Cycle life improvement of $LiMn_2O_4$ cathode in rechargeable lithium batteries

Zhaolin Liu [a,*], Aishui Yu [a], J.Y. Lee [b]

[a] *Institute of Materials Research and Engineering, National University of Singapore, 10 Kent Ridge Crescent, Singapore 119260, Singapore*
[b] *Department of Chemical Engineering, National University of Singapore, 10 Kent Ridge Crescent, Singapore 119260, Singapore*

Abstract

Spinel $LiMn_2O_4$ and $LiCo_{0.1}Mn_{1.9}O_4$ were synthesized by solid state reactions and were used as the positive electrode in liquid cells with Li as the negative electrode. Through extensive ball milling of the spinel with carbon black during the preparation of the cathodic mix, significant decrease in contact resistance between the oxide phase and carbon particles was achieved. The spinel $LiCo_{0.1}Mn_{1.9}O_4$ cathode so prepared showed good cyclability and rate capability. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Rechargeable lithium battery; $LiMn_2O_4$ cathode; Solid state reaction

1. Introduction

Spinel $LiMn_2O_4$ has been investigated extensively as a cathode material for rechargeable lithium batteries because of its low cost, environmental benignity and its relative ease of preparation from solid state reactions [1–3]. It has electrochemical properties that satisfy the basic requisites of a 4 V cathode material. However, $LiMn_2O_4$ has a lower specific capacity (compared to $LiCoO_2$) and most undesirably, suffers from a progressive capacity loss upon cycling. The origin for this capacity loss has not been clearly identified, but several possibilities exist: (1) reactions between the electrolyte and the electrode in the charged state, (2) a structural transformation due to Jahn–Teller distortions of the spinel in the discharged state, (3) Mn dissolution through a disproportionate reaction [4].

Much work has been directed to the stabilization of the spinel structure to obtain lithiated manganese oxide cathodes with improved cycle life and application performance [5,6]. Considerable success has been obtained by the partial substitution of Mn(III) with M(III) admetals, as proposed by Li et al. [7]. The capacity fade can be slowed down but not completely eliminated by such approach.

Since spinel $LiMn_2O_4$ has low electronic conductivity, it has to be mixed with a conducting additive such as carbon powder to make a working cathode. When the carbon content in the cathode is low, Mn dissolution is inhibited, but the capacity loss is severe [8]. Nishizawa et al. [9] reported recently that composites of manganese oxide particles and polypyrrole (PPy) can be prepared by adding pyrrole into an acidic aqueous suspension of the oxide. The resulting composites can have a higher specific capacity than oxides mixed with carbon power. Our results here will show that an excess of carbon can be advantageous to cyclability, although the energy and power densities of the resulting batteries are necessarily lower.

In this paper, we report the preparation and electrochemical behaviour of spinel $LiMn_2O_4$ and $LiCo_{0.1}Mn_{1.9}O_4$. Electrochemical impedance spectroscopy was used to determine the dominant factor for the capacity loss on repeated cycling. It was found that the contact areas between oxide and carbon particles could be increased through prolonged ball milling. The contact resistance and electrode reaction resistance were decreased by such mechanical means, resulting in cathodes of improved cyclability and rate capability.

2. Experimental

Spinel $LiMn_2O_4$ and quaternary spinel $LiCo_{0.1}Mn_{1.9}O_4$ were prepared by heating stoichiometric amounts of Li_2CO_3 and $MnCO_3$ or Li_2CO_3, $MnCO_3$ and $CoCO_3$ in

* Corresponding author. Fax: + 65-8720785; e-mail: zl-liu@imre.org.sg.

air for 24 h at 450°C, followed by another 24 h at 750°C, before they were furnace-cooled. The crystal structure of the product was determined by X-ray diffraction (XRD) using a Siemens D-5000 X-ray diffractometer, CuKα radiation and a graphite monochromator.

