

The effects of heat-treatment temperature on the retention capacities of spinels prepared by the Pechini process

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Abstract

Stoichiometric LiMn_2O_4 was prepared by the Pechini method and heat-treated at temperatures between 600 and 800 °C for 8 h. Crystalline structures and the electrochemical properties of the prepared samples were investigated. The sample heat-treated at 600 °C shows a trace amount of Mn_2O_3 with predominant spinel, whereas those prepared at temperatures between 700 and 800 °C show exclusively spinel with similar lattice constants. The crystallinity index calculated from the (1 1 1) peak of XRD pattern increases with increasing heat-treatment temperature. All of the prepared samples show similar capacity fading rate. On the same cycle number, the specific capacity increases with increasing temperature of heat-treatment. It is found that samples with similar lattice constant exhibit similar specific discharging capacity on the same cycle number and similar fading rate at the high voltage plateau. The crystallinity index and the initial specific discharge capacity on the low-voltage plateau increase with increasing heat-treatment temperature.

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Keywords: LiMn_2O_4 spinel; Electrochemical properties; Lattice constant; Crystallinity index

1. Introduction

Spinel LiMn_2O_4 has been studied by many researchers [1–4] and becomes an attractive cathode material for rechargeable lithium-ion batteries for the advantages of easier preparation, less toxicity, lower cost, and higher safety than LiCoO_2 and LiNiO_2 [4–7]. The electrochemical properties of spinel LiMn_2O_4 are highly dependent on composition [8–10], starting materials [8,11,12], synthesis method [11,13], and thermal history [8,9,12–18] of the samples. The effects of heat-treatment conditions on the crystalline structure and oxygen stoichiometry of the spinel powder had been studied [14–18], and the influences of lattice constant and crystallinity on the electrochemical properties of spinel LiMn_2O_4 had also been investigated [16–18]. However, many works are still needed to construct a firm relationship among them.

Wet chemical methods [13,16,18–20] have been developed to synthesize small particle-sized, well-crystallized LiMn_2O_4 powders with high homogeneity in compositions and particle sizes at lower temperatures and/or shorter duration of heat-treatment than those of the conventional solid-state reaction methods. Smaller particle size leads to

shorter Li^+ ion diffusion length. Hence, the conductivity of Li^+ ions in the LiMn_2O_4 powders is enhanced by the powder having been prepared by wet chemical routes [19]. The Pechini process has been proved to be an effective wet-chemical method for the preparation of the LiMn_2O_4 -based cathode materials for lithium-ion batteries [20].

In the present study, stoichiometric LiMn_2O_4 cathode powders are prepared by Pechini method. The effects of heat-treatment temperature on the spinel lattice constant and crystallinity are studied. The relationship among the specific capacities of the low- and the high-voltage plateaus of the 4 V region, the lattice constant of spinel, and the crystallinity of the prepared LiMn_2O_4 powders are also investigated.

2. Experimental

Stock solutions of LiNO_3 (s grade, Wako Pure Chem. Ind. Ltd.) and $\text{Mn}(\text{NO}_3)_2$ (s grade, Wako Pure Chem. Ind. Ltd.) are prepared as the cationic sources, and their concentrations are determined by atomic absorption spectroscopy (Spectr AA 300 plus, Varian Techtron Pty. Ltd.). Citric acid (s grade, Wako Pure Chem. Ind. Ltd.) and ethylene glycol (s grade, Wako Pure Chem. Ind. Ltd.) are used as the monomers for the formation of the polymeric matrix. Proper amounts of stock solutions of metal nitrates are added to a mixture of citric acid and ethylene glycol (molar ratio = 1:4) such that

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the starting solution contained stoichiometric amounts of Li^+ and Mn^{2+} cations. Details of the synthetic procedure of Pechini process are described elsewhere [20]. The derived polymeric gel is calcined in air at $200\text{ }^\circ\text{C}$ for 6 h, followed by heat treating in air with heating rate of $5\text{ }^\circ\text{C}/\text{min}$ to various temperature ($600\text{--}800\text{ }^\circ\text{C}$) and holding at that temperature for 8 h. The powder then is oven-cooled to room temperature.

XRD patterns of the heat-treated powders are recorded at room temperature using Rigaku D/Max-III A X-ray diffractometer. Lattice constants are calculated by iterative least square refinements using silicon as an internal standard. The crystallinity index is determined by following the definition given by Ahn and Song [17], however, the strongest peak of (1 1 1) face is used in this study to determine the index instead of the much weaker (4 0 0) peak. Morphologies and particle sizes of the LiMn_2O_4 powders are observed with a scanning electron microscopy (S-800 FESEM, Hitachi Instruments, Inc.).

