

# Charge and discharge performances of lithiated metal oxide cathodes in organic electrolyte solutions with different compositions

Masayuki Morita<sup>\*</sup>, Otoo Yamada, Masashi Ishikawa

*Department of Applied Chemistry and Chemical Engineering, Yamaguchi University, 2557 Tokiwadai, Ube 755-8611, Japan*

## Abstract

The charge and discharge characteristics of  $\text{LiNiO}_2$  and  $\text{LiMn}_2\text{O}_4$  have been investigated in mixed carbonate-based electrolyte solutions. The discharge capacity depended on the electrolytic salt. The order of the capacity,  $\text{LiCF}_3\text{SO}_3 < \text{LiPF}_6 \leq \text{LiClO}_4$ , which is common to both electrodes, is partly consistent with that of the ionic conductivity of the solution. The solvent composition also affected the charge and discharge behavior. However, the order in the capacity did not strictly coincide with that of the ionic conductivity of the electrolyte. Moreover the details of the influence of the electrolyte composition was somewhat different between the oxide electrodes. The ac impedance at the electrode/electrolyte interface varied with the electrolyte composition. It showed that higher discharge capacities are obtained in electrolyte solutions which show lower interfacial resistances. © 1999 Elsevier Science S.A. All rights reserved.

*Keywords:* Lithium ion battery; Metal oxide cathodes; Organic electrolytes; Ac impedance

## 1. Introduction

Much attention has been focused on the improvement of the electrode performances of lithiated metal oxides such as  $\text{LiNiO}_2$  and  $\text{LiMn}_2\text{O}_4$ , the most promising replacements of the  $\text{LiCoO}_2$ -based cathodes in the present lithium-ion battery systems [1,2]. The discharge capacity and the cyclability of the oxide cathode depend on the composition and structure of the oxide. For instance, partial substitution of the host metal (Ni and Mn, respectively) by other divalent/trivalent metal cations is quite effective to improve the cyclability without significant loss of the discharge capacity [3–10].

On the other hand, it is also recognized that the sort of the electrolyte system affects the charge and discharge performances of the batteries which consist of these oxide cathodes [11–14]. Tarascon and Guyomard [12,13] have examined several combinations of organic solvents and lithium salts for a carbon/ $\text{LiMn}_2\text{O}_4$  cell. They obtained good cell performances when using a  $\text{LiPF}_6$  solution with mixed solvent of ethylene carbonate (EC)–dimethyl carbonate (DMC). However, the details of the effects of the electrolyte composition on the battery performances are

still unknown. We have also been interested in the role of the electrolyte system in the design of battery systems, and observed that the composition of the organic electrolyte solution has significant effects on the charge and discharge performances of the  $\text{LiNiO}_2$ -based [15,16] and  $\text{LiMn}_2\text{O}_4$ -based cathodes [17]. In this paper, common feature and differences of the cathodic behavior are discussed for  $\text{LiNiO}_2$  and  $\text{LiMn}_2\text{O}_4$  in organic electrolyte solutions with various compositions.

## 2. Experimental

The test electrode consisted of the powdered active material ( $\text{LiNiO}_2$ : Nihon Kagaku Sangyo,  $\text{LiMn}_2\text{O}_4$ : Tosoh) [15,17], acetylene black as a conducting support, and a PTFE binder, in a mass ratio of 20/10/3. Each component was well-mixed and then pressed onto a current collector of stainless steel screen (13 mm diameter). The resulting test electrodes were dried at 120°C for 5 h or longer under a vacuum prior to use.

The electrolyte solvents were binary mixed carbonate systems, i.e., high permittivity cyclic esters, EC and propylene carbonate (PC), mixed with low viscosity linear alkyl carbonate, DMC or diethyl carbonate (DEC), in a volumetric ratio of 50/50. These component solvents were used as received from Mitsubishi Chemical (Battery Grade, water

<sup>\*</sup> Corresponding author. Tel.: +81-836-35-9416; Fax: +81-836-35-9933; E-mail: morita@po.cc.yamaguchi-u.ac.jp

content: < 10 ppm). Well-dehydrated  $\text{LiClO}_4$ ,  $\text{LiPF}_6$  or  $\text{LiCF}_3\text{SO}_3$  was dissolved in the mixed solvent to form  $1 \text{ mol dm}^{-3}$  (1 M) solution.

