

Spinel-type lithium–manganese oxide cathodes for rechargeable lithium batteries

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Abstract

Dissolution of Mn ions and capacity loss of spinel-type Li–Mn oxide cathodes in LiPF₆-containing electrolytic solutions at 60°C were investigated. The amounts of dissolved Mn decreased with the increase in the Li/Mn molar ratios in Li–Mn oxides. The dissolution reaction of Mn ions was enhanced on charged cathodes, resulting in a cathode capacity loss and a contraction of the lattice parameter. An increase of the polarization voltage was considered to cause a capacity loss on the charged cathodes during the course of immersion at 60°C, as well as the dissolution of Mn ions. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

Rechargeable lithium batteries using LiCoO₂ cathodes and carbon anodes are well-known secondary battery systems in mobile devices, camcorder, handy telephones, portable personal computers, etc. LiCoO₂ exhibits a relatively stable cyclability and an excellent rate performance. However, Co metal is much less abundant in nature and highly expensive, and these problems are obstacles to applications of LiCoO₂ as cathodes for large-scale lithium batteries for load-leveling systems and electric vehicles. For these applications, Li–Mn oxides such as spinel-type LiMn₂O₄ are one of the most promising materials, because Mn is rich in natural resources and inexpensive as compared with Co. In addition, Mn oxides are relatively inert and safe, as they are widely used in primary batteries.

Performances of spinel-type Li–Mn oxide cathodes at elevated temperature have been under development to realize the large-scale lithium batteries. One of the major problems is dissolution of Mn ions from LiMn₂O₄ cathodes, followed by a cathode capacity loss. Thackeray et al. proposed the disproportionation reaction of Mn³⁺ yielding Mn⁴⁺ and releasing Mn²⁺ into electrolytic solutions [1]. There are a number of reports in terms of the dissolution mechanisms which account for dissolution reactions of Mn ions were enhanced by HF [2], H₂O [3], solvents in electrolytic solutions [4,5], carbons of electric conductors

in cathodes [4,5], etc. Xia and Yoshio indicated that an unstable Li–Mn oxide species formed in the two-phase region of charged cathodes released Mn ions into electrolytic solutions and resulted in the capacity loss [6]. Oxygen evolution accompanied by dissolution of Mn ions was suggested by Gao and Dahn [7]. However, dissolution of Mn ions and its subsequent reactions which are responsible for cathode capacity loss have not been elucidated and in controversy. For prevention of the dissolution of Mn ions, durable cathode materials were produced through a partial substitution of Mn sites by the other transition elements [8–10], surface treatments with lithium borate glasses, and complexing agents on Li–Mn oxides [3], etc. In this work, cathodes of spinel-type Li–Mn oxides with Li-rich compositions were developed for suppression of dissolution of Mn ions and capacity loss of cathodes. Capacity loss reactions induced by dissolution of Mn ions and decomposition of solvents on the cathodes were also discussed.

2. Experimental

Spinel-type Li–Mn oxide powders with different Li/Mn molar ratios (denoted as $R_{\text{Li/Mn}}$) were prepared by calcination of electrochemically produced manganese dioxides (EMD) and Li salts such as Li₂CO₃, LiNO₃, etc. Their crystal structures and lattice parameters were analyzed by X-ray diffraction (XRD) method using Cu-K α 1 (0.1540562 nm). Mixtures of the Li–Mn oxides, graphite and poly-

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(vinylene difluoride) binder were coated on Al foil as test electrodes.

Charge and discharge experiments of these electrodes were conducted at 0.5 mA/cm^2 between 3.0 and 4.3 V vs. Li counter electrodes in electrolytic solutions containing LiPF_6 as an electrolyte. The solvents in use were binary mixture solutions of ethylene carbonate (EC) and ethylmethyl carbonate (EMC). The charged electrodes were immersed into the solutions added in the sealed stainless steel vessels, and thermostated at 60°C . After the immersion, the charged cathodes were discharged to 3.0 V at 0.5 mA/cm^2 in order to measure remaining capacity densities.

Lattice parameters of the Li–Mn oxide cathodes in discharged state were determined by XRD before and after the immersion. Total amounts of Mn ions in solutions were measured by inductive coupled plasma (ICP) method and given in ppm as the concentration in electrolytic solutions.