In the preparation of the composite cathode, spinel powder is mixed with acetylene black (100%, Strem Chem., Inc.) followed by dispersion in NMP (ISP Technologies, Inc.) solution with PVDF (Kynar 740, ATOFINA Chemicals, Inc.) dissolved in it. The slurry obtained is tape-cast on aluminum foil, followed by vacuum drying at $110\text{ }^\circ\text{C}$ for 8 h, punching into disc sample of diameter of 10 mm, and pressing. The coin-type cells for capacity retention studies are assembled in a argon-filled glove-box with Li metal (99.9%, Aldrich Chem. Co., Inc.) as anode, 1 M LiPF_6 in ethylene carbonate (EC)/diethylene carbonate (DEC) (1:1 volume ratio) (Tomiya Pure Chem. Ind. Ltd.) as electrolyte, Celgard 2400 membrane (Hoechst Celanese Corp.) as separator, and the LiMn_2O_4 -based composites as cathodes. The capacity retention tests are carried out galvanostatically between 3 and 4.5 V at a constant current of 0.1 mA at room temperature.

3. Results and discussion

The XRD patterns of the stoichiometric LiMn_2O_4 powders heat-treated at temperatures ranging between 600 and $800\text{ }^\circ\text{C}$ for 8 h are shown in Fig. 1. The spinel phase predominates in the $600\text{ }^\circ\text{C}$ sample with trace a amount of body-centered cubic Mn_2O_3 . Nevertheless, when the powders are heat-treated at temperatures between 700 and $800\text{ }^\circ\text{C}$ for 8 h, pure spinel is exhibited exclusively. These observations are different from the works done by Liu et al. with the same method [20]. They found the samples remained amorphous after the calcinations at $230\text{ }^\circ\text{C}$ and became spinel after the samples that had been heat-treated at temperatures between 250 and $800\text{ }^\circ\text{C}$ for a few hours. Variations of the calculated spinel lattice constant and crystallinity index (I_{max}/B) of the prepared crystalline samples with heat-treatment temperature are illustrated in Fig. 2. The lattice constant of the prepared samples increases

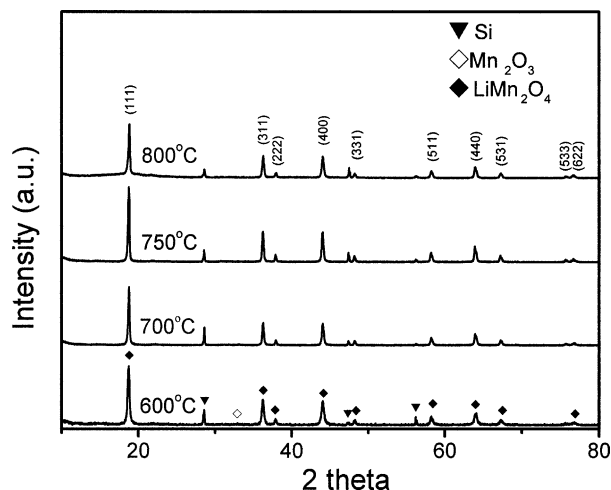


Fig. 1. The XRD patterns of the LiMn_2O_4 powders heat-treated at various temperatures for 8 h.

abruptly as the heat-treatment temperature increases from 600 to $700\text{ }^\circ\text{C}$, however, the samples prepared at temperatures between 700 and $800\text{ }^\circ\text{C}$ exhibit similar values that closely approximate the theoretical value of 8.247 \AA . Nevertheless, the crystallinity index increases linearly with increasing temperature of heat-treatment. From scanning electron micrographs of the prepared samples, shown in Fig. 3, it is found that particle size of the prepared spinel powder increases significantly with increasing heat-treatment temperature. The diameter of primary particle increases from about 30 nm in diameter in $600\text{ }^\circ\text{C}$ sample to $0.2\text{--}0.6\text{ }\mu\text{m}$ in $800\text{ }^\circ\text{C}$ sample. The growth in the particle size will lead to increasing crystallinity.

