Electrochemical characteristics of a carbon electrode with gel polymer electrolyte for lithium-ion polymer batteries

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Abstract

A study of the electrochemical performance of a carbon electrode prepared with mesocarbon microbeads is carried out in a new polymer electrolyte for application as the negative electrode in rechargeable lithium-ion polymer batteries. The polymer electrolyte is prepared by solution casting from a homogeneous mixture containing 18 wt.% acrylonitrile–methyl methacrylate–styrene (AMS) terpolymer, 73 wt.% 1 M $LiClO_4$ in ethylene carbonate (EC)/dimethyl carbonate (DMC) and 9 wt.% silica. The lithium/polymer electrolyte/carbon half cell has a reversible capacity of 305 mA h^{-1} g in the voltage range 0.01 to 1.5 V at the C/10 rate and shows an attractive coulombic efficiency which is higher than 99% after the first three cycles. Good cycling performance of a lithium-ion polymer cell which comprises a carbon anode, an AMS-based polymer electrolyte and a lithium intercalation cathode ($LiNi_{0.83}Co_{0.17}O_2$) has been achieved. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

Lithium polymer batteries are now being widely studied and developed as rechargeable, high energy density devices [1–5]. These batteries use a lithium or a carbon negative electrode (anode) in combination with a high-voltage intercalation positive electrode (cathode) and a polymer electrolyte. The use of polymer electrolyte should permit development of cells which increase safety and provide greater flexibility of battery shape. In a recent publication [5], we reported the cycling performance of rechargeable $Li/LiMn_2O_4$ cells which use acrylonitrile–methyl methacrylate–styrene (AMS)-based polymer electrolytes [5]. It is essential, however, to avoid plating lithium dendrites as the growth of dendrites on lithium metal reduces cycle life and leads to safety problems during charge–discharge cycling. Carbon material can be an alternative anode for lithium metal in rechargeable lithium polymer batteries. There have been a large number of studies on the electrochemical characteristics of various carbon materials for use as negative electrodes in rechargeable lithium batteries. Most of these studies have been performed in a liquid electrolyte [6–10]. Only a few research groups have demonstrated the use of carbon electrodes with a solid polymer electrolyte based on poly(ethylene oxide) (PEO) at high temperature [11–13], and even less have studied the electrochemical characteristics of carbon electrodes in the gel polymer electrolytes at ambient temperature.

In this study, we have prepared gel polymer electrolytes composed of AMS terpolymer, liquid electrolyte and silica powder. A composite carbon electrode based on mesocarbon microbeads (MCMB) has also been prepared. With these materials, we have assembled lithium/polymer electrolyte/carbon half cells and have investigated their electrochemical characteristics and cycling performance at room temperature.

2. Experimental

2.1. Preparation of gel polymer electrolytes

Poly(acrylonitrile-co-methyl methacrylate-co-styrene), abbreviated as AMS in this paper, was prepared by emulsion polymerization with a small amount of potassium persulfate as an initiator, as previously described [5]. The

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final product was obtained as a white powder. From the ^{1}H NMR spectroscopy, the molar composition of AN, MMA and ST was determined to be 57:27:16. Gel polymer electrolytes consisted of AMS, plasticizing electrolyte solution and silanized fumed silica. The AMS was first dissolved in anhydrous tetrahydrofuran (THF). After the polymer had completely dissolved, predetermined amounts of liquid electrolyte and silanized fumed silica (Cabot) were added and the solution was further stirred. The organic liquid electrolyte used was 1 M LiClO$_4$ in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1 by volume) solution (Mitsubishi Chemical, battery grade). The resulting viscous solution was cast with a doctor blade apparatus on to a release paper, and then the solvent was evaporated slowly at room temperature. After evaporation of THF, the film was separated from the release paper. The thickness of the cast film was 60 to $\sim$ 140 μm. All procedures for preparing polymer electrolytes were carried out in a dry-box which was filled with argon gas.