The spinel was mixed with 10% of carbon black (except where otherwise specified) and 5% of polytetrafluoroethylene (PTFE), and pressed onto 13 mm diameter Al disks. In addition, spinel $LiCo_{0.1}Mn_{1.9}O_4$ and 10% of carbon black was milled in an automatic mortar with stainless steel balls, using alcohol as the dispersing liquid to form a slurry. The powder resulting from drying the slurry at 100°C was mixed with 5% of PTFE and similarly pressed onto Al disks of 13 mm diameter.

The electrolyte was 1 M $LiPF_6$ in a 1:1 mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC). Lithium metal foils were used as the counter and the reference electrodes for the electrochemical measurements. Cyclic voltammetry and battery cycling were carried out on an EG&G model 273 potentiostat/galvanostat using the control software from the vender. The electrochemical impedance of the cells was measured over the frequency range of 0.01 Hz to 100 kHz by connecting the EG&G 273 to an EG&G model 5210 lock-in amplifier. Impedance readings were taken at the open-circuit condition after the cell was charged to 4.2 V. All measurements were carried out at 25°C.
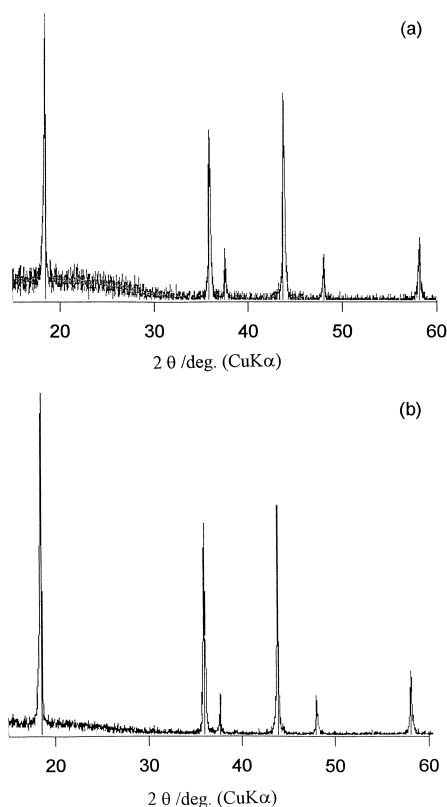

Fig. 1. X-ray powder diffraction pattern for spinel (a) $LiMn_2O_4$, (b) $LiCo_{0.1}Mn_{1.9}O_4$.

3. Results and discussion

3.1. XRD patterns of $LiMn_2O_4$ and $LiCo_{0.1}Mn_{1.9}O_4$

The XRD patterns of $LiMn_2O_4$ and $LiCo_{0.1}Mn_{1.9}O_4$ synthesized by the solid state reactions are shown in Fig. 1. All the diffraction peaks are characteristic of the spinel structure of $LiMn_2O_4$ without discernable impurities. The cubic lattice parameter of the spinel as calculated by the Rietveld program was 8.215 Å for $LiCo_{0.1}Mn_{1.9}O_4$ and 8.245 Å for $LiMn_2O_4$.

