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# Electrochemical characterization of layered $\text{LiCoO}_2$ films prepared by electrostatic spray deposition

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## Abstract

$\text{LiCoO}_2$  thin-film cathode was deposited on Pt-coated alumina substrate by the electrostatic spray deposition method. The average film weight of  $\text{LiCoO}_2$  increased linearly with the deposition time. Electrochemical characterization was carried out by cyclic voltammetry and charge/discharge tests. These tests revealed that single phase HT- $\text{LiCoO}_2$  films could be obtained by the ESD method at temperature as low as  $600^\circ\text{C}$  and the  $\text{LiCoO}_2$  film deposited by the ESD method showed very stable cycling characteristics. The crystallinity of the  $\text{LiCoO}_2$  layers increased with increasing annealing temperature. XANES results showed that the  $\text{LiCoO}_2$  film deposited by the ESD method does not show any changes of the local geometry and electronic structure around Co atoms after electrochemical cycling. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Electrostatic spray deposition;  $\text{LiCoO}_2$ ; Thin-film; XANES; Microbatteries

## 1. Introduction

Advances in the microelectronics industry have reduced the current and power requirements of electronic devices. This has made possible the use of thin-film rechargeable microbatteries as power sources for these devices. Encouraged by this practical importance, the fabrication of thin-film electrodes has received considerable attention in recent years. This type of electrode is also of great interest in investigating the intrinsic electrochemical properties of lithiated transition metal oxides, because it has a simple geometric form without additives such as polymer binder and conducting materials and its simple geometric form makes the theoretical analysis of the electrochemical behaviors easier.

$\text{LiCoO}_2$  is most widely used as the cathode material for both Li rechargeable batteries and thin-film microbatteries due to its advantages including high specific capacity, high operating voltage, and long cycle life [1–4].  $\text{LiCoO}_2$  thin-films have been fabricated by several methods, such as r.f. magnetron sputtering, pulse laser deposition, and chemical vapor deposition. Recently, Schoonman et al. have developed the electrostatic spray deposition (ESD) method and

applied it to fabricating thin-film cathode of rechargeable microbatteries [5–7]. The ESD method uses a very fine aerosol of a precursor solution, which is electrohydrodynamically generated, to deposit a film on a heated electrode substrate. The ESD method offers many advantages over some conventional deposition techniques, such as a simple and low cost set-up, high deposition efficiency, low temperature synthesis, and easy control of the composition and surface morphology of the deposited films. However, compared to conventional deposition techniques such as r.f. magnetron sputtering, pulse laser deposition, and chemical vapor deposition, there have been only a few reports of the fabrication of thin-film cathodes by the ESD method. In the present study, we prepared  $\text{LiCoO}_2$  thin-films by the electrostatic spray deposition (ESD) method. The structure and its electrochemical properties were studied by X-ray diffraction (XRD), X-ray absorption near edge spectroscopy (XANES), cyclic voltammetry (CV), and galvanostatic charge/discharge experiments.

## 2. Experimental

A stoichiometric amount of lithium nitrate and cobalt nitrate with the cationic ratio of  $\text{Li}:\text{Co} = 1:1$  was dissolved

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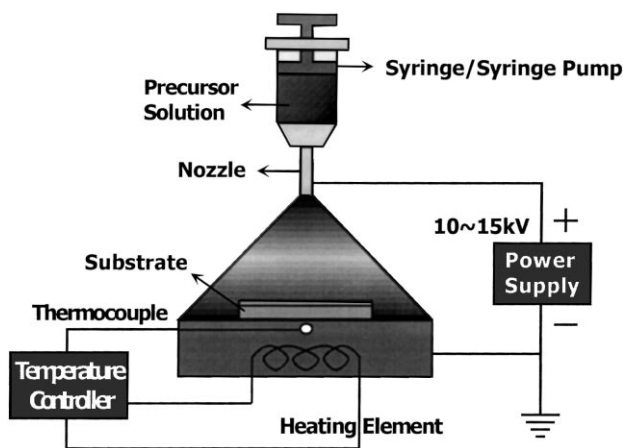


Fig. 1. A schematic diagram of the electrostatic spraying deposition (ESD) system.

in absolute ethanol and mixed to obtain a precursor solution. A schematic diagram of the ESD system is illustrated in Fig. 1. The working principles of the ESD method have been described in the literature [5–7]. A high voltage between the nozzle and the substrate makes the precursor solution atomized at the orifice of the nozzle generating a fine aerosol spray. The temperature of the substrate was kept at 300°C during the deposition. An ethanol precursor solution of 0.04 M LiNO<sub>3</sub> and 0.04 M Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O was pumped at 2 ml/h rate for 1 h through a nozzle placed 4 cm above the substrate. All LiCoO<sub>2</sub> films were deposited on 3000 Å thick Pt current collectors on alumina substrates.

