

Electrochemical and structural comparison of doped lithium manganese spinels

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Accepted 28 June 1999

Abstract

Lithium cobalt mixed doped lithium manganese spinels $\text{Li}_1(\text{Mn}_{1.9-x}\text{Co}_{0.1}\text{Li}_x)\text{O}_4$ ($0 \leq x \leq 0.1$) were prepared by heat treatment (750°C for 12 h) of solution precipitated precursors. Samples were characterised structurally and electrochemically by XRD and galvanostatic cycling. Permanent cycling, storage in the charged state, and storage in the discharged state were tested. Under the cycling conditions of this study, mixed doped lithium manganese spinels present better cycling and storage stabilities than a respective Co-doped spinel. There are hints for a considerable occupation of site 16c by lithium ions. The electrochemical behaviour is similar to that of an undoped spinel for low values of x and is similar to that of lithium doped spinels for high values of x . © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Electrochemical comparison; Structural comparison; Doped lithium manganese spinels

1. Introduction

Lithium manganese spinel is a promising 4-V cathode material for lithium-ion rechargeable batteries. It presents advantages in economy, ecology, and safety. The main disadvantage in application of this material is the loss of capacity during cycling and during storage in the electrolyte, especially at elevated temperatures. The reasons for the capacity loss are not totally clarified yet; but many models are proposed:

- Jahn–Teller distortion [1,2]
- disproportionation reaction [1,2]
- change of lattice constant at cycling [3]
- electrolyte oxidation [4,5]
- formation of an oxygen rich spinel [6]
- site exchange between Li and Mn [7]

Improvement of capacity retention has been achieved in three ways:

- partial substitution of manganese ions by trivalent or divalent cations like Co, Cr, Al, Mg, etc. [1,3,8–10]
- substitution of Mn by excess Li [1,11,12].
- synthesising cation deficient (= oxygen-rich) spinels at lower temperatures [1,11,12].

In this paper, the effects of a mixed doping by cobalt and excess lithium ions are investigated.

2. Experimental

2.1. Sample preparation

Precursors for mixed doped spinel samples of the nominal composition series $\text{Li}_1(\text{Mn}_{1.9-x}\text{Co}_{0.1}\text{Li}_x)\text{O}_4$ ($0 \leq x \leq$

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0.1) were prepared by a solution precipitation technique. Further details are described elsewhere [13]. The precursors were heated in air for 12 h at a temperature of 750°C and cooled down within about 2 h.

2.2. Structural characterisation

X-ray diffraction profiles of the samples were measured with a Siemens D5000 diffractometer (Cu K_{α} radiation, graphite secondary monochromator). Powder samples were pressed into standard sample holders. Electrodes were torn away from the aluminium grid and fixed on a silicon single crystal plate. Lattice constants were refined from the reflection positions by the programme LCLSQ (Burnham, Cambridge). All observed reflections could be indexed according to space group Fd3m.

2.3. Electrochemical characterisation

Each electrode mass (15 wt.% carbon SAB, 5 wt.% PTFE) was rolled out to a thin foil. Pieces of 10 mm in diameter and of weight between 10 and 20 mg were cut out, pressed into strips of aluminium grid, and dried for 12 h under vacuum at 150°C. Pieces of lithium metal foil (Aldrich 99.9%), about 1 cm² in area, were pressed onto strips of nickel grid and were used as reference and counter electrodes. Electrodes were mounted in polyethylene cells in a parallel three-electrode arrangement. The electrolyte was a 1 M solution of LiPF₆ in a mixture of organic carbonates. Cell assembly and electrochemical measurements took place in a glove box under argon atmosphere at room temperature. Test cells were galvanostatically cycled (Ionic systems P 1.0). For every sample,

three cells were assembled and cycled under different conditions:

- Permanent cycling for 3 weeks between 3.0 and 4.5 V vs. Li/Li⁺ at current rate C/10. After each charge or discharge process, current was switched off for 2 h
- Storage in the discharged state for 3 weeks. At the beginning and after each of the three weeks, the cell was cycled one time under the same conditions as in case (a).
- As case (b), but storage in the charged state. One charge process was added to each of the cycles in order to equalise self discharge.

Additional electrodes for ex situ X-ray diffraction were also cycled between 3.0 and 4.5 V vs. Li/Li⁺ at current rate C/10. Cycling was stopped after the first discharge or after the second charge process. After equilibration for about 12 h, electrodes were taken out of the cells and washed in ethanol.