Fig. 4 shows the galvanostatic charge/discharge curves of the coin-type cells measured at a constant current of 0.1 mA. The two distinctive plateaus, characteristic of the well-defined spinel LiMn_2O_4 cathode, are observed for all samples except for the $600\text{ }^\circ\text{C}$ prepared spinel powder. Variation of the specific discharging capacity with cycle

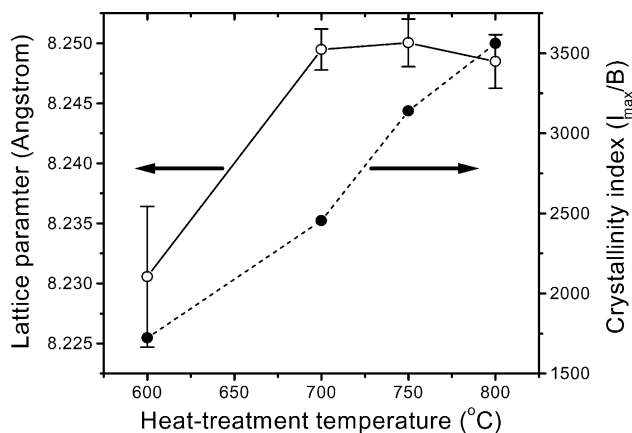


Fig. 2. Variations of the spinel lattice constant and the crystallinity index of the prepared powders with the heat-treatment temperature.

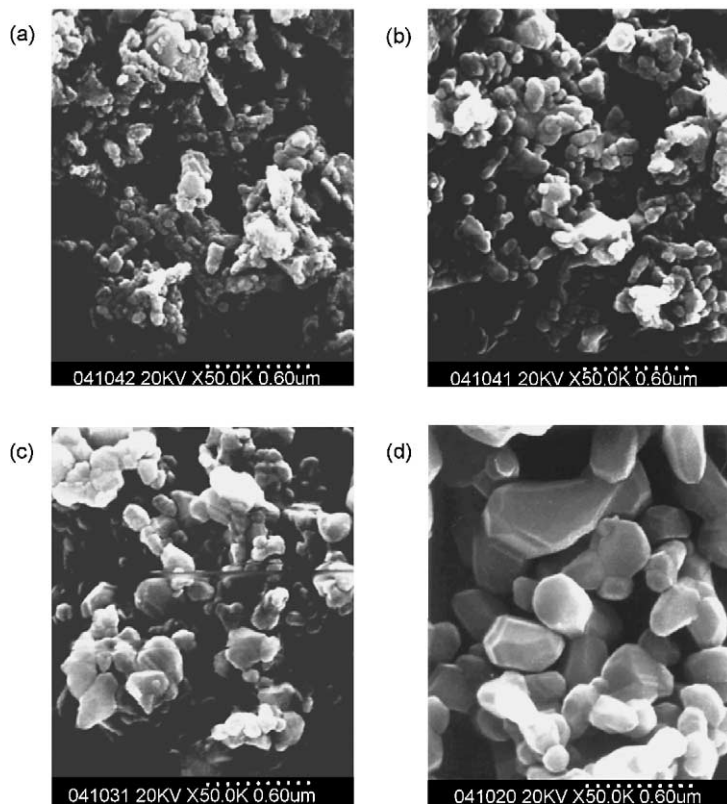


Fig. 3. Scanning electron micrographs of LiMn_2O_4 heat-treated at (a) 600 °C, (b) 700 °C, (c) 750 °C, and (d) 800 °C for 8 h.

number for the cells is shown in Fig. 5. The abnormally low values in the discharging capacities of the 1st cycle for 700 and 750 °C prepared samples may be induced by improper assembling of the coin cells or insufficient swelling of the cathode by electrolyte solution. Ignoring the abnormality, it is found that the specific discharging capacity of the prepared samples increases with increasing heat-treatment temperature on the same cycle number. All of the prepared

samples exhibit similar fading trend in the specific discharging capacity. The differential chronopotentiometric curves [9], shown typically in Fig. 6, were calculated for every 5th cycle from the results of retention studies for each prepared sample. The discharging curves can be divided into high- and low-voltage plateaus by a voltage at which the second derivative of the specific discharging capacity with respect to voltage, d^2Q/dV^2 , equates to zero. The specific