The crystal structure of LiCoO<sub>2</sub> films annealed at various temperatures was characterized by X-ray diffraction patterns using Cu K $\alpha$  radiation in a Rigaku diffractometer. XANES measurements were performed in fluorescence mode at beamline 3C1 of Pohang Light Source (PLS) using a Si(1 1 1) double-crystal monochromator. The storage ring was operated with an electron energy of 2 GeV and a current between 80 and 120 mA. Calibration was carried out prior to all measurements using the first inflection point of the spectrum of Co foil, i.e. Co K-edge = 7709 eV, as a reference.

A three-electrode electrochemical cell was employed for electrochemical measurements in which lithium foil was used for both reference and counter electrodes. The electrolyte used was 1 M LiClO<sub>4</sub> in propylene carbonate (PC) solution. Cyclic voltammetry (CV) and galvanostatic charge/discharge experiments were carried out using a multichannel potentiostat/galvanostat (WBCS 3000, Wonatech, Korea). All the electrochemical experiments were carried out at room temperature in a glove box filled with purified argon gas.

### 3. Results and discussion

The relation between the weight of LiCoO<sub>2</sub> films and the deposition time is shown in Fig. 2. The amount of deposit was determined by weighing the electrode substrates before

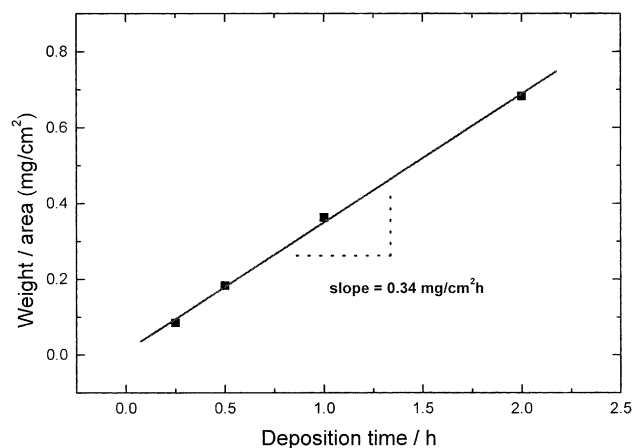


Fig. 2. The relation between the weight of LiCoO<sub>2</sub> films and the deposition time. Deposition conditions are given in the experimental section.

and after the deposition. It was found that a linear relation exists between the weight of the film and the deposition time. The weight growth rate was about 0.34 mg/cm<sup>2</sup> h under the specific conditions as given in experimental section. The film thickness growth rate is calculated to be about 0.67  $\mu$ m/h under the assumption that the LiCoO<sub>2</sub> films are fully dense with the theoretical density of 5.06 g/cm<sup>3</sup>.

Fig. 3 shows XRD patterns for the LiCoO<sub>2</sub> layers annealed at various temperatures in air for 0.5 h. In order to minimize interference from the diffraction peaks of the alumina substrate and Pt current collector, near grazing angle scans were made in which the angle of the incident radiation with respect to the plane of the substrate was fixed at 5° while the detector with a parallel-beam thin-film attachment placed in front of it was moved through the 2 $\theta$  angle. All diffraction peaks can be indexed by assuming the structure to be a hexagonal lattice of the  $\alpha$ -NaFeO<sub>2</sub> type. The diffraction peaks became sharper as the annealing temperature increased. This indicates an increase in crystallinity and a gradual growth in the average particle size.