A three electrode system with a glass beaker cell was employed for electrochemical measurements [16]. The reference and the counterelectrodes were a lithium tip ( $\text{Li}/\text{Li}^+$ ) and a large surface area lithium foil ( $3.0 \text{ cm} \times 2.5 \text{ cm}$ ), respectively. The volume of the electrolyte solution was  $50 \text{ cm}^3$ . The cell was cycled under constant current conditions, typically with a current density of  $1.0 \text{ mA cm}^{-2}$  and cut-off potential of  $4.2 \text{ V}$  (vs.  $\text{Li}/\text{Li}^+$ , on charge) to  $2.5 \text{ V}$  (on discharge) for the  $\text{LiNiO}_2$  test electrode, and with a current density of  $0.5 \text{ mA cm}^{-2}$ , cut-off potential of  $4.4 \text{ V}$  (on charge) to  $3.5 \text{ V}$  (on discharge) for  $\text{LiMn}_2\text{O}_4$ , at room temperature ( $18\text{--}25^\circ\text{C}$ ). A frequency response analyzer (Solartron 1250) coupled with an electrochemical interface was used for the ac impedance measurements. The frequency was scanned from  $65 \text{ kHz}$  to  $5 \text{ mHz}$  with an amplitude of  $\pm 5 \text{ mV}$ . The measurements were carried out under open circuit voltage (OCV) conditions before and after the constant current charge and discharge.

### 3. Results and discussion

Fig. 1 shows the charge and discharge curves of the  $\text{LiNiO}_2$  electrode in  $\text{LiClO}_4$  solutions using various solvents under constant current polarization ( $1.0 \text{ mA cm}^{-2}$ ). The discharge capacity depended on the electrolyte solvent in the order of  $\text{PC} + \text{DMC} < \text{EC} + \text{DEC} < \text{EC} + \text{DMC}$ . The capacity depended also on the electrolytic salt when we used  $\text{EC} + \text{DMC}$  as the common solvent. The order of the discharge capacity was  $\text{LiCF}_3\text{SO}_3 < \text{LiPF}_6 \leq \text{LiClO}_4$  [15]. Figs. 2 and 3 show the dependence of the charge and discharge profile on the electrolyte composition observed for the  $\text{LiMn}_2\text{O}_4$  cathode. Similar trend was observed as those obtained for  $\text{LiNiO}_2$ . However, the detail of the composition dependency on the electrode performance is somewhat different from the case of  $\text{LiNiO}_2$ . That is, the

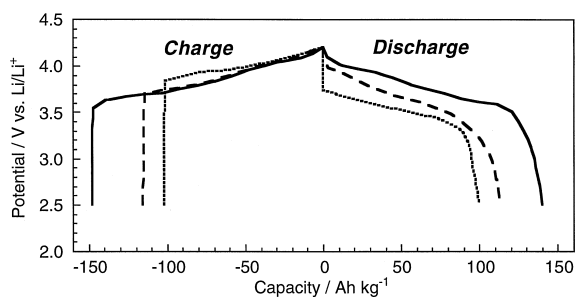


Fig. 1. Charge and discharge profiles for  $\text{LiNiO}_2$  electrode in mixed carbonate solutions containing  $1 \text{ mol dm}^{-3}$   $\text{LiClO}_4$ . Solid line:  $\text{EC} + \text{DMC}$ , broken line:  $\text{EC} + \text{DEC}$ , dotted line:  $\text{PC} + \text{DMC}$ , Current density:  $1.0 \text{ mA cm}^{-2}$ .