2.2. Fabrication of Li / polymer electrolyte / carbon cells

The composite carbon electrode was prepared by coating the slurry of graphite, polymer electrolyte and super-P carbon on a copper foil with a doctor blade. Graphite was purchased from Osaka Gas; it was treated at 2800°C and coded MCMB-2528. The thickness of the carbon electrode ranged from 60 to 80 μm. A lithium metal of 50-μm thickness (Cyprus Foote Mineral) was used as an anode. A lithium/polymer electrolyte/carbon half cell of cross-sectional area 4 cm^2 was assembled by sandwiching the polymer electrolyte between the lithium anode and the composite carbon electrode. The cell was then enclosed in a metallized plastic bag and vacuum sealed in order to permit testing outside of a dry box. The composite cathode contained the same polymer electrolyte and an electronic conductor along with the intercalation compound LiNi$_{0.83}$Co$_{0.17}$O$_2$ (Sumitomo Chemical); it was cast on aluminum foil. All cells were assembled in a dry-box filled with argon gas.

2.3. Electrical measurements

The A.C. impedance measurements were performed by means of a Zahner Elektrik IM6 impedance analyzer over a frequency range of 10 Hz to 100 kHz for conductivity measurements of the polymer electrolyte, and 1 mHz to 100 kHz for investigations of the electrode interface. Blocking cells with stainless-steel (SS) electrodes were used for conductivity measurements, and non-blocking cells with lithium or carbon electrodes were used to investigate interface phenomena. The charge and discharge cycling tests of the lithium/polymer electrolyte/carbon cell were conducted in the voltage range 0.01 to 1.5 V at a constant current by means of battery test equipment. In this study, charge and discharge of the cell refer to the de-inter-

calation and the intercalation of lithium into the carbon electrode, respectively.

3. Results and discussion

The capacity to retain electrolyte solution and the mechanical state of the polymer electrolyte film was found to be dependent on the AN/MMA/ST molar composition of the AMS terpolymer. To prepare polymer electrolytes with high ionic conductivity and mechanical stability, the AN/MMA/ST molar composition was maintained at 57:27:16, as previously reported [5]. The polymer electrolyte was prepared by solution casting from a homogeneous mixture which contained 18 wt.% AMS terpolymer, 73 wt.% 1 M LiClO$_4$ in EC/DMC and 9 wt.% silica. The polymer electrolytes were free-standing films which exhibit good mechanical properties. An A.C. impedance spectrum of the SS/polymer electrolyte/SS cell at room temperature is shown in Fig. 1. The plot consists of a spike displaced from the origin; this represents a resistor in series with a capacitor. The intercept (5.9 Ω) on the real axis gives the electrolyte resistance. The ionic conductivity is calculated to be 5.1×10^{-4} S cm^{-1} from the electrolyte resistance determined from this data.

To determine the efficacy of the composite carbon anode with AMS-based gel polymer electrolyte in rechargeable lithium-ion polymer batteries, we fabricated lithium/polymer electrolyte/carbon cells. The open-circuit potential of the cell was $\sim$ 3.2 V. The discharge (intercalation)–charge (de-intercalation) curves of lithium/polymer electrolyte/carbon cell at a constant current density of 0.2 mA cm^{-2} (C/10) during the first two cycles are presented in Fig. 2. As lithium ions are inserted into the carbon electrode, the cell voltage falls rapidly to
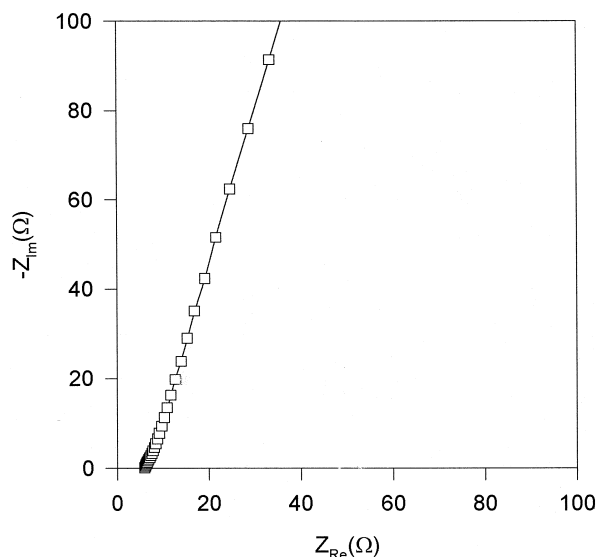