3.2. Charge and discharge profiles

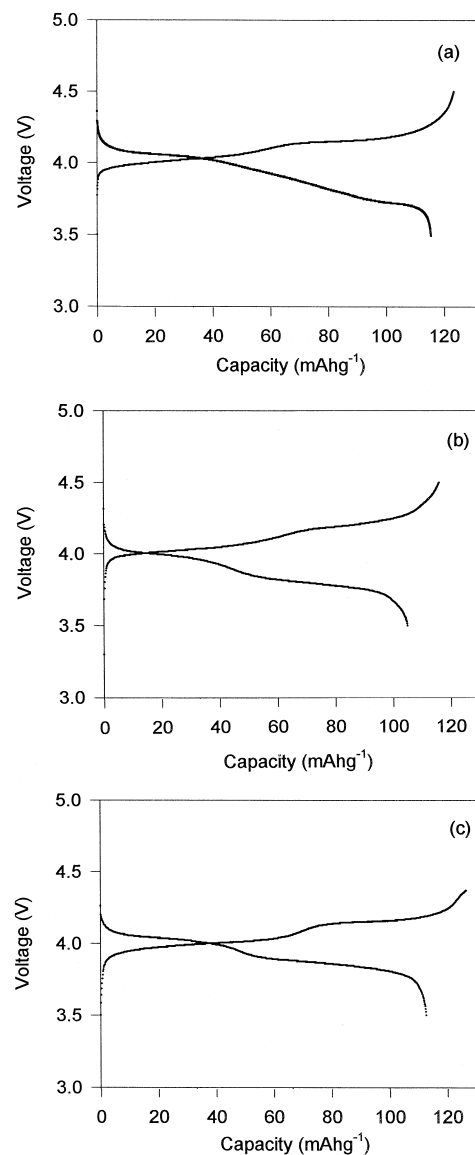Fig. 2 shows the initial charge/discharge curves of cells tested at the current density of 0.2 mA cm^{-2} (20

Fig. 2. The first charge and discharge curves of $Li/LiMn_2O_4$ and $Li/LiCo_{0.1}Mn_{1.9}O_4$ cells between 3.5 V and 4.5 V at a current density of 0.2 mA cm^{-2} (20 mA/g): (a) $LiMn_2O_4$, (b) $LiCo_{0.1}Mn_{1.9}O_4$, (c) $LiCo_{0.1}Mn_{1.9}O_4$ mixed and ground with 10% carbon black during the cathode formulation stage.

mA/g), with cut-off voltage limits of 4.5 V and 3.5 V. The discharge capacity was found to be almost equal to the charge capacity, indicating a coulombic efficiency close to 100%. The initial specific capacities of $LiMn_2O_4$ and $LiCo_{0.1}Mn_{1.9}O_4$ were determined to be 119 mAh g^{-1} and 107 mAh g^{-1}, respectively. As expected, cobalt doping reduces the initial capacity because of the decrease of Mn in the $+3$ state due to the presence of Co^{3+} (the valence of manganese in $LiCo_{0.1}Mn_{1.9}O_4$ is 3.53). The lower initial capacity of the quaternary oxide could be compensated in principle by any effort that reduces the electrode polarization. This was done in this work by improving the electrical contact between the oxide and carbon particles through extensive impact grinding. The result is shown in Fig. 2c, where the initial discharge capacity of $LiCo_{0.1}Mn_{1.9}O_4$ is increased to 118 mAh g^{-1}.