3. Results and discussion

In Fig. 1, the lattice constant a is shown for the nominal composition series Li₁(Mn_{1.9-x}Co_{0.1}Li_x)O₄ ($0 \leq x \leq 0.1$). The lattice constant decreases for increasing degree of lithium doping. For low values of x , the lattice constant decreases slightly slower than for high values (Note that sample $x = 0.04$ is an outlier also in the electrochemical characterisation!). Since lattice constant and manganese oxidation state are highly correlated, this observation may indicate a slower increase of the manganese oxidation state for low values of x than for high values.

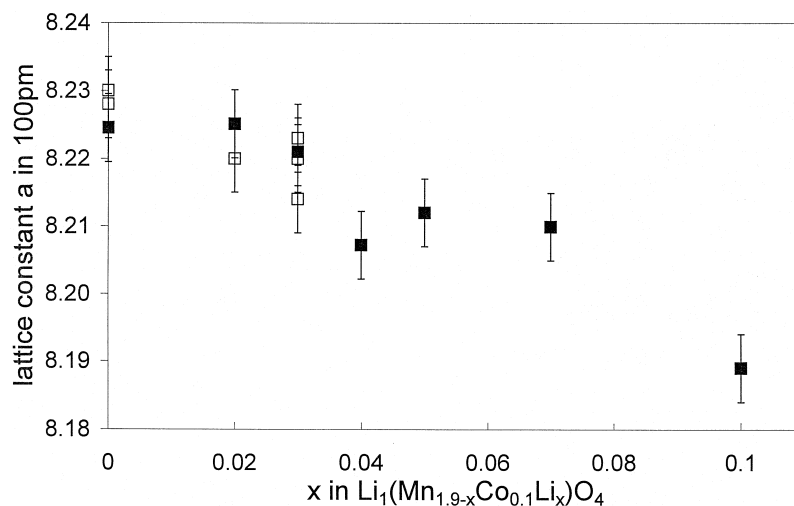


Fig. 1. Lattice constant a of Li–Co–mixed doped spinels for increasing Li doping. □: data from Ref. [15]; ■: this study.

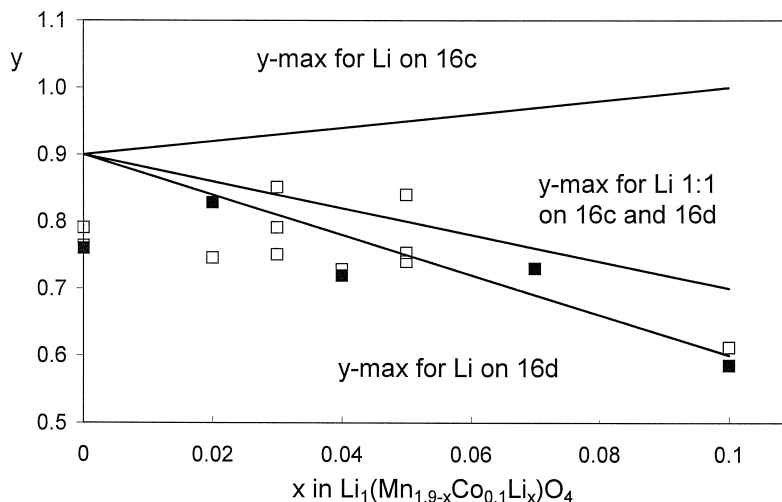


Fig. 2. Theoretical and measured number y of cyclable lithium ions per formula unit. □: data from Ref. [15]; ■: this study.

In Fig. 2, the number y of cyclable lithium ions per formula unit is depicted. It is calculated from the first discharge capacity according to following relation:

$$y = \frac{C_m M}{F} \quad (1)$$

wherein C_m is the measured specific capacity, M is the molar mass of the respective spinel referred to one formula unit, and F is the Faraday constant. In Fig. 2, the number y of cyclable lithium ions stays more or less constant for about $x < 0.06$. Above $x \cong 0.06$, it decreases. Since the number of extractable lithium ions is correlated with the manganese oxidation state in the discharged state, this observation may indicate an approximately constant manganese oxidation state for $x < 0.06$, more or less in accordance with the behaviour of the lattice constant.

A possible explanation for an uneven behaviour of the manganese oxidation state could be a partial occupation of the empty site 16c by excess lithium ions besides the manganese site 16d (space group Fd3m). Providing that there are no vacancies on the manganese site, the occupation of 16c reduces the manganese oxidation state and counterbalances the effects of manganese substitution by lithium ions. There are hints by neutron diffraction for a simultaneous lithium occupation of site 16c and site 16d in a ratio of about 1:1 at least for a sample of $x = 0.1$ [14]. But the observed behaviour of lattice constant and number of extractable lithium ions implies that this ratio should be even higher for lower values of x . Further evaluation of neutron diffraction data is currently being performed, in order to test this assumption.