3. Results and discussion

3.1. Dissolution reaction of Mn ions on spinel-type Li–Mn oxide powders (discharged state)

Fig. 1 shows the amounts of dissolved Mn in LiPF_6 -containing EC + EMC solutions for spinel-type Li–Mn oxide powders with different $R_{\text{Li}/\text{Mn}}$ values as the function of immersion time at 60°C . The $R_{\text{Li}/\text{Mn}}$ of each specimen were given in the figure. The amount of dissolved Mn was found to be largest on the cathode with R of 0.527 among the samples. This reaction did not terminate during the time scale given in Fig. 1. The amounts of dissolved Mn for the powders at Li-rich compositions ($R_{\text{Li}/\text{Mn}} = 0.55\text{--}0.572$) were appreciably suppressed. The amounts of dissolved Mn were reduced by 1/4 times or less by increasing $R_{\text{Li}/\text{Mn}}$ over 0.55, and the minimum value was obtained for Li–Mn oxide powder with $R_{\text{Li}/\text{Mn}}$ of 0.55 among the samples in use. This powder was

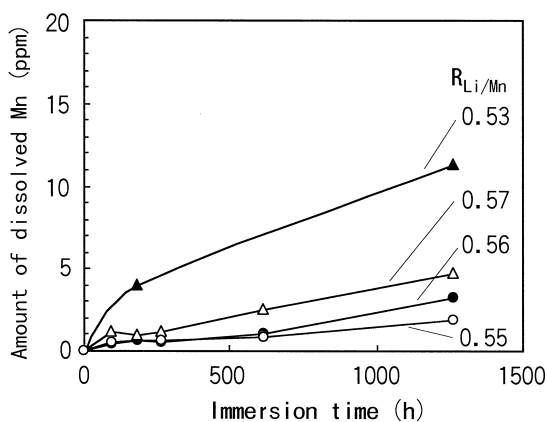


Fig. 1. The amounts of dissolved Mn from spinel-type Li–Mn oxide powders with various $R_{\text{Li}/\text{Mn}}$ values as the function of the immersion time in LiPF_6 -containing EC + EMC solutions at 60°C .

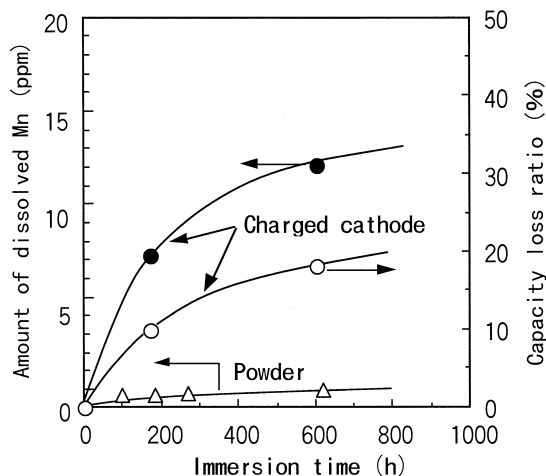


Fig. 2. Time dependences of the capacity loss ratio and the amount of dissolved Mn for the charged spinel-type Li–Mn oxide cathodes with $R_{\text{Li}/\text{Mn}}$ of 0.55 during the immersion in LiPF_6 -containing EC + EMC solutions at 60°C .

examined in detail to clarify capacity loss reactions induced by the dissolution of Mn ions and the crystallographic change of Li–Mn oxide cathodes at the charged state.

3.2. Dissolution of Mn ions on charged spinel-type Li–Mn oxide cathodes

The amounts of Mn dissolved from charged cathodes using Li–Mn oxides with $R_{\text{Li}/\text{Mn}}$ of 0.55 were presented in Fig. 2 as the function of the immersion time. The amount of dissolved Mn was significantly increased by 10–20 times for the charged cathode (closed circles), comparing to the original powder (open triangles). The capacity loss ratios were evaluated as the relative values of decreased capacity densities against the initial capacity density. The rate of Mn dissolution was fast in the early stage of immersion and decreased with the immersion time. The capacity loss ratio increased with increasing the immersion time in a similar behavior. This may suggest the dissolution of Mn ions involved in the capacity loss reaction for the charged cathode.