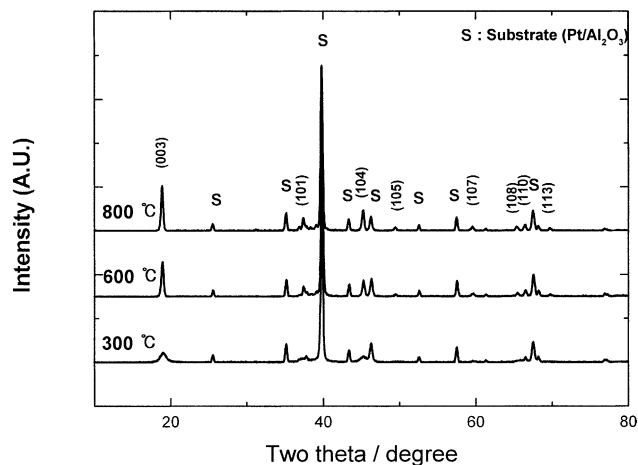


Fig. 3. XRD patterns for the LiCoO<sub>2</sub> layer annealed at various temperatures in air for 0.5 h.

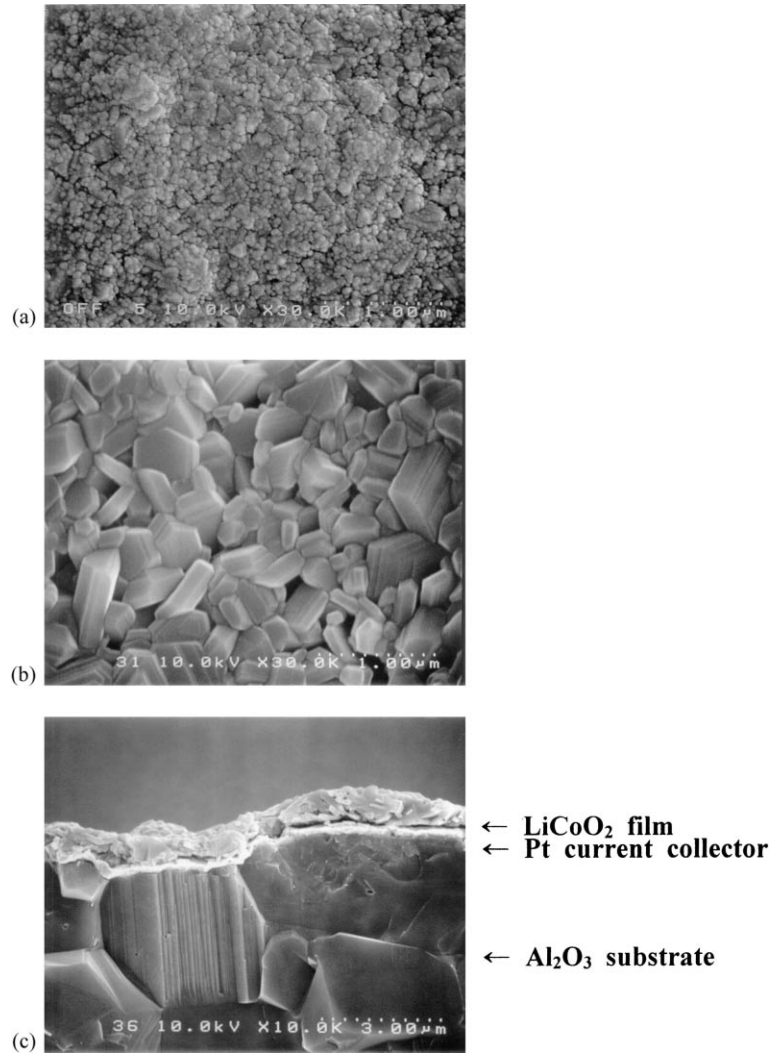


Fig. 4. SEM of the  $\text{LiCoO}_2$  films deposited at  $300^\circ\text{C}$  for 1 h at 2 ml/h rate: (a) plane view of  $\text{LiCoO}_2$  films annealed at  $600^\circ\text{C}$ ; (b) plane view of  $\text{LiCoO}_2$  films annealed at  $800^\circ\text{C}$ ; (c) cross-section of  $\text{LiCoO}_2$  films annealed at  $800^\circ\text{C}$ .

Scanning electron micrographs of the  $\text{LiCoO}_2$  films annealed at various temperatures in air for 0.5 h are shown in Fig. 4. The  $\text{LiCoO}_2$  films deposited by the ESD method showed uniform thickness, grain size, and smooth surface. This morphology could be obtained by controlling deposition conditions such as deposition temperature, spraying rate, precursor solution, and bias voltage between nozzle and substrate. There was a trend that the grain size of the films increased with increasing the annealing temperature.