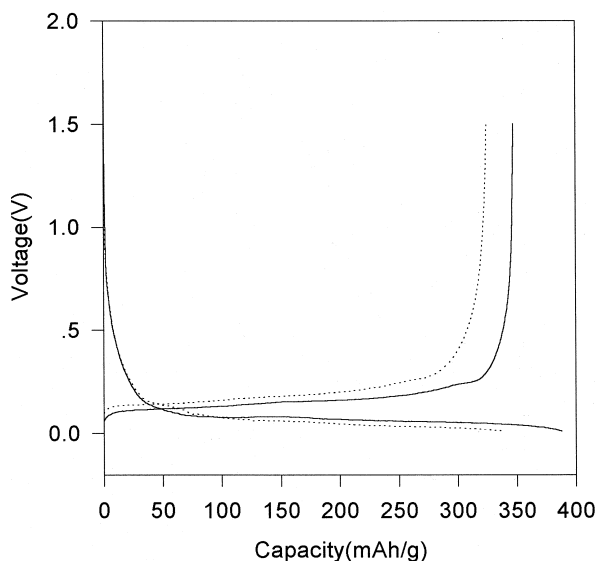Fig. 1. A.C. impedance spectrum of SS/polymer electrolyte/SS cell at 25°C.

Fig. 2. Charge–discharge curves for lithium/polymer electrolyte/carbon half-cell at a constant current density of 0.2 mA cm^{-2} (C/10 rate). Solid and dotted lines correspond to the first and second cycle, respectively.
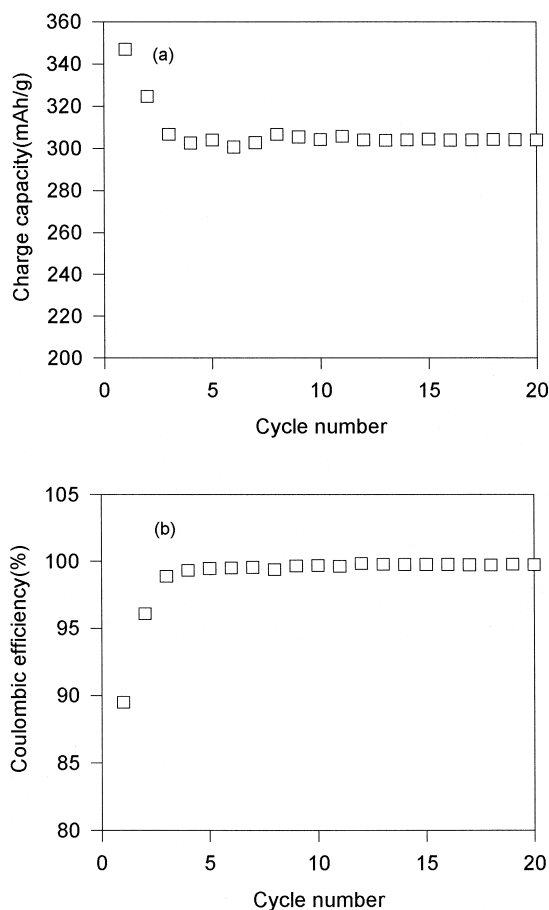
reach ∼ 0.2 V, and then a long plateau is observed to 0.01 V, which means that lithium intercalation occurs mainly at a potential below 0.2 V. The charge curve is essentially similar with a long plateau from 0.01 to 0.2 V and an abrupt increase to 1.5 V. The coulombic efficiencies of the first and second cycle are calculated to be 89.6 and 96.1%, respectively. The large irreversible capacity observed in the first cycle is due to the formation of a passivating film on the surface of the carbon electrode as a result of the decomposition of electrolyte, as previously reported by other authors [14,15]. The wettability of the carbon electrode is relatively poor when a polymer electrolyte is used in place of a liquid electrolyte. This can also account for the low coulombic efficiency during the initial cycle. The lithium/polymer electrolyte/carbon half-cell initially delivered 347 mA h g^{-1} based on MCMB active material.