3.3. Cyclic voltammetric measurements

Figs. 3 and 4 show the cyclic voltammograms of $Li/LiMn_2O_4$ and $Li/LiCo_{0.1}Mn_{1.9}O_4$ cells in the potential range of 3.4 to 4.7 V vs. Li. The three electrode technique allows one to study only the contribution of the spinel oxide/electrolyte interface and to avoid any phenomenon occurring on the Li electrode. The two redox pairs in Fig. 3 are typical of the two step reversible transformation of the spinel. Their voltammetric features agree well with the observation of Guyomard and Tarascon [2]. It is only when the high voltage limit was increased above 4.7 V vs. Li, that the oxidation current would increase without any corresponding cathodic feature on the reverse scan. The electrolyte is therefore stable up to 4.7 V vs. Li against oxidation in the presence of $LiMn_2O_4$ and $LiCo_{0.1}Mn_{1.9}O_4$. In Fig. 4, two pairs of clearly separated redox peaks were also observed, indicating that the reversibility of Li^+ deintercalation/intercala-
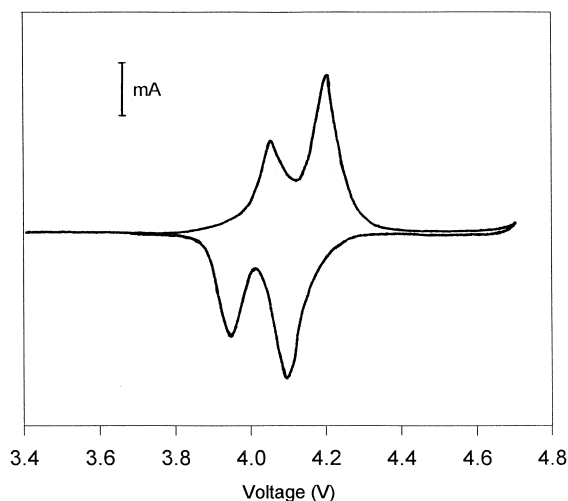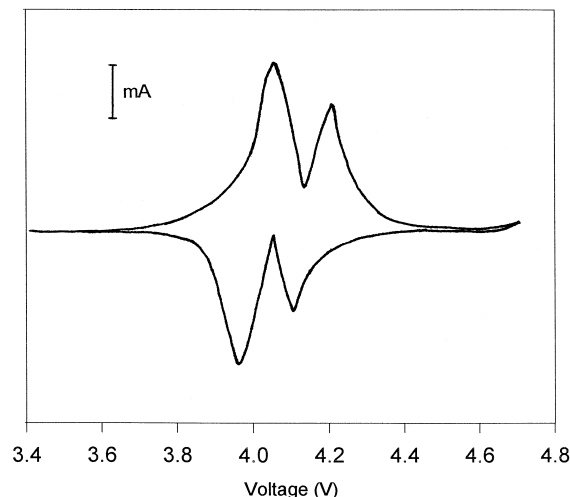

Fig. 4. Cyclic voltammogram for a $LiCo_{0.1}Mn_{1.9}O_4$ cell at a scan rate of 0.1 mV s^{-1} between 3.4 and 4.7 V.

tion reaction in the spinel host between 3.4 and 4.7 V (vs. Li) was not compromised by cobalt addition. However, the peak at 4.05 V is higher than that at 4.2 V on the anodic scan, and the peak at 4.1 V is lower than that at 3.95 V on the cathodic scan. Interestingly doping also lengthens the first voltage plateau in the discharge curve of the spinel. These observations which can be used to differentiate between doped and undoped $LiMn_2O_4$ are probably due to the substitution of some Mn–O linkages in the spinel by Co–O. Although there is lack of binding energy data for the M–O bonds, some first estimates can be obtained by comparing the binding energies of MO_2. From thermodynamic calculations that are based on the Born–Haber cyclic process, the binding energies of MnO_2 and CoO_2 were calculated to be 946 and 1067 kJ mol^{-1}, respectively [7]. The octahedral sites in the spinel should be more stable in the presence of the stronger Co–O bonds.

3.4. Cycling behaviour

Fig. 5 shows the cycling behaviour of $Li/LiMn_2O_4$ (a), $Li/LiCo_{0.1}Mn_{1.9}O_4$ (b) and $Li/LiCo_{0.1}Mn_{1.9}O_4$ after prolonged ball milling with carbon black (c). The cells were cycled between 3.5 and 4.5 at the current density of 0.2 mA cm^{-2} (20 mA/g). The initial capacity of an electrode based on $LiMn_2O_4$ was 119 mAh g^{-1} which decreased rapidly to 85 mAh g^{-1} after 50 cycles. In contrast, the capacity of $LiCo_{0.1}Mn_{1.9}O_4$ powder showed better capacity retention and the capacity decrease was from an initial value of 107 to 92 mAh g^{-1} after 50 cycles. The fact that the cycle performance was improved by substitution of Mn by adatoms could be rationalized in terms of the enhanced stability of the octahedral sites in the spinel skeleton [7]. Additionally, Co–O bond is stronger than the Mn–O bond, and this helps to increase the robustness of the spinel host structure. In Fig. 5c, the cathode prepared from an exten-
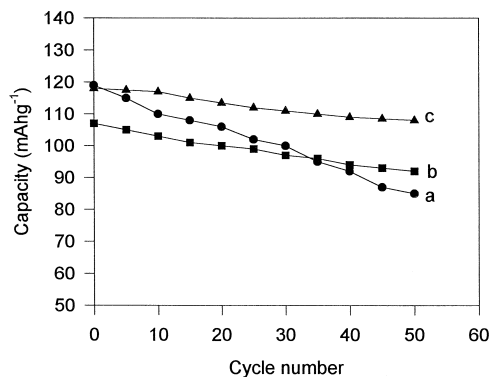