In Fig. 2 for comparison, theoretical values for the maximum number y of cyclable lithium ions are added to

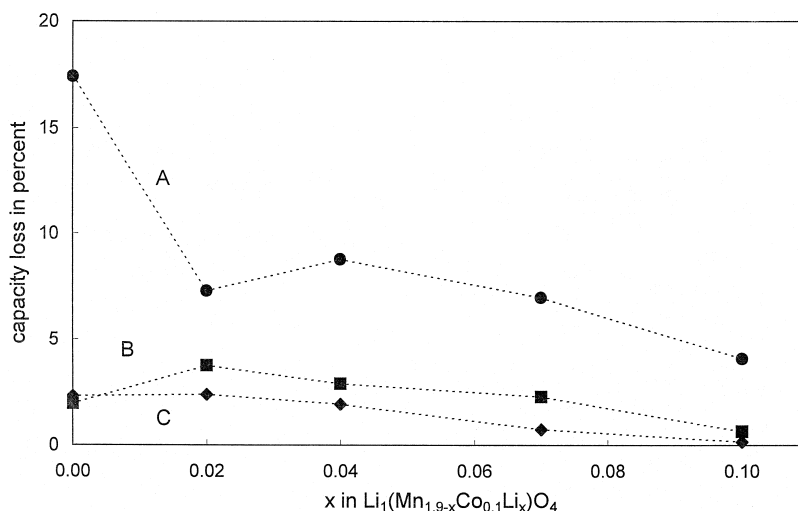


Fig. 3. Total relative capacity loss after three weeks for three kinds of cycling. (A) Permanent cycling, (B) cycling and storage in the discharged state, (C) cycling and storage in the charged state.

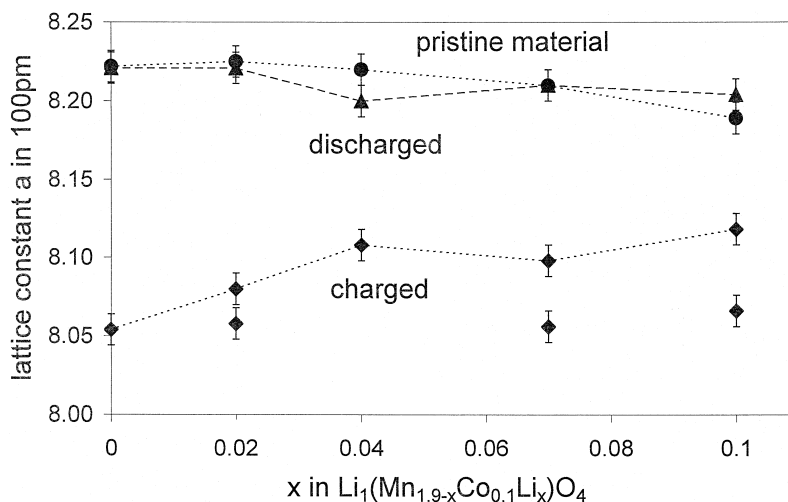


Fig. 4. Lattice constant a after first cycle.

the plot for three structure models: $x_1 = x$; $x_1 = x_2 = x/2$; $x_2 = x$; for $(\text{Li}_1)_{8a}(\text{Mn}_{1.9-x_1}\text{Co}_{0.1}\text{Li}_{x_1})_{16d}(\text{Li}_{x_2})_{16c}\text{O}_4$ and $x_1 + x_2 = x$. The theoretical values follow Eq. (2):

$$y(\text{max}) = 0.9 - 3x_1 + x_2 \quad (2)$$

In the plot of Fig. 2, there is a high degree of scattering as well as in Fig. 1. Reproducibility tests have shown that this effect neither results from the electrochemical nor from the XRD measurements, but from reproducibility problems in the synthesis of the samples. This corresponds to synthesis problems described in the literature for a pure lithium doping [11,12].

In Fig. 3, the total relative capacity loss after 3 weeks is depicted for all tested samples and kinds of cycling. the storage stability in the charged state is improved for an increasing additional lithium doping. Also, the storage stability in the discharged state increases for increasing lithium doping, but there is a decrease for $x = 0.02$. The cycling stability is generally improved for an increasing

lithium doping. This can be explained by the decrease in the change of the lattice constant at cycling (Fig. 4). Except for the sample $x = 0.04$, all mixed doped samples consist of two cubic phases in the charged state, like an undoped spinel. The reason for the inconsistency at $x = 0.04$ is not known. For mixed doped spinels, the existence of a phase transition in the high potential range seems not to be as detrimental to the capacity retention, as it is commonly thought to be for the undoped spinel [6].