The charge capacity and coulombic efficiency of the lithium/polymer electrolyte/carbon half-cell are given in Fig. 3 as a function of cycle number between 0.01 and 1.5

Fig. 3. Charge capacity and coulombic efficiency of lithium/polymer electrolyte/carbon half-cell as a function of cycle number at 0.2 mA cm^{-2}: (a) charge capacity vs. cycle number; (b) coulombic efficiency vs. cycle number.
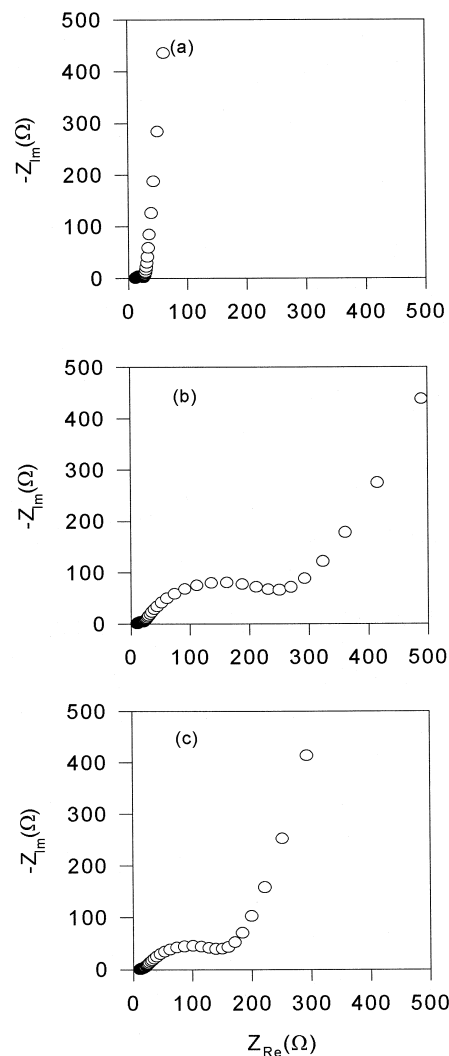

Fig. 4. A.C. impedance spectra of lithium/polymer electrolyte/carbon half-cell in fully charged state: (a) after being assembled; (b) after 1 charge–discharge cycle; (c) after 20 charge–discharge cycles.

V at a constant current density of 0.2 mA cm^{-2}. Following the fall in capacity over the early cycles, a stage is reached at which the decline is much more gradual. Thus, after three cycles, a respectable level of reversible capacity, viz. 305 mA h g^{-1} is achieved. The coulombic efficiency is estimated to be almost 100% except for the first three cycles, as shown in Fig. 3(b).

The A.C. impedance technique provides useful information on the charge transfer and diffusion of lithium ions in the electrodes. The A.C. impedance spectra of a lithium/polymer electrolyte/carbon half-cell in a fully charged state are given in Fig. 4. For a freshly made cell, only one small arc appeared and thus the equivalent circuit comprises an electrolyte resistance and an interface resistance. After the first charge–discharge cycle, the spectrum displays two arcs. The first, at middle frequency, can be associated with an ionically conducting surface layer which grows on the carbon electrode. The low-frequency semicircle is related to charge transfer between the surface layer and the electrode. These conclusions are confirmed by the fact that a low-frequency semicircle can be observed after charge–discharge cycling. This behaviour can be ascribed to an initial poor interfacial contact between the polymer electrolyte and the carbon electrode before charge–discharge cycling, which means that current flow is necessary to activate initially the polymer electrolyte/carbon electrode interface, as previously reported for a lithium/polymer electrolyte/LiV$_3$O$_8$ cell [16]. Since the total interfacial resistance is shown to be many times greater than the electrolyte resistance, it is of crucial importance to minimize the resistance for practical applications. The A.C. impedance diagram is completed by a Warburg line which is related to the diffusion of Li-ions in carbon electrode, and is qualitatively similar to that obtained in the intercala-
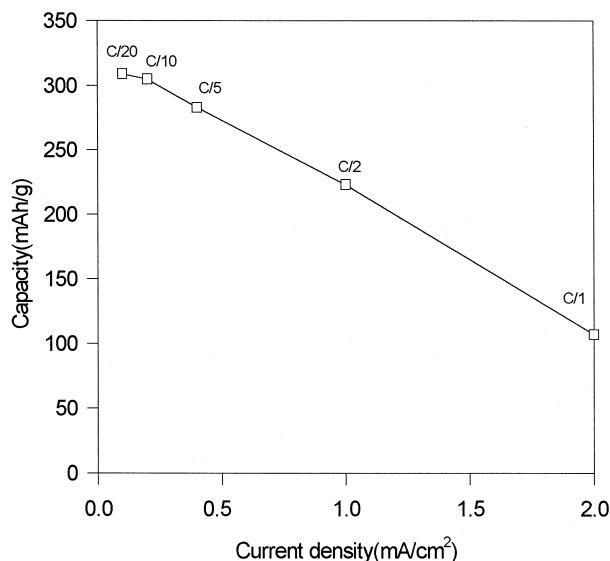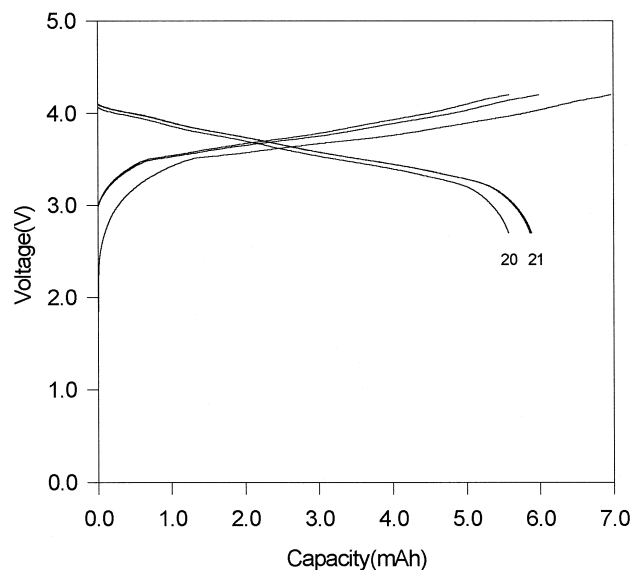