Fig. 3. Cyclic voltammogram for a $Li/LiMn_2O_4$ cell at a scan rate of 0.1 mV s^{-1} between 3.4 and 4.7 V.

Fig. 5. Variation in the capacity of $Li/LiMn_2O_4$ and $Li/LiCo_{0.1}Mn_{1.9}O_4$ cells as a function of cycle number using a charge/discharge current of 0.2 mA cm^{-2} (20 mA/g) between 3.5 and 4.5 V. (a) $LiMn_2O_4$, (b) $LiCo_{0.1}Mn_{1.9}O_4$, (c) a cathode prepared from an extensively ground mixture of $LiCo_{0.1}Mn_{1.9}O_4$ and carbon black.

sively milled mixture of $LiCo_{0.1}Mn_{1.9}O_4$ and carbon black shows the best cyclability, with the capacity decreasing from an initial value of 118 to 108 mAh g^{-1} after 50 cycles. Fig. 6 shows the discharge capacity of $Li/LiCo_{0.1}Mn_{1.9}O_4$ cells at various current densities. The capacity decrease is again the lowest for the cathode using the extensively milled mixture of $LiCo_{0.1}Mn_{1.9}O_4$ and carbon black. Two factors could be at work here: a better material utilization in small particles of high surface area and the decrease in contact resistance between oxide and carbon particles as enabled by extended impact grinding.

3.5. Analysis of capacity loss in cathode and electrochemical impedance measurements

The carbon black content in the cathode was systematically varied. Fig. 7 shows clearly the benefits of a high carbon loading on cyclability. Between the 45% and the 10% carbon loaded cathodes, the former exhibits a near
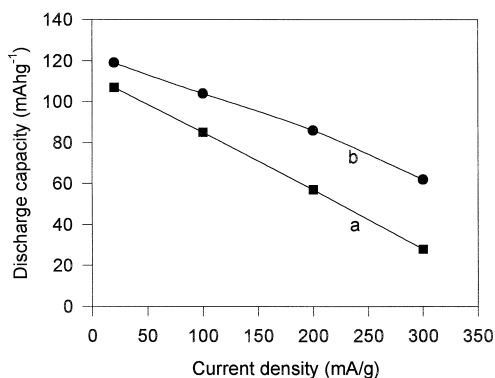

Fig. 6. Discharge capacity of $Li/LiCo_{0.1}Mn_{1.9}O_4$ cells at different current densities: (a) no grinding; (b) grinding of $LiCo_{0.1}Mn_{1.9}O_4$ with carbon black during electrode formulation.
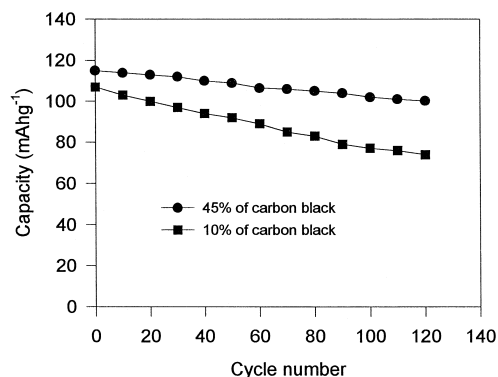

Fig. 7. Variation in the capacity of $Li/LiCo_{0.1}Mn_{1.9}O_4$ cells of different carbon contents as a function of cycle number.

perfect capacity retention. The results imply that excess carbon is advantageous to cyclability. This advantage is however realized at the expense of lower energy and power contents of the resulting cells, as electrically conductive but electrochemically inactive carbon necessarily adds weight and volume to the cells. A good capacity retention may be obtained in practice with a 10% carbon loading and prolonged milling of the spinel and carbon to ensure an intimate mix of the two phases.