The deposition mechanism of the ESD method is similar to the synthesis mechanism of a sol–gel process. In the case of the sol–gel process, metal ions mixed at atomic scale exist in a sol precursor solution and then a dried gel precursor decomposes and crystallizes simultaneously through pyrolysis [8–10]. The electrostatic spray deposition method usually atomizes a precursor solution containing metal ions mixed at atomic scale into an aerosol, which is then directed to a heated substrate. Desired films are formed on the heated substrate by simultaneous decomposition of the precursor

solution and synthesis of metal oxide. The two methods make possible a better mixing of the elements and, therefore, a better reactivity of the mixture, which then allows a lower reaction temperature and a shorter reaction time. Single phase HT- $\text{LiCoO}_2$  films could be obtained by the ESD method at temperature as low as  $600^\circ\text{C}$ . Fig. 5 presents cyclic voltammograms obtained from the  $\text{LiCoO}_2$  films annealed at various temperatures. In  $\text{LiCoO}_2$  films annealed at  $600^\circ\text{C}$  or above, typical cyclic voltammograms of HT- $\text{LiCoO}_2$  were observed, which were characterized by three sets of well-defined current peaks [11]. The  $\text{LiCoO}_2$  films annealed at  $600^\circ\text{C}$  or above display the main lithium intercalation and deintercalation peaks near 3.9 V, which is due to the coexistence of two pseudo-phases of an Li-dilute  $\alpha$ -phase and an Li-concentrated  $\beta$ -phase [12]. Two high voltage peaks observed above 4 V may result from phase transition between ordered and disordered lithium ion arrangements in the  $\text{CoO}_2$  framework [13]. An irreversible oxidation peak at about 3.83 V is shown in the  $\text{LiCoO}_2$  films

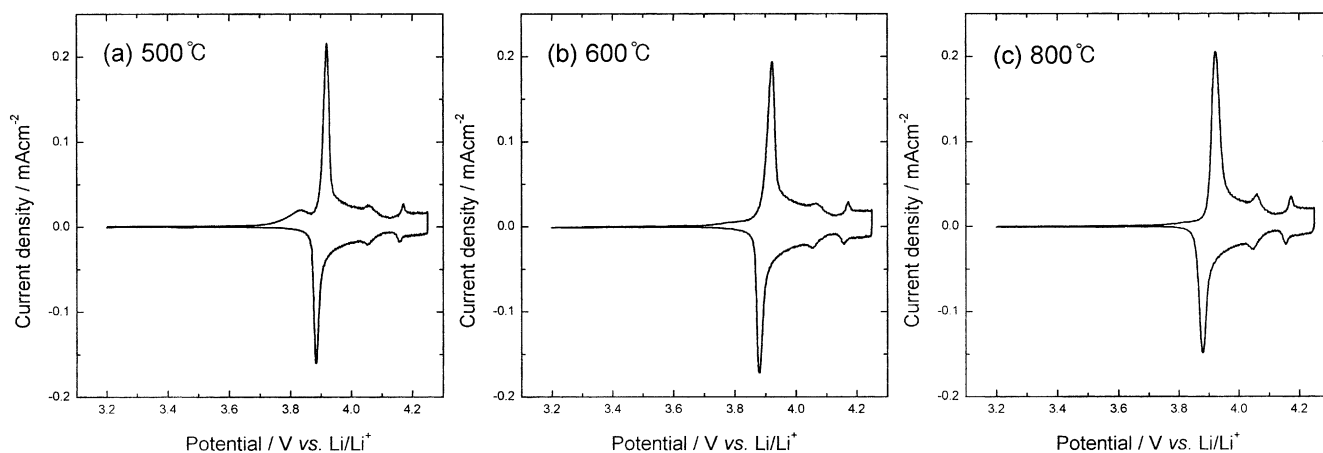


Fig. 5. Cyclic voltammograms obtained from the  $\text{LiCoO}_2$  films annealed at various temperatures at a scan rate of 0.1 mV/s.

annealed at  $500^\circ\text{C}$ , and this indicates that the  $\text{LiCoO}_2$  film is an intermediate phase between HT- $\text{LiCoO}_2$  and LT- $\text{LiCoO}_2$ .