Fig. 6. Charge–discharge curves for carbon/polymer electrolyte/ LiNi$_{0.83}$Co$_{0.17}$O$_2$ cell at a constant current density of 0.3 mA cm^{-2} (C/5 rate).

tion cathode [17]. This indicates that the kinetics of the electrochemical intercalation process may become diffusion-controlled. After 20 charge–discharge cycles, the charge-transfer resistance at low frequency is decreased. This is a convincing indication of a good interfacial contact in composite carbon electrode, and thus capacity loss on cycling due to the degradation of the carbon interface can be considered to be negligible in the systems developed here.

The reversible capacity of a lithium/polymer electrolyte/carbon half-cell obtained at different current densities is presented in Fig. 5. The cell delivers a reversible capacity of 309 mA h g^{-1} at 0.1 mA cm^{-2}. It also yields an attractive capacity of 283 mA h g^{-1} at 0.4 mA cm^{-2}. It
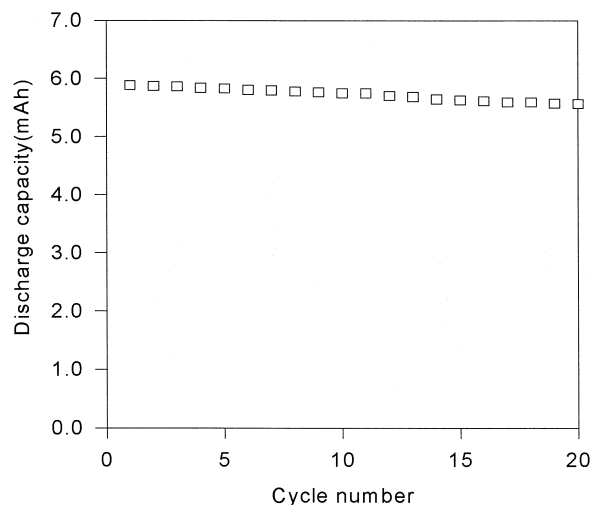

Fig. 5. Reversible capacity of lithium/polymer electrolyte/carbon half-cell as a function of current density at 25°C.

Fig. 7. Discharge capacities of carbon/polymer electrolyte/ LiNi$_{0.83}$Co$_{0.17}$O$_2$ cell as a function of cycle number at 0.3 mA cm^{-2}.

is found, however, that the reversible capacity decreases as the current rate increases; it falls to 107 mA h g^{-1} at 2.0 mA cm^{-2}. The reduced capacity in the lithium/polymer electrolyte/carbon half-cell at high rates can be related to the lower diffusion rate of lithium ions in the polymer electrolyte as compared with that in liquid electrolyte.