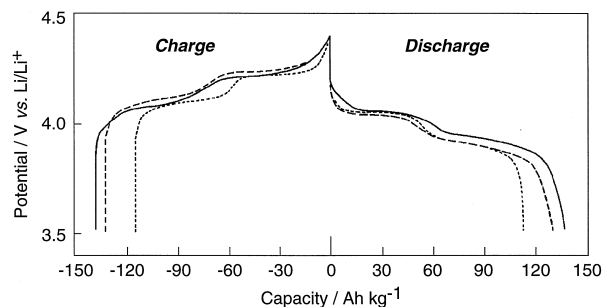


Fig. 2. Charge and discharge profiles for  $\text{LiMn}_2\text{O}_4$  electrode in mixed carbonate solutions containing  $1 \text{ mol dm}^{-3}$   $\text{LiClO}_4$ . Solid line:  $\text{EC} + \text{DMC}$ , broken line:  $\text{EC} + \text{DEC}$ , dotted line:  $\text{PC} + \text{DMC}$ , Current density:  $0.5 \text{ mA cm}^{-2}$ .

polarization during the charge and discharge processes is not so different among the solvents, while it significantly varies with the electrolytic salt for the  $\text{LiMn}_2\text{O}_4$  cathode. The voltammetric responses of the oxide electrodes corresponded to these results on the discharge capacity under constant current polarization [15,17].

Generally speaking, the above tendency of the charge and discharge capacity depending on the electrolyte composition is partly consistent with the order of the ionic conductance of the solution. Table 1 summarizes a comparison of the ionic conductivity of the electrolytic solution at  $25^\circ\text{C}$  where the salt concentration is  $1 \text{ mol dm}^{-3}$ . The conductivity varied with the order of  $\text{EC} + \text{DEC} \leq \text{PC} + \text{DMC} < \text{EC} + \text{DMC}$  for every electrolytic solute. With respect to the salt, the order of the conductivity was  $\text{LiCF}_3\text{SO}_3 < \text{LiClO}_4 < \text{LiPF}_6$  without any exception. The ionic conductance of the electrolyte apparently has an effect on the utilization of such bulk electrode as PTFE-bonded oxide powder because the rate capability would be influenced by the mass transfer in the pore structure of the electrode. That is, an electrolyte with higher ionic conductance tends to give higher rate capability (higher discharge capacity even at a high discharge rate). However, the above order of the discharge capacity does not strictly coincide with that of the ionic conductivity of the electrolyte. Moreover the details of the influence of the elec-

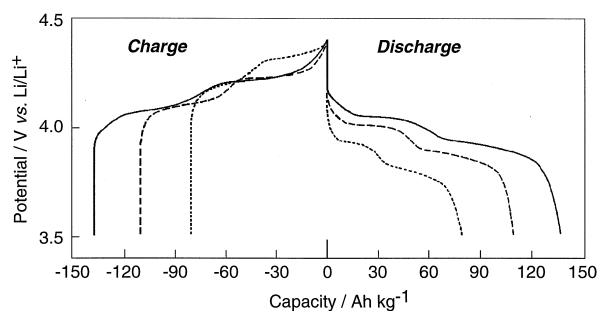


Fig. 3. Charge and discharge profiles for  $\text{LiMn}_2\text{O}_4$  electrode in  $\text{EC} + \text{DMC}$  solutions containing  $1 \text{ mol dm}^{-3}$  lithium salts. Solid line:  $\text{LiClO}_4$ , broken line:  $\text{LiPF}_6$ , dotted line:  $\text{LiCF}_3\text{SO}_3$ , Current density:  $0.5 \text{ mA cm}^{-2}$ .