Crystallographic changes of charged Li–Mn oxide cathodes examined after the immersion treatment at 60°C . Fig. 3 exhibits the time dependence of lattice parameters measured by XRD after the immersed cathodes were discharged up to 3.0 V in a newly prepared LiPF_6 -containing EC + EMC solution at room temperature. The lattice parameter shown at zero on the abscissa was the datum of the cathode obtained without immersion at 60°C and charge/discharge cycling. A cubic structure of spinel-type Li–Mn oxides was detected without any other different crystal structures for all samples by XRD analyses. The lattice parameters decreased in a proportional manner with the amount of dissolved Mn. According to the dispropor-

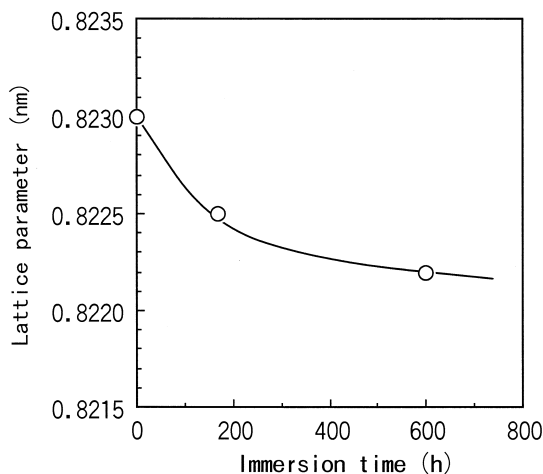
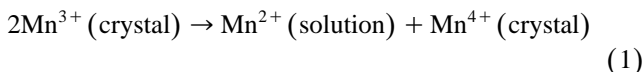


Fig. 3. The lattice parameter of the spinel-type Li–Mn oxide cathodes with $R_{\text{Li}/\text{Mn}}$ of 0.55 as the function of the immersion time in LiPF_6 -containing EC+EMC solutions at 60°C.

tion reaction model expressed by Eq. (1), the residual Mn^{3+} ions in the Li–Mn oxide crystal was oxidized to Mn^{4+} ions, releasing Mn^{2+} into solutions [1].



As the ionic radius of Mn^{4+} (0.067 nm) is smaller than that of Mn^{3+} (0.079 nm), the increase in the mole fraction of small Mn^{4+} ions is likely to cause the contraction of the Li–Mn oxide crystals, which is associated with the results observed in Fig. 3.

3.3. Relationship between dissolution of Mn ions and capacity loss of charged spinel-type Li–Mn oxide cathodes

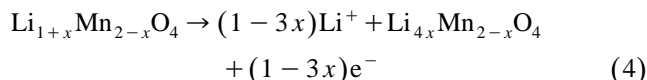
Capacity loss reactions of charged cathodes at elevated temperatures have not been clarified. Factors of the capacity loss of spinel-type Li–Mn oxide cathodes are discussed below according to the data of the dissolution of Mn ions obtained in this work. Assuming that the Li–Mn oxides used in this work had no oxygen vacancy, the general formula of the Li–Mn oxides is represented $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ where x is the excess molar fraction of Li^+ ions. On the basis of this assumption, the molar fraction of Mn^{3+} ions in $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ cathodes in discharge state can be calculated from Eq. (2) expressing the charge neutralization rule:

$$1 \times (1+x) + 3\alpha + 4 \times (2-x-\alpha) = 2 \times 4 \quad (2)$$

where α denotes the Mn^{3+} molar fraction in $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ oxides. Terms in the left hand exhibits the sum of positive charges of Li^+ , Mn^{3+} and Mn^{4+} , whereas a term in the right hand is the negative charge of O^{2-} . Eq. (2) leads Eq. (3) which expresses α with a function of x

$$\alpha = 1 - 3x. \quad (3)$$

Then the full charge reaction of spinel-type Li–Mn oxide crystals, namely, the oxidation of all Mn^{3+} ions to Mn^{4+} ions, is represented in Eq. (4):