Fig. 8 shows the 1st and the 50th charge/discharge cycles of $LiCo_{0.1}Mn_{1.9}O_4$ cathode loaded with the 10%
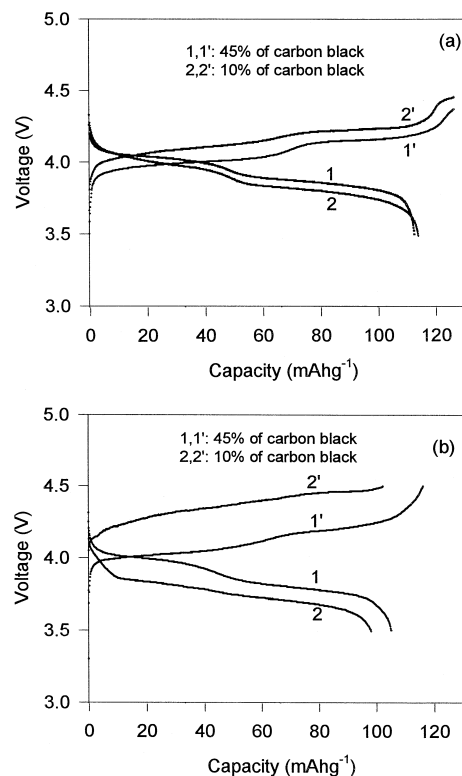

Fig. 8. The charge and discharge curves of $Li/LiCo_{0.1}Mn_{1.9}O_4$ cells: (a) the 1st charge/discharge curves and (b) the 50th cycle curves.
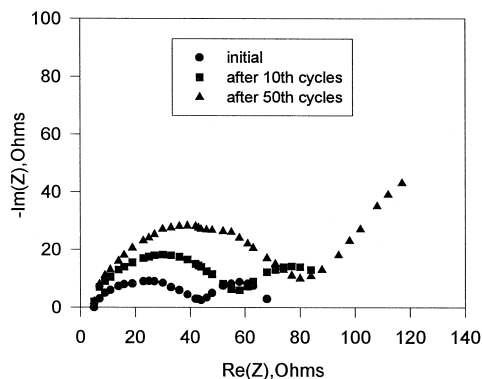
Fig. 9. Electrochemical impedance spectra for $LiCo_{0.1}Mn_{1.9}O_4$ with 10% carbon black loading at various cycle times.

Fig. 10. Electrochemical impedance spectra for $LiCo_{0.1}Mn_{1.9}O_4$ with 45% carbon black loading at various cycle times.

and 45% of carbon black. The 1st cycle profiles are similar irregardless of the carbon content, indicating similarity in the initial cathode properties of the two electrodes. In the 50th profiles, the 45% loaded cathode shows similar charge/discharge profile amidst some small capacity loss. In contrast, the 10% carbon black loaded cathode experiences a substantial capacity loss due to incomplete charging. During the 50th recharge cycle, the charging reaction had ended in the middle of the second voltage plateau because of the prescribed cutoff limit of 4.5 V. Consequently, the discharge capacity, which should be proportional to the charging capacity, was correspondingly lower. The incomplete charging was caused by high cathode polarization resulting from a deteriorating electrical contact between the oxide particles and the carbon particles.

Electrochemical impedance spectroscopy was used to investigate the interfacial resistance in the electrode. Typical impedance spectra at the open-circuit voltage (OCV) for two fully charged composite cathodes loaded with different amounts of carbon black are shown in Figs. 9 and 10. Two semicircular arcs were found. In accordance with common assignments, the high frequency arc can be attributed to effects arising from the resistance and capacitance of the electrolyte/electrode interface, and the low frequency arc to mostly Li^+ ion diffusion from the surface of the electrode to the interior of the oxide spinel host [10]. The initial diameters of the high frequency arc were nearly the same for the 10% carbon black loaded and the 45% carbon black loaded cathodes. Upon repeated cycling, the diameters increased steadily, but were faster for the 10% loaded cathode. This is a clear indication of the increase in cathode resistance.