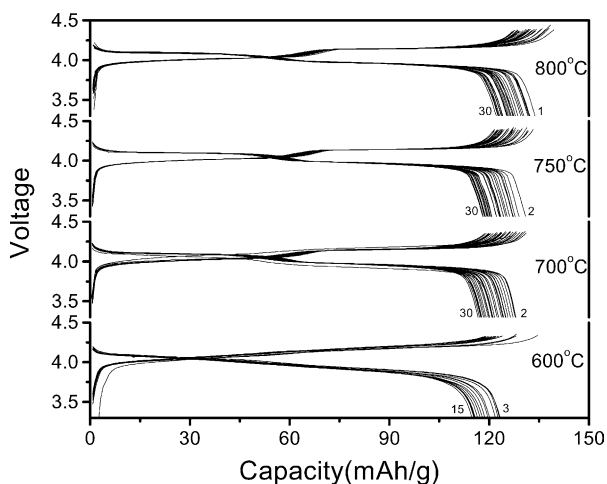


Fig. 4. The charge/discharge curves at constant current of 0.1 mA of the $\text{Li}|\text{1 M LiPF}_6$ in EC:DEC (1:1)| LiMn_2O_4 coin cells comprised with cathodes had been heated at various temperatures for 8 h.

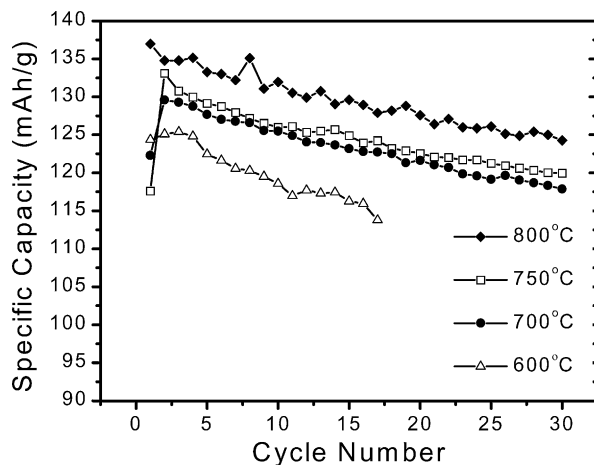


Fig. 5. Variation of the specific discharging capacity with the number of cycles for the $\text{Li}|\text{1 M LiPF}_6$ in EC:DEC (1:1)| LiMn_2O_4 coin cells comprised with LiMn_2O_4 powders heat-treated at various temperatures. Cycling was carried out galvanostatically at a constant current of 0.1 mA between 3.0 and 4.5 V.

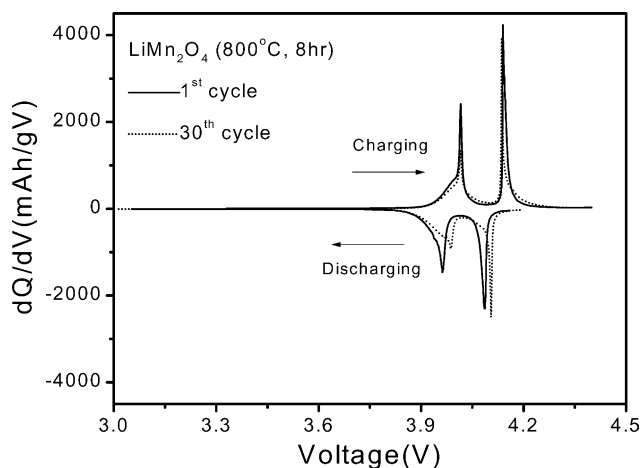


Fig. 6. The dQ/dV vs. V plots of the discharging curves of the 1st and 30th cycle of the coin cell comprised with LiMn_2O_4 heat-treated at 800°C for 8 h.

capacities of the low- and high-voltage plateaus determined for each prepared samples are shown in Figs. 7 and 8, respectively. All of the prepared samples exhibit similar capacity fading rates at the low-voltage plateau. The specific discharging capacity of the low-voltage plateau increases with increasing heat-treatment temperature of the sample on the same cycle number. Moreover, all except the 600°C sample show not only similar fading trend but also similar values in the specific discharging capacity at the high voltage plateau on the same cycle number.

It is believed that the relative amount of Mn^{3+} in the LiMn_2O_4 spinel plays a key role in the determining of electrochemical properties. The specific capacity of spinel increases with increasing $\text{Mn}^{3+}/\text{Mn}^{4+}$ ratio or decreasing average oxidation state of manganese [16,18]. However,