The x -value of the $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ powder used in Fig. 2 was evaluated to be 0.0695 from the equation of Li/Mn molar ratio ($R_{\text{Li}/\text{Mn}} = 0.55$) as shown in Eq. (5):

$$(1+x)/(2-x) = 0.55. \quad (5)$$

Thus the Mn^{3+} molar fraction (α) was calculated to be 0.792 by substituting 0.0695 for x in Eq. (3). If 0.792 mole of electrons is released in Eq. (4), the theoretical capacity density of 120 (mAh)/g is obtained. On the contrary, the capacity density of the cathodes used in Fig. 2 were 113–115 (mAh)/g. Thus it can be speculated that 94–96% of the initial molar fraction of Mn^{3+} ions contributed in the charge/discharge reaction, and the residual Mn^{3+} ions with 4–6% of the initial molar fraction (0.792) were considered to undergo the disproportionation reaction of Eq. (1) on the charged cathode in Fig. 2. On the other hand, the amount of Mn ions dissolved as described in Eq. (1) was presumed to be larger for Li–Mn oxide powder at the discharged state than the charged cathodes, as the Mn^{3+} molar fraction of the powder was much larger than that of the charged cathode. On the contrary, the amount of dissolved Mn for the powder was smaller by 1/10 or less than the charged cathode (Fig. 2). This result suggests that Eq. (1) is unlikely and the other dissolution reactions of Mn ions may take place on the charged cathodes studied in this work.

To clarify the factors that cause capacity loss of charged cathodes, the relationship between the amount of dissolved Mn and the capacity loss ratio was examined in Fig. 4 using the data in Fig. 2. The slope of capacity loss ratio

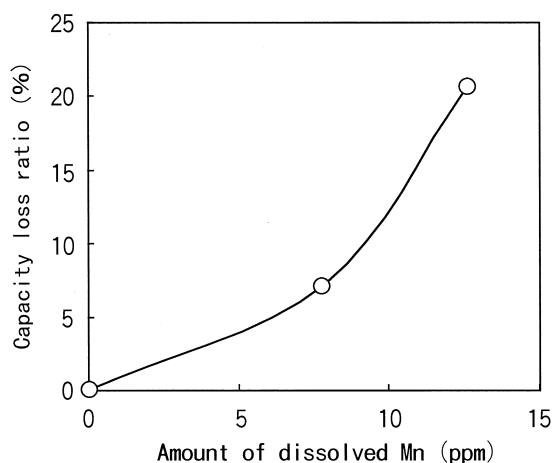


Fig. 4. The relationship between the amount of dissolved Mn and the capacity loss ratio of the charged spinel-type Li–Mn oxide cathodes with $R_{\text{Li}/\text{Mn}}$ of 0.55 after the immersion in LiPF_6 -containing EC+EMC solutions at 60°C.

against the amount of dissolved Mn increased with the amount of dissolved Mn. This result also supports the speculation that other capacity loss reactions except for the dissolution of Mn ions may also take place on the charged cathodes.

To clarify the other capacity loss reactions except for the dissolution of Mn ions on charged spinel-type Li–Mn cathodes, changes of charge and discharge curves of the Li–Mn oxide cathodes were discussed below in more detail. Fig. 5 shows the charge and discharge curves obtained before and after the immersion in LiPF_6 -containing EC + EMC solutions at 60°C . Each charge curve showed a voltage step around a half of the capacity density obtained after a full charge up to 4.3 V. These charge curves can be divided into the two stages such as stages I and II. In the former stage, Li–Mn oxides in two different structures including an unstable species were considered to coexist [6]. The charging curves shifted gradually to a high potential region with an increase of the immersion time, resulting in a decrease of the capacity density. An increase of the polarization voltage with the immersion time can be