Table 1

Electrolytic conductivity of the carbonate-based solutions containing 1 mol dm<sup>-3</sup> lithium salt at 25°C

Lithium salt (1 mol dm <sup>-3</sup> )	Conductivity (10 <sup>-3</sup> S cm <sup>-1</sup> ) Solvent (50+50 by volume)		
	EC+DMC	ED+DEC	PC+DMC
LiPF <sub>6</sub>	11.2	7.8	10.0
LiClO <sub>4</sub>	10.1	6.4	6.8
LiCF <sub>3</sub> SO <sub>3</sub>	3.1	2.1	2.2

trolyte composition is somewhat different between the oxide electrodes. For the LiNiO<sub>2</sub> cathode, the effect of the solvent was more significant than the salt, while the cycling performance of LiMn<sub>2</sub>O<sub>4</sub> is much more affected by the electrolytic salt. These suggest that the factors determining the charge and discharge performance may be different between these cathodes.

Tarascon and Guyomard previously reported similar solvent effects on the voltammetric response of LiMn<sub>2</sub>O<sub>4</sub> and discussed them from the viewpoint of the electrochemical stability of the solvents [12,13]. They indicated that the stability of the electrolytic solution depends not only on the electrolytic salt but also on the electrode material. However, it is difficult to determine quantitatively how stable (or unstable) the electrolyte in question is, because the anodic decomposition of the electrolyte on the oxide usually proceeds under a competition with the battery reaction of the oxide itself. An onset potential where the decomposition current starts to flow has generally been used as a measure of the electrolyte stability. In this respect, EC + DMC dissolving LiCF<sub>3</sub>SO<sub>3</sub> is reported being unstable on LiMn<sub>2</sub>O<sub>4</sub> under anodic polarization [12]. This may be one of the causes that the discharge capacity of the spinel is the lowest in LiCF<sub>3</sub>SO<sub>3</sub>/(EC + DMC).

The ac impedance technique is useful to analyze such an electrode process that includes competitive reactions. Fig. 4 shows a Cole–Cole plot (Nyquist plot: Imaginary component,  $-Z''/\Omega$ , vs. Real component,  $Z'/\Omega$ ) of the ac

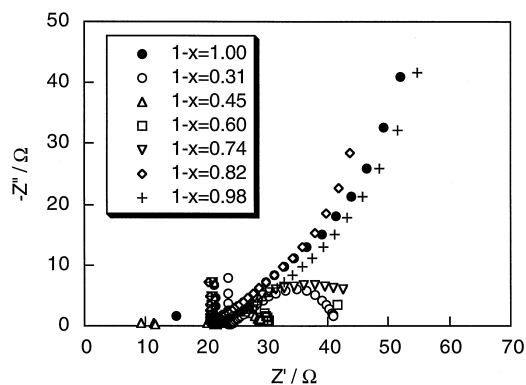


Fig. 4. Cole–Cole plots for ac impedance of Li<sub>1-x</sub>NiO<sub>2</sub> before ( $1-x=1.00$ ) and after the charge ( $1-x=0.31$ ) and discharge in 1 mol dm<sup>-3</sup> LiClO<sub>4</sub>/(EC+DMC).

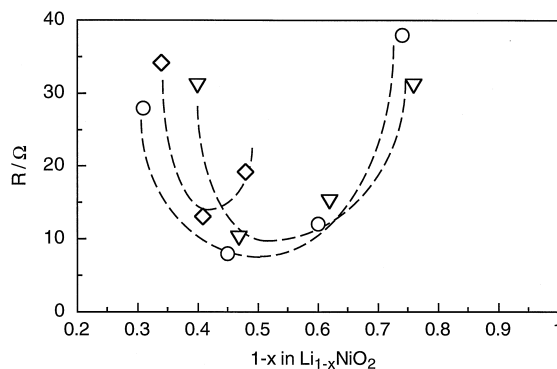


Fig. 5. Interface resistance of the Li<sub>1-x</sub>NiO<sub>2</sub> electrode in 1 mol dm<sup>-3</sup> LiClO<sub>4</sub> solution. Circle: LiClO<sub>4</sub>/(EC+DMC), triangle: LiClO<sub>4</sub>/(ED+DEC), square: LiClO<sub>4</sub>/(PC+DMC).

