Cycle life of undoped and 10 mol% cobalt-doped lithium manganese oxide spinel.

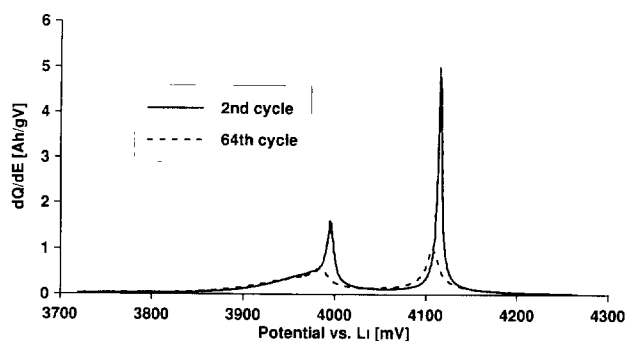


Fig. 6. Differential capacity of undoped lithium manganese oxide spinel (cycle numbers 2 and 64).

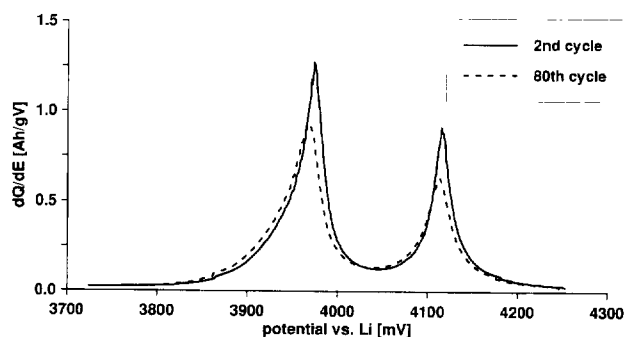


Fig. 7. Differential capacity of 10 mol% cobalt-doped lithium manganese spinel (cycle numbers 2 and 80).

plots with cycling are presented in Figs. 6 and 7. A significant broadening of the peaks and a shift to lower potentials is observed for LiMn_2O_4 . By contrast, the cobalt-doped sample shows no change in peak potential and half-width with cycle number.

4. Conclusions

The results of this study illustrate that the partial substitution of manganese by cobalt cations leads to a stabilization of the spinel structure. XRD studies and electrochemical measurements have shown that the cobalt content strongly influences the ordering/disordering phase transformation of the lithium ions. The samples show much better capacity retention upon cycling, if the two-phase reaction in the upper potential region can be avoided.

Acknowledgements

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