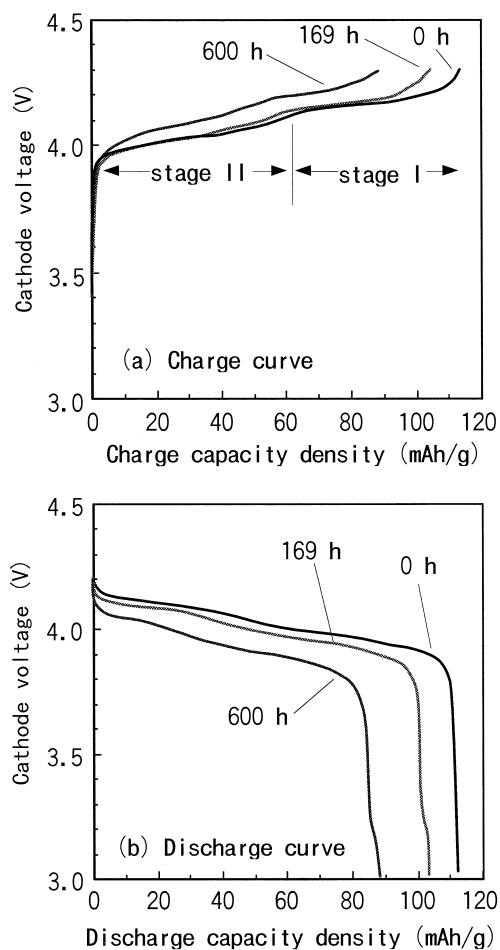


Fig. 5. (a) Charge and (b) discharge curves of the spinel-type Li–Mn oxide cathodes with $R_{\text{Li}/\text{Mn}}$ of 0.55 before and after the immersion in LiPF_6 -containing EC + EMC solutions at 60°C .

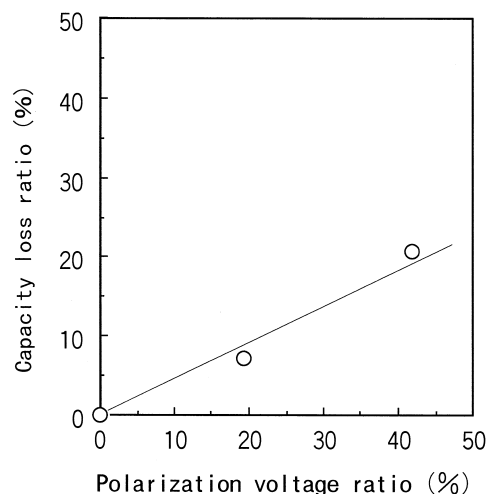


Fig. 6. The capacity loss ratio of the spinel-type Li–Mn oxide cathodes with $R_{\text{Li}/\text{Mn}}$ of 0.55 after the immersion in LiPF_6 -containing EC + EMC solutions at 60°C as the function of the polarization voltage ratio evaluated with respect to the initial value (93 mV) before the immersion.

also observed for the discharging curves of Li–Mn oxide cathodes (Fig. 5(b)).

Effect of the polarization voltage on capacity densities of charged spinel-type Li–Mn oxide cathodes was examined. The polarization voltage was evaluated as the voltage gap between the charge cutoff voltage (4.3 V) and the rest potential measured after 0.5 h passed since the charge of Li–Mn oxide cathode was terminated. Fig. 6 exhibits the relationship between the polarization voltage ratio and the capacity loss ratio of charged Li–Mn oxide cathodes with the Li/Mn molar ratio of 0.55. The polarization voltage ratio was estimated as a ratio of the polarization voltage measured after the immersion of charged cathodes against the initial value (93 mV) obtained before the immersion. The capacity loss ratio was evaluated as a relative capacity density obtained after the immersion against the value before the immersion. As the capacity loss ratio increased with the polarization voltage ratio in a proportional manner, the polarization voltage is considered to be one of the major factors to cause the capacity loss of charged spinel-type Li–Mn oxide cathodes.

Capacity losses in stages I and II after the immersion of the charged cathodes were investigated to make clear the effect of the unstable Mn oxide species formed in stage I [6] on capacity loss reactions. Voltages of the charge curves in Fig. 5(a) were differentiated by the charge capacity density to determine the capacity density at which stages I and II were separated. The data were given in Fig. 7(a) as the function of the charge capacity density. Capacity densities at peaks observed in the differentiated polarization voltage curves were presented in the figure, and stage I and II were separated at these peaks. The charge capacities gained in the stages I and II were plotted in Fig. 7(b) as the function of the immersion time. In this work, the charged cathodes underwent the capacity loss reaction