impedance obtained for Li<sub>1-x</sub>NiO<sub>2</sub> ( $0.3 < 1-x \leq 1.0$ ) in LiClO<sub>4</sub>/(EC + DMC) [16]. The impedance was measured under an OCV condition after the constant current polarization with given quantity of electricity (charge and discharge) in its first cycle. The depth of charge or discharge is presented as  $1-x$  in Li<sub>1-x</sub>NiO<sub>2</sub>, which is formally determined by the quantity of electricity passed. In every electrolyte system, the plot for the LiNiO<sub>2</sub> electrode before charging ( $x=0$  in Li<sub>1-x</sub>NiO<sub>2</sub>) showed almost linear relation over a wide frequency range, which implies that the electrode reaction at  $x=0$  ( $1-x=1$ ) is simply controlled by a diffusion process. When the electrode was anodically charged to  $1-x=0.4$  or less, the plots formed arcs or flat semicircles. The size of the arc or semicircle once decreased with the discharging, and then increased with the increase in the depth of discharge. Finally, for the electrodes with  $1-x \geq 0.8$ , the plots came back to the initial linear relations. Similar variations in the Cole–Cole plot with the depth of charge and discharge also reported for LiNiO<sub>2</sub> and related oxides [18–20].

We can assume that the ac impedance obtained for the oxide with  $0.4 \leq 1-x \leq 0.8$  is equivalent to a series combination of two parallel R–C circuits [16]. In that case, the diameter of the arc in the Cole–Cole plot is regarded as an interfacial resistance of the oxide/organic electrolyte system. Fig. 5 shows the variations in the interfacial resistance,  $R$ , with the electrode composition,  $1-x$  in Li<sub>1-x</sub>NiO<sub>2</sub>, in different solvent compositions. The resistance had a minimum around  $1-x=0.5$  in every electrolyte system. The same feature was already reported by Yamada et al. [18] and Choi et al. [19]. They had related the variation in the resistance with the  $1-x$  value to the changes in the interlayer distance of the crystal lattice [18] and in the concentrations of lithium and electron near the surface region of the oxide [19]. We observed that the resistance also depended on the electrolyte composition, which means the interface resistance including the contribution of the effects of the electrolyte solution. Electrolyte solutions with lower interfacial resistances tend to give higher discharge capacities for the LiNiO<sub>2</sub> cathode.

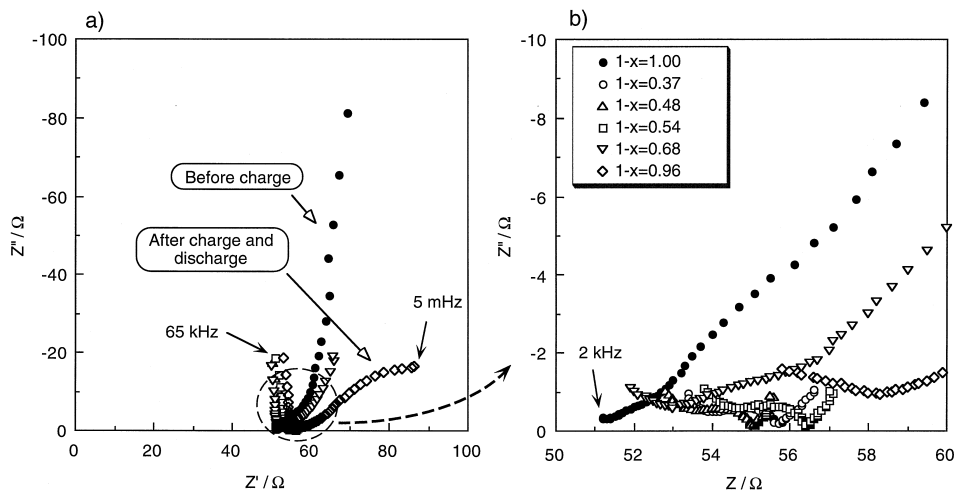


Fig. 6. Cole–Cole plots for ac impedance of  $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$  before ( $1-x=1.00$ ) and after the charge ( $1-x=0.37$ ) and discharge in  $1 \text{ mol dm}^{-3}$   $\text{LiClO}_4/(\text{EC} + \text{DMC})$ .