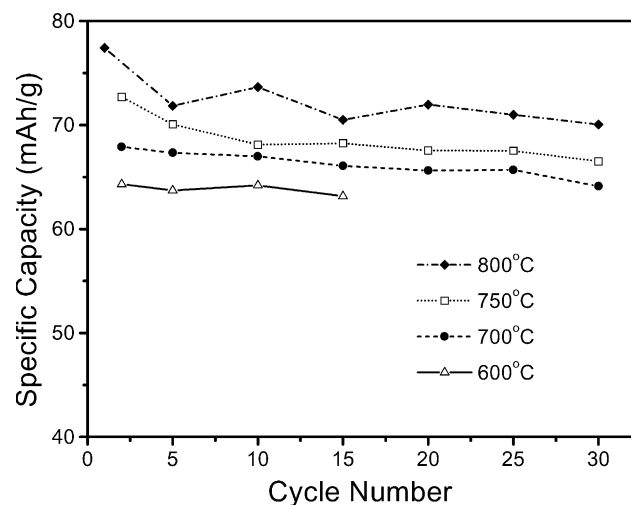


Fig. 7. Variation of the calculated specific discharging capacity of the low-voltage plateau at 4 V region with the number of cycles for the coin cells comprised with LiMn_2O_4 powders heat-treated at various temperatures.

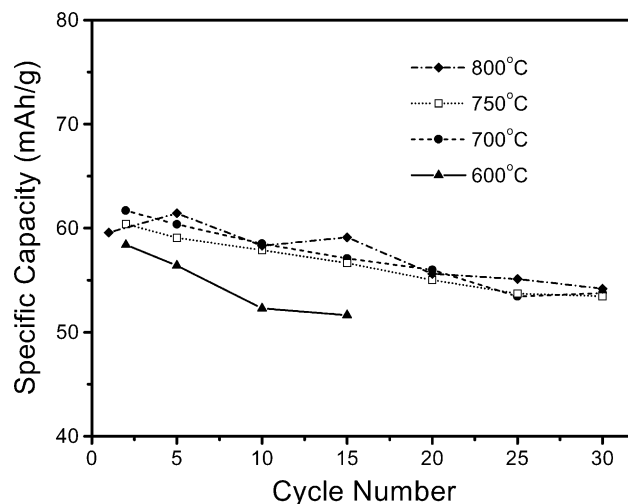


Fig. 8. Variation of the calculated specific discharging capacity of the high voltage plateau at 4 V region with the number of cycles for the coin cells comprised with LiMn_2O_4 powders heat-treated at various temperatures.

it is difficult to determine the relative amount of Mn^{3+} by chemical titration method. It has been discovered that there is a good relationship among the lattice constant, the relative amount of Mn^{3+} , and the specific capacity [16,18]. The lattice constant of spinel can be used to deduce the electrochemical properties of LiMn_2O_4 . On the other hand, Ahn and Song [17] introduced a parameter named the “crystalline index (I_{max}/B)” and found that the sample with the highest crystallinity and largest grain size has the largest first-discharging capacity and shows the best cycling performance among samples. From the results shown in Figs. 2, 7 and 8, the samples prepared at temperatures between 700 and 800°C exhibit close values in the spinel lattice constant and also in the specific discharging capacity at high voltage plateau on the same cycle number. However, the crystallinity index and the specific discharging capacity at low-voltage plateau increase with increasing heat-treatment temperature. A classic lattice-gas model with short-range interactions is applied to explain the phenomena. This model was found to be an appropriate approximation for exploring the effect of ordering of lithium-ion on the thermodynamic and kinetic properties of lithium intercalation and de-intercalation of a $\text{Li}_{1-\delta}\text{Mn}_2\text{O}_4$ electrode [21,22]. The 8a sites in the spinel form a diamond lattice, which can be considered as two interpenetrating fcc sublattices separated by $1/4$ $1/4$ $1/4$. For each Li atom, there are four nearest 8a neighbors in the other sublattice and six next nearest 8a neighbors within the same sublattice. During discharging, at the voltage of the first peak in the dQ/dV versus V plot, the intercalated Li^+ ions prefer to enter the next nearest neighbor sites regularly in the same sublattice at the high voltage plateau for negative interaction energy (J_{NNN}) which means attractive Li^+-Li^+ interaction [23]. The amount of available sites for Li ion is determined by the ratio of $\text{Mn}^{3+}/\text{Mn}^{4+}$ in the original cathode powder before de-intercalation that can be manifested by lattice constant of spinel. Consequently, samples exhibit similar

lattice constant for similar $\text{Mn}^{3+}/\text{Mn}^{4+}$ ratio and show similar specific discharging capacity and fading rate at the high voltage region. As the amount of the intercalated Li^+ increases further and the voltage approaches 4.0 V, this orderly intercalation is discouraged because there are not enough vacancies. Finally, Li^+ ions intercalate randomly into the nearest neighboring 8a sites in the other sublattice with repulsive interaction energy, J_{NN} , at the second peak (the lower voltage) in dQ/dV versus V plot. Since the nearest neighbor sites intercalated at the low-voltage plateau are in the other sublattice, the amount of the available sites in the other sublattice for lithium intercalation might be presumed to increase with increasing crystallinity of the spinel powder. Hence, the initial specific discharging capacity of the low-voltage plateau also increases with increasing crystallinity index. After cycling, the crystallinity of the cathode material might decrease with increasing cycle number, thus the capacity fading occurs.