The change in the diameter of the low frequency arc is also similar. With repeated cycling, Fig. 9 reveals that the low frequency semicircular arc could disappear into a sloping 'spur'. This is indicative of the increasing difficulty of Li^+ ion diffusion from the electrode surface into the spinel interior. The situation is more aggravated for an electrode with a large ohmic polarization. Increase in electrode resistance could account for most of the high cell
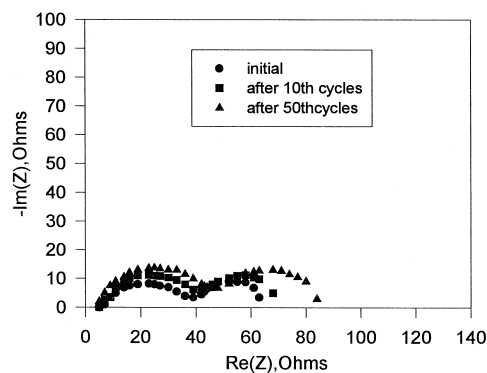
polarization that leads to the premature termination of the recharge operation.

4. Conclusions

Spinel $LiMn_2O_4$ and $LiCo_{0.1}Mn_{1.9}O_4$ for use in lithium rechargeable batteries were prepared by solid state reactions and their electrochemical behaviour was investigated by cyclic voltammetry, constant current charge/discharge, and electrochemical impedance spectroscopy. $LiMn_2O_4$ and $LiCo_{0.1}Mn_{1.9}O_4$ of initial discharge capacities of 119 and 107 mAh g^{-1} could be easily produced. The initial discharge capacity of $LiCo_{0.1}Mn_{1.9}O_4$ could be further increased to 118 mAh g^{-1} through extensive impact grinding of spinel and carbon black. For the same carbon black loading in cathode, the cycle performance of $LiCo_{0.1}Mn_{1.9}O_4$ was better than that of $LiMn_2O_4$, but the cathode prepared from an extensively milled mix of $LiCo_{0.1}Mn_{1.9}O_4$ and carbon black showed the best cyclability. Cathode polarization could arise from poor electrical contact between the active oxide phase and carbon particles, leading to incomplete charging of the cathode after some time. Such problem could be overcome by milling the spinel with carbon particles over an extended period of time during the preparation of the cathode mix.

Acknowledgements

References

[1] J.M. Tarascon, D. Guyomard, J. Electrochem. Soc. 138 (1991) 2864.
[2] D. Guyomard, J.M. Tarascon, J. Electrochem. Soc. 139 (1992) 937.
[3] J.M. Tarascon, W.R. McKinnon, F. Coowar, T.N. Bowmer, G. Amatucci, D. Guyomard, J. Electrochem. Soc. 141 (1994) 1421.

[4] R.J. Gummow, A. de Kock, M.M. Thackeray, Solid State Ionics 69 (1994) 59.

[5] J.M. Tarascon, E. Wang, F.K. Shokoohi, W.R. McKinnon, S. Colson, J. Electrochem. Soc. 138 (1991) 2859.

[6] R. Bittihn, R. Herr, D. Hoge, J. Power Sources 43–44 (1993) 223.

[7] G. Li, H. Ikuta, T. Uchida, M. Wakihara, J. Electrochem. Soc. 143 (1996) 178.

[8] D.H. Jang, Y.J. Shin, S.M. Oh, J. Electrochem. Soc. 143 (1996) 2204.

[9] M. Nishizawa, K. Mukai, S. Kuwabata, C.R. Martin, H. Yoneyama, J. Electrochem. Soc. 144 (1997) 1923.

[10] L. Feng, Y. Chang, L. Wu, T. Lu, J. Power Sources 63 (1996) 149.