Figs. 6 and 7 are Cole–Cole plots obtained for  $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$  in EC + DMC that dissolved  $\text{LiClO}_4$  and  $\text{LiPF}_6$  salts, respectively. In the  $\text{LiClO}_4$  solution, the variation in the diagram with the depth of discharge gave a similar feature to that obtained for the  $\text{LiNiO}_2$  system (Fig. 4) though there are some differences in the low frequency region between the two electrode systems. Small semicircles or arcs were observed for the electrodes with  $0.37 \leq 1-x \leq 0.68$  at medium frequency regions although they are accompanied by large diffusion impedance components at lower frequency regions. On the other hand, in the  $\text{LiPF}_6$  electrolyte, the impedance spectra had no semicircle on the complex plane although the total impedance at the lowest frequency region was almost the same as that in  $\text{LiClO}_4$ . This result suggests that the electrode process in the  $\text{LiPF}_6$  solution includes much more complicated parts. In fact,

after the impedance experiment, the  $\text{LiPF}_6$  solution was colored to pale pink and a small amount of deposit was observed on the lithium counterelectrode. The dissolution of manganese species from the oxide probably leads to these results, and would be a cause of such a complex profile of the impedance plot as shown in Fig. 7.

In the  $\text{LiCF}_3\text{SO}_3$  solution, the lower resistance to the anodic oxidation of the salt [12], as well as low ionic conductivity, will be the possible reason of the lower capacities. Unfortunately we could not analyze the impedance responses of the  $\text{LiMn}_2\text{O}_4$  system in these electrolyte solutions. For the present, we suppose that the differences in the effects of the electrolyte composition between  $\text{LiNiO}_2$  and  $\text{LiMn}_2\text{O}_4$  are attributable to the differences in the catalytic activity of the oxides toward the anodic decomposition of the electrolyte [12,16,21] as

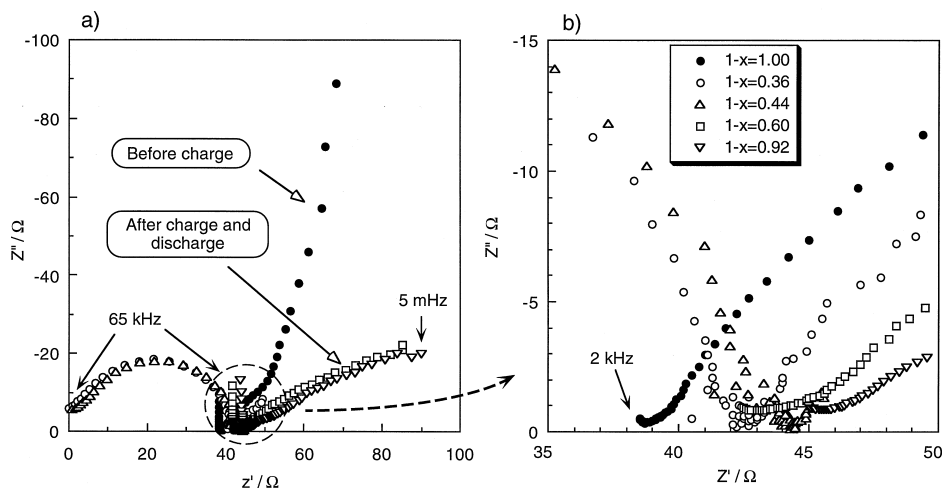


Fig. 7. Cole–Cole plots for ac impedance of  $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$  before ( $1-x=1.00$ ) and after the charge ( $1-x=0.36$ ) and discharge in  $1 \text{ mol dm}^{-3}$   $\text{LiPF}_6/(\text{EC} + \text{DMC})$ .

well as differences in the diffusivity of  $\text{Li}^+$  in the oxides [2,12,22]. Further discussion will be made with a help of quantitative analysis in the near future.