To demonstrate the rechargeability of  $\text{LiCoO}_2$  film, test cells were cycled at a current density of  $50 \mu\text{A}/\text{cm}^2$  between 3.0 and 4.2 V at room temperature. Fig. 6 shows the discharge capacity vs. cycle number of  $\text{LiCoO}_2$  film annealed at  $800^\circ\text{C}$  in air for 0.5 h. The initial discharge capacity per unit of area and thickness was  $70 \mu\text{Ah}/\text{cm}^2 \mu\text{m}$  which is close to the theoretical value of  $69 \mu\text{Ah}/\text{cm}^2 \mu\text{m}$  for exchange of 0.5 Li per  $\text{CoO}_2$  in a fully dense film. As shown in Fig. 6, the  $\text{LiCoO}_2$  film deposited by the ESD method shows very stable cycling characteristics.

Fig. 7 shows the normalized Co K-edge XANES spectra for pristine  $\text{LiCoO}_2$  film and  $\text{LiCoO}_2$  film after 50 cycles. The K-edge XANES spectra originate from transitions of the 1s core level of the metal to excited vacant states of proper symmetry involving metal orbitals [14–16]. The small pre-edge absorption, A peak, represents the transition of 1s electron to an unoccupied 3d orbital of  $\text{Co}^{3+}$  ion with the

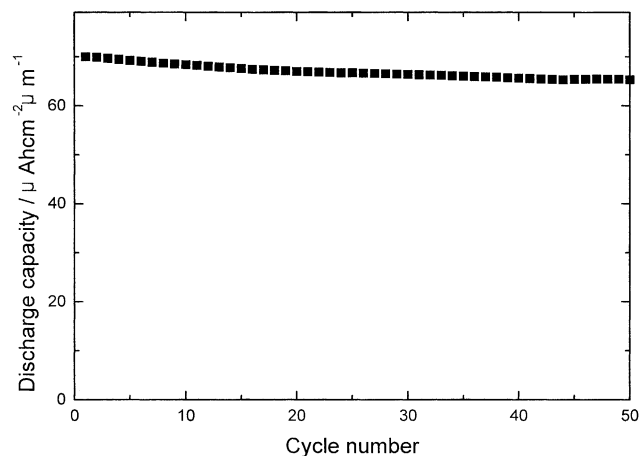


Fig. 6. Discharge capacity vs. cycle number of  $\text{LiCoO}_2$  film annealed at  $800^\circ\text{C}$  in air for 0.5 h.

low spin ( $t_{2g}^6 e_g^0$ ) electronic configuration. Although, the  $1s \rightarrow 3d$  transition is electric dipole-forbidden transition in an ideal octahedral symmetry, the appearance of small absorption peak results from pure electric quadrupole coupling and  $3d-4p$  orbital mixing by the noncentrosymmetric environment of its slightly distorted  $\text{CoO}_6$  octahedral site. The first strong absorption, B peak, is assigned to a shake-down process involving the  $1s \rightarrow 4p$  transition followed by ligand to metal charge transfer. The strongest absorption, C peak, is purely dipole-allowed  $1s \rightarrow 4p$  transition. Namely, the B and C peaks correspond to two final states of a  $1s1c3d^7L4p^1$  with a shakedown process by ligand to metal charge transfer (LMCT) and a  $1s1c3d^64p^1$  without

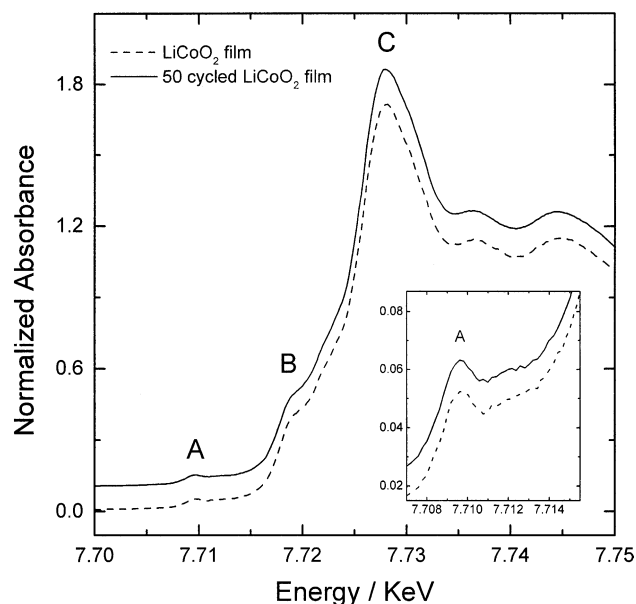


Fig. 7. The normalized Co K-edge XANES spectra for pristine  $\text{LiCoO}_2$  film and  $\text{LiCoO}_2$  film after 50 cycles. The inset shows an expanded view of the region of the spectrum containing  $1s \rightarrow 3d$  transitions. For clarity, each spectrum is shifted to y-scale by the 0.1 value (and 0.01 value for the inset).