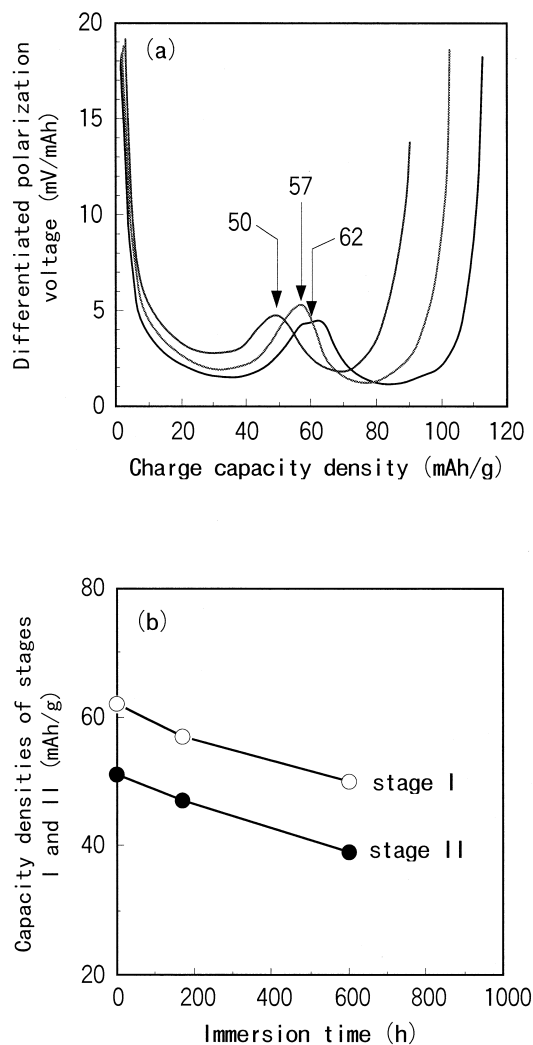


Fig. 7. Changes of (a) polarization voltage and (b) capacity densities obtained in the stages I and II of the spinel-type Li–Mn oxide cathodes with $R_{\text{Li}/\text{Mn}}$ of 0.55 after the immersion in LiPF_6 -containing EC+EMC solutions at 60°C .

in stage I during the immersion in electrolytic solutions. The capacity densities of stages I and II were similarly reduced with an increase of the immersion time. This result indicates that the capacity loss reaction affected on the whole charging processes of stages I and II to the same degree. Accordingly, the formation of unstable Mn oxide species [6] seemed to be a minor factor to give rise to the capacity loss of the Li–Mn oxide cathodes used in this work, but an increase of the polarization voltage was

considered to be a major factor. The increase of the polarization voltage is probably due to formation of surface films or accumulation of by-products on the charged cathodes through decomposition of the electrolytic solutions [9].

4. Conclusions

Capacity loss reactions related to dissolution reaction of Mn ions on spinel-type Li–Mn oxide cathodes were investigated by immersing the charged cathodes into electrolytic solutions at 60°C . The amount of dissolved Mn was effectively reduced by increasing the $R_{\text{Li}/\text{Mn}}$ -values of Li–Mn oxides not less than 0.55. The dissolution reaction of Mn ions was accelerated on the charged cathodes, involving the capacity loss and the contraction of Li–Mn oxide crystals. An increase of the polarization voltage of cathodes was considered to cause the capacity loss during the course of the immersion, as well as the dissolution of Mn ions. It is speculated that solvent decomposition reactions may take place on the charged cathodes increasing the polarization voltage.

Acknowledgements

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References

- [1] M.M. Thackeray, P.J. Johnson, L.A. De Picciotto, P.G. Bruce, J.B. Goodenough, *Mat. Res. Bull.* 19 (1984) 179.
- [2] A. Blyr, C. Sigala, G. Amatucci, J.M. Tarascon, Meeting Abstract of 191st Society Meeting, Montreal, 1997, p. 108.
- [3] G.G. Amatucci, A. Blyr, C. Sigala, P. Alfonse, J.M. Tarascon, *Solid State Ionics* 104 (1997) 13.
- [4] D.H. Jang, Oh, *J. Electrochem. Soc.* 143 (1996) 2204.
- [5] D.H. Jang, Oh, *J. Electrochem. Soc.* 144 (1997) 3342.
- [6] Y. Xia, M. Yoshio, *J. Power Sources* 66 (1997) 129.
- [7] Y. Gao, J.F. Dahn, *Solid State Ionics* 69 (1996) 33.
- [8] J.M. Tarascon, W.R. McKinnon, F. Coowar, T.N. Bowner, G.G. Amatucci, D. Guyomard, *J. Electrochem. Soc.* 141 (1994) 1421.
- [9] R.J. Gummow, A. de Kock, M.M. Thackeray, *Solid State Ionics* 69 (1994) 59.
- [10] L. Guohua, H. Ikuta, T. Uchida, M. Wakihara, *J. Electrochem. Soc.* 143 (1996) 178.