### Acknowledgements

This work was supported by Grant-in-Aid for Scientific Research (Nos. 08650980, 09237250, 09650907) from the Ministry of Education, Science, Sports and Culture.

### References

- [1] T. Ohzuku, in: G. Pistoia (Ed.), *Lithium Batteries—New Materials, Developments and Perspectives*, Chap. 6, Elsevier, Amsterdam, 1994, p. 239.
- [2] M. Wakihara, G. Li, H. Ikuta, in: M. Wakihara, O. Yamamoto (Eds.), *Lithium Ion Batteries, Fundamentals and Performance*, Chap. 2, Kodansha, Wiley-VCH, Tokyo, 1998, p. 26.
- [3] H. Arai, S. Okada, H. Ohtsuka, M. Ichimura, J. Yamaki, *Solid State Ionics* 80 (1995) 261.
- [4] Y. Fujita, K. Amine, J. Murata, H. Yasuda, *J. Power Sources* 68 (1997) 126.
- [5] T. Ohzuku, T. Yanagawa, M. Kouguchi, A. Ueda, *J. Power Sources* 68 (1997) 131.
- [6] M. Okada, K. Takahashi, T. Mouri, *J. Power Sources* 68 (1997) 545.
- [7] K. Kubo, M. Fujiwara, S. Yamada, S. Arai, M. Kanda, *J. Power Sources* 68 (1997) 553.
- [8] Y. Nishida, K. Nakane, T. Satoh, *J. Power Sources* 68 (1997) 561.
- [9] J.M. Tarascon, E. Wang, F.K. Shokoohi, W.R. McKinnon, S. Colson, *J. Electrochem. Soc.* 138 (1991) 2859.
- [10] G. Li, H. Ikuta, T. Uchida, M. Wakihara, *J. Electrochem. Soc.* 143 (1996) 178.
- [11] L.A. Dominey, in: G. Pistoia (Ed.), *Lithium Batteries—New Materials, Developments and Perspectives*, Chap. 4, Elsevier, Amsterdam, 1994, p. 137.
- [12] M. Tarascon, D. Guyomard, *Solid State Ionics* 69 (1994) 293.
- [13] D. Guyomard, J.M. Tarascon, *J. Power Sources* 54 (1995) 92.
- [14] Z.X. Shu, I.J. Davidson, R.S. McMillan, J.J. Murray, *J. Power Sources* 68 (1997) 618.
- [15] M. Morita, O. Yamada, M. Ishikawa, Y. Matsuda, *J. Appl. Electrochem.* 28 (1998) 209.
- [16] O. Yamada, M. Ishikawa, M. Morita, *Electrochim. Acta* 44 (1999) 1607.
- [17] M. Morita, O. Yamada, K. Adachi, M. Ishikawa, *J. Electrochem. Soc. Jpn., Denki Kagaku* 66 (1998) 1304.
- [18] S. Yamada, M. Fujiwara, M. Kanda, *J. Power Sources* 54 (1995) 209.
- [19] Y.-M. Choi, S.-I. Pyun, J.-S. Bae, S.-I. Moon, *J. Power Sources* 56 (1995) 25.
- [20] D. Aurbach, M.D. Levi, E. Levi, B. Markovsky, G. Salitra, H. Teller, in: C.F. Holmes, A.R. Landgrebe (Eds.), *Proc. of the Symposium on Batteries for Portable Applications and Electric Vehicles*, Vol. 97-18, Electrochemical Society, Pennington, 1997, p. 941.
- [21] K. Kanamura, S. Toriyama, S. Shiraishi, Z. Takehara, *J. Electrochem. Soc.* 143 (1996) 2548.
- [22] P.G. Bruce, A. Lisokowa-Oleksiak, M.Y. Saidi, C.A. Vincent, *Solid State Ionics* 57 (1992) 353.