4. Conclusions

LiMn_2O_4 spinel cathode materials were prepared by the Pechini process with heat-treatment at temperatures between 600 and 800 °C for 8 h. The lattice constant of the spinel increases as heat-treatment temperature increases from 600 to 700 °C and remains nearly constant for samples prepared at temperatures between 700 and 800 °C. However, the crystallinity index increases with increasing heat-treatment temperature. The specific discharging capacity on the low-voltage plateau increases with increasing heat-treatment temperature that might be caused by increasing crystallinity index. On the other hand, the similarity in the specific discharging capacity of the high voltage plateau might be induced by having nearly the same lattice constant in the samples prepared at temperatures between 700 and 800 °C.

Acknowledgements

The authors are grateful for the financial support from Tatung University and Tatung Company.

References

- [1] T. Ohzuku, M. Kitagawa, T. Hirai, *J. Electrochem. Soc.* 137 (1990) 769.
- [2] J.M. Tarascon, D. Guyomard, *J. Electrochem. Soc.* 138 (1991) 2864.
- [3] M.M. Thackeray, A. de Kock, M.H. Rossouw, D. Liles, *J. Electrochem. Soc.* 139 (1992) 363.
- [4] J.M. Tarascon, D. Guyomard, G.L. Baker, *J. Power Sources* 43–44 (1993) 689.
- [5] D. Guyomard, J.M. Tarascon, *Solid State Ionics* 69 (1994) 222.
- [6] J.R. Dahn, E.W. Fuller, M. Obrovac, U. von Sacken, *Solid State Ionics* 69 (1994) 265.
- [7] D.D. MacNeil, T.D. Hatchard, J.R. Dahn, *J. Electrochem. Soc.* 148 (2001) A663.
- [8] Y. Xia, H. Takeshige, H. Noguchi, M. Yoshio, *J. Power Sources* 56 (1995) 61.
- [9] Y. Gao, J.R. Dahn, *J. Electrochem. Soc.* 143 (1996) 100.
- [10] J.M. Tarascon, F. Coowar, G. Amatucci, F.K. Shokoohi, D.G. Guyomard, *J. Power Sources* 54 (1995) 103.
- [11] S.-H. Kang, J.B. Goodenough, *J. Electrochem. Soc.* 147 (2000) 3621.
- [12] V. Manev, B. Banov, A. Momchilov, A. Nassalevska, *J. Power Sources* 57 (1995) 99.
- [13] B.J. Hwang, R. Santhanam, D.G. Liu, *J. Power Sources* 101 (2001) 86.
- [14] A. Yamada, K. Miura, K. Hinokuma, M. Tanaka, *J. Electrochem. Soc.* 142 (1995) 2149.
- [15] M.M. Thackeray, M.F. Mansuetto, J.B. Bates, *J. Power Sources* 68 (1997) 153.
- [16] Y.K. Sun, K.H. Lee, S.I. Moon, I.H. Oh, *Solid State Ionics* 112 (1998) 237.
- [17] D.S. Ahn, M.Y. Song, *J. Electrochem. Soc.* 147 (2000) 874.
- [18] H.T. Chung, S.T. Myung, T.H. Cho, J.T. Son, *J. Power Sources* 97–98 (2001) 454.
- [19] L. Chen, X. Huang, E. Kelder, J. Schoonman, *Solid State Ionics* 76 (1995) 91.
- [20] W. Liu, G.C. Farrington, F. Chaput, B. Dunn, *J. Electrochem. Soc.* 143 (1996) 879.
- [21] S.-W. Kim, S.-I. Pyun, *Electrochim. Acta* 46 (2001) 987.
- [22] W.C. Wong, J. Newman, *J. Electrochem. Soc.* 149 (2002) A493.
- [23] Y. Gao, J.N. Reimer, J.R. Dahn, *Phys. Rev. B* 54 (1996) 3878.