In Fig. 5, the potential curves for the second discharge process are shown for three selected samples. The respective differential capacity curves are shown in Fig. 6. Note that the specific capacity is higher for the sample with $x = 0.02$ (120 mAh/g) than for the pure Co-doped sample (110 mAh/g) and that this sample offers a better cycling stability, contradicting the general trend of a decreasing capacity for an increasing capacity retention. However, the specific capacity for the sample with $x = 0.1$ is reduced again (90 mAh/g). For $x = 0.02$, the potential curve and the differential capacity curve look like those for an un-

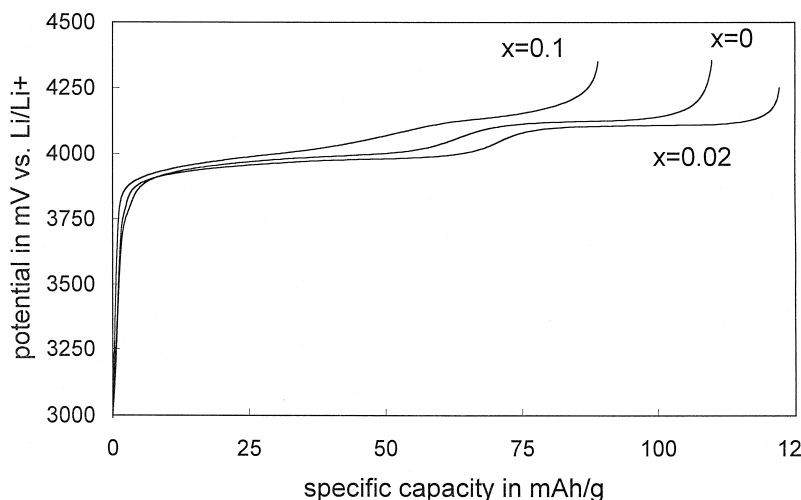


Fig. 5. Potential curves of the second discharge process for $\text{Li}_1(\text{Mn}_{1.9-x}\text{Co}_{0.1}\text{Li}_x)\text{O}_4$.

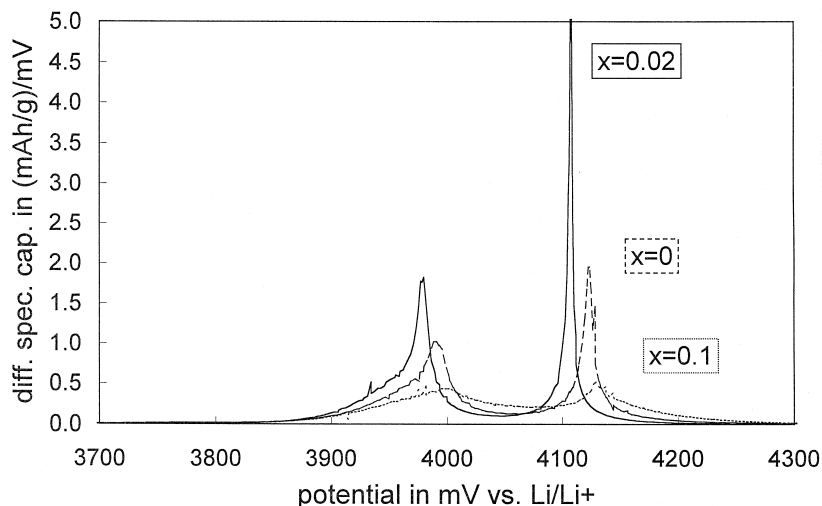


Fig. 6. Differential capacity curves of the second discharge process for $\text{Li}_1(\text{Mn}_{1.9-x}\text{Co}_{0.1}\text{Li}_x)\text{O}_4$.

doped spinel, due to the flat high potential range and the sharp second peak respectively. It seems, that the effects of Co doping are partially equalised by excess lithium ions occupying site 16c. For $x = 0.1$, however, the curves are similar to those of lithium doped spinels [11,12]. The potential curve is steeper and is smeared out, the differential capacity curve shows two low and broad peaks. It seems, that in this case the behaviour is strongly determined by lithium ions occupying site 16d.

4. Conclusions

Under the cycling conditions of this study, mixed doped spinels $\text{Li}_1(\text{Mn}_{1.9-x}\text{Co}_{0.1}\text{Li}_x)\text{O}_4$ ($0 \leq x \leq 0.1$) present better cycling and storage stabilities than a respective Co doped spinel. There are hints for a considerable occupation of site 16c by lithium ions. The electrochemical behaviour is similar to that of an undoped spinel for low values of x and is similar to that of lithium doped spinels for high values of x . The reproducibility in the synthesis of these materials is rather poor.

Acknowledgements

This work was supported by the German Ministry of Education, Research, Technology, and Science (BMBF)

under contract 03N 3007 E7 in cooperation with VARTA Battery, Kelkheim.

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