In order to investigate the effectiveness of a composite carbon anode when combined with an intercalation cathode in a lithium-ion polymer battery, a carbon/polymer electrolyte/LiNi$_{0.83}$Co$_{0.17}$O$_2$ cell has been constructed. The cycling tests were performed at a constant current density of 0.3 mA cm^{-2}(0.2 C) and with cut-off voltages of 4.2 and 2.7 V for the upper and lower limits, respectively. The charge–discharge curves of a carbon/polymer electrolyte/LiNi$_{0.83}$Co$_{0.17}$O$_2$ cell are given in Fig. 6. This cell has an average voltage of 3.5 V and a discharge capacity of ~5.88 mA h (1.47 mA h^{-1} cm^{-2}) on the first cycle. From the value of discharge capacity with weight of electrode active material, the specific discharge capacity of the carbon anode and the LiNi$_{0.83}$Co$_{0.17}$O$_2$ cathode are estimated to be 198 and 153 mA h g^{-1}, respectively. The cycle efficiency is 84.6% on the first cycle. With the repeated cycling, the discharge capacity decreases slightly, while the cycling efficiency increases.

The discharge capacity of the carbon/polymer electrolyte/LiNi$_{0.83}$Co$_{0.17}$O$_2$ cell as a function of cycle number is shown in Fig. 7. The discharge capacity is 5.57 mA h g^{-1} on the 20 the cycle, which is 95% of the initial capacity. The charge–discharge efficiency is about 100%, except for the first three cycles. From these results, it is concluded that the composite carbon anode with AMS-based gel polymer electrolyte as an electrolyte exhibits satisfactory performance in a lithium-ion polymer battery. More detailed studies on the electrical performance of the lithium-ion polymer cells employing AMS-based gel polymer electrolyte are in progress and will be reported in the near future.

4. Conclusions

The capacity and cycle life of a carbon electrode has been investigated using gel polymer electrolytes based on AMS terpolymer. A composite carbon electrode prepared with graphitic carbon shows promise as an anode with the new polymer electrolytes for a lithium-ion polymer battery. In combination with LiNi$_{0.83}$Co$_{0.17}$O$_2$ as a cathode, good cycling performance has been achieved.

References

[1] R. Koksbang, I.I. Olsen, P.E. Tonder, N. Kundsen, D. Fauteux, J. Appl. Electrochem. 21 (1991) 301.

[2] D. Peramunage, D.M. Pasquariello, K.M. Abraham, J. Electrochem. Soc. 142 (1995) 1789.

[3] G.B. Appetecchi, G. Dautzenberg, B. Scrosati, J. Electrochem. Soc. 143 (1996) 6.

[4] Y. Aihara, M. Kodama, K. Nakahara, O. Okise, K. Murata, J. Power Sources 65 (1997) 143.

[5] D.W. Kim, Y.K. Sun, J. Electrochem. Soc. 145 (1998) 1958.

[6] J.R. Dahn, R. Fong, M.J. Spoon, Phys. Rev. B 42 (1990) 6424.

[7] T. Ohzuku, Y. Iwakoshi, K. Sawai, J. Electrochem. Soc. 140 (1993) 2490.

[8] A. Mabuchi, K. Tokumitsu, H. Fujimoto, T. Kasuh, J. Electrochem. Soc. 142 (1995) 1041.

[9] D. Aurbach, Y. Ein-Eli, J. Electrochem. Soc. 142 (1995) 1746.

[10] K. Tatsumi, T. Akai, I. Imamura, K. Saghib, N. Iwashita, S. Higuchi, Y. Sawada, J. Electrochem. Soc. 143 (1996) 1923.

[11] R. Yazami, K. Zaghib, M. Deschamps, J. Power Sources 52 (1994) 55.

[12] K. Zaghib, Y. Choquette, A. Guerfi, M. Simoneau, A. Belanger, M. Gauthier, J. Power Sources 68 (1997) 368.

[13] F. Coowar, D. Billaud, J. Ghanbaja, P. Baudry, J. Power Sources 62 (1996) 179.

[14] R. Fong, U. von Sacken, J.R. Dahn, J. Electrochem. Soc. 137 (1990) 2009.

[15] J.M. Tarascon, D. Guyomard, J. Electrochem. Soc. 138 (1991) 2864.

[16] A. Selvaggi, F. Croce, B. Scrosati, J. Power Sources 32 (1990) 389.

[17] Y. Xia, H. Takeshige, H. Noguchi, M. Yoshio, J. Power Sources 56 (1995) 61.