shakedown process, respectively, where  $c$  and  $L$  are a 1s core hole and a ligand hole. The strong B peak occurs as a shoulder on the lower energy region with respect to the main absorption C peak since the 1s core electron of  $3d^7L$  state is less bound to the more screened nucleus with respect to that of  $3d^6$  state. As shown in Fig. 7, both the edge structures of pristine  $\text{LiCoO}_2$  film and  $\text{LiCoO}_2$  film after 50 cycles are identical, and this indicates that the  $\text{LiCoO}_2$  film deposited by ESD method does not show any changes of the local geometry and electronic structure around Co atoms after electrochemical cycling.

#### 4. Conclusions

We have prepared  $\text{LiCoO}_2$  films on Pt-coated alumina substrate by the electrostatic spray deposition technique. The average film weight of  $\text{LiCoO}_2$  increased linearly with the deposition time. The ESD method allowed us to prepare single phase HT- $\text{LiCoO}_2$  films at temperature as low as  $600^\circ\text{C}$ . SEM and XRD results showed an increase in crystallinity and a gradual growth in the average particle size with increasing the annealing temperature. Cycling test showed that the  $\text{LiCoO}_2$  film deposited by the ESD method shows very stable cycling characteristics. From the observation of Co K-edge XANES spectra of cycled  $\text{LiCoO}_2$ , it is found that the  $\text{LiCoO}_2$  film deposited by the ESD method does not show any changes of the local geometry and electronic structure around Co atoms after electrochemical cycling.

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#### References

- [1] K. Mizushima, P.C. Jones, P.C. Wiseman, J.B. Goodenough, *Mater. Res. Bull.* 15 (1980) 783.
- [2] T. Nagaura, K. Tozawa, *Progr. Batt. Solar Cells* 9 (1991) 209.
- [3] M. Antaya, J.R. Dahn, J.S. Preston, E. Rossen, J.N. Reimers, *J. Electrochem. Soc.* 140 (1993) 575.
- [4] B. Wang, J.B. Bates, F.X. Hart, B.C. Sales, R.A. Zuhr, J.D. Robertson, *J. Electrochem. Soc.* 143 (1996) 3203.
- [5] C. Chen, E.M. Kelder, M.J. Kelder, M.J.G. Jak, J. Schoonman, *Solid State Ionics* 86-88 (1996) 1301.
- [6] C. Chen, E.M. Kelder, P.J.J.M. van der Put, J. Schoonman, *J. Mater. Chem.* 6 (1996) 765.
- [7] C. Chen, E.M. Kelder, J. Schoonman, *J. Electrochem. Soc.* 144 (1997) L289.
- [8] P.A. Lessing, *Ceram. Bull.* 68 (1989) 1002.
- [9] E. Zhecheva, R. Stoyanova, M. Gorova, R. Alcantara, J. Morales, J.L. Tirado, *Chem. Mater.* 8 (1996) 1429.
- [10] W.-S. Yoon, K.-B. Kim, *J. Power Sources* 81-82 (1999) 517.
- [11] I. Uchida, H. Saito, *J. Electrochem. Soc.* 142 (1995) L139.
- [12] Y.M. Choi, S.I. Pyun, J.S. Bae, S.I. Moon, *J. Power Sources* 56 (1995) 25.
- [13] J.N. Reimers, J.R. Dahn, *J. Electrochem. Soc.* 139 (1992) 2091.
- [14] I.J. Pickering, G.N. George, J.T. Lewandowski, A.J. Jacobson, *J. Am. Chem. Soc.* 115 (1993) 4137.
- [15] I.J. Pickering, G.N. George, *Inorg. Chem.* 34 (1995) 3142.
- [16] M.C. Martins Alves, J.P. Dodelet, D. Guay, M. Ladouceur, G. Tourillon, *J. Phys. Chem.* 96 (1992) 10898.