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Short communication

Characterization of $LiMn_2O_4$-coated $LiCoO_2$ film electrode prepared by electrostatic spray deposition

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Abstract

$LiMn_2O_4$-coated $LiCoO_2$ film was synthesized by the ESD technique. The bulk structure and its electrochemical property were studied by X-ray diffraction (XRD) and cyclic voltammetry (CV) and the surface structure were characterized using soft XAS at the O K-edge and the Mn L-edge. The bulk structure and the electrochemical property of the $LiMn_2O_4$-coated $LiCoO_2$ film do not show substantial difference compared to the bare $LiCoO_2$ film. The thermal stability of $LiCoO_2$ film is improved by $LiMn_2O_4$ coating on the surface of the $LiCoO_2$ film. The Mn L-edge and O K-edge results suggest that the structure at the surface of $LiMn_2O_4$-coated $LiCoO_2$ film is a spinel $LiCo_xMn_{2-x}O_4$.

Keywords: $LiMn_2O_4$ coating; Soft X-ray absorption spectroscopy; ESD; Lithium rechargeable batteries; Thin film

1. Introduction

$LiCoO_2$ 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 [1–3]. $LiCoO_2$ 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 [4,5]. The ESD technique 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.

Recently, novel approaches that coat surface of cathode materials for Li batteries by various oxides have been conducted to improve electrode performance such as thermal stability, cyclability, high temperature capacity, and so on [6,7]. Similar approach has been also applied to the thin-film electrode for Li microbatteries [8]. These report clearly showed that the electrode performance is improved not by doping but by coating. Characterizations of the coated surface structure play an important role in understanding the improved electrochemical property by surface coating. Since these surface coatings on the cathode materials have nanoscale dimension, electronic and structural characterizations of the layer on the surface of the materials might not be easy.

Soft X-ray absorption spectroscopy (XAS) has been applied in the investigation of the electronic structure of electrode materials for Li rechargeable batteries [9–11]. Soft X-ray absorption spectra can be obtained in both the electron yield and fluorescence modes. The electron yield mode is surface sensitive (within ~50 Å) while the fluorescence yield mode is suitable for bulk studies (more than ~2000 Å) [12]. Therefore, soft XAS using electron yield mode can be an useful tool to characterize surface structure of those oxide-coated electrode materials. In this work, we prepared $LiMn_2O_4$-coated $LiCoO_2$ films by the ESD technique. The bulk structure and its electrochemical property were studied by X-ray diffraction (XRD) and cyclic voltammetry (CV) and the surface structure were characterized using soft XAS at the O K-edge and the Mn L-edge.

2. Experimental

The ESD set-up used here and its working principles have been described in the literature [5,13]. A high dc voltage is

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applied between an electrically conductive substrate and a metal capillary nozzle, which is connected to a precursor solution. Under a suitable flow rate, the precursor solution is atomized at the orifice of the nozzle, generating a fine spray. The spray moves toward the heated substrate under the electrostatic force and, due to pyrolysis of the precursors, a thin layer is deposited on the substrate surface. An ethanol solution of $LiNO_3 + Mn(NO_3)_2$ with a molar ratio Li:Mn = 1:2 was used as the precursor solution (0.04 M). The precursor solution was pumped at a rate of 2 ml h^{-1} to a stainless steel nozzle, which placed 4 cm above $LiCoO_2$ film substrate. The total amount of Mn in the precursor solution corresponded to 3 mol% of $LiCoO_2$ film. The deposition temperature was chosen generally between 200 and 400 °C. $LiMn_2O_4$ film on the $LiCoO_2$ substrate was annealed at 400 °C. Electrochemical measurements ware carried out using a three-electrode cell with 1 M $LiClO_4$/propylene carbonate (PC) solution in a glove box. Li foils were used as the counter and reference electrodes.

The soft XAS measurements of the $LiMn_2O_4$-coated $LiCoO_2$ films were performed on U7 beamline in the storage ring of 2.5 GeV with the ring current of 120–160 mA at Pohang Light Source (PLS) [14]. The U7 beamline, which consists of 4.3 m long, 7 cm period undulator and the variable-included angle plane-grating monochromator, provides the highly brilliant and monochromatic linear-polarized soft X-ray for the high resolution spectroscopy [15]. The O K-edge and Mn $L_{II,III}$-edge XAS data were taken in a total electron yield mode, recording the sample current. The experimental spectra were normalized by reference signal from Au mesh with 90% transmission. The energy calibrations for O K-edge and Mn $L_{II,III}$-edge were made using the L-edges data of pure V and Mn metal foils, respectively. According to the measured photon absorption spectra specified as the inner shell electron excitation for the Ar, N_2 and Ne gases, the energy resolving power ($E/\Delta E$) in entire measurement range was greater than 3000. The base pressure of the experiment chamber was in 10^{-8} mbar range.

3. Results and discussion

The $LiMn_2O_4$ was successfully coated on $LiCoO_2$ film electrode by electrostatic spray deposition technique. Fig. 1 shows XRD patterns for (a) $LiCoO_2$ and (b) $LiMn_2O_4$-coated $LiCoO_2$ film on Pt/Al_2O_3 substrate. All diffraction peaks can be indexed by assuming the structure to be a hexagonal lattice of the α-$NaFeO_2$ type. There is no substantial difference between XRD patterns for $LiCoO_2$ and $LiMn_2O_4$-coated $LiCoO_2$ film. This indicates that bulk structure of both samples is a well-developed layered HT-$LiCoO_2$. Cyclic voltammogram (CV) for $LiMn_2O_4$-coated $LiCoO_2$ film at a scan rate of 0.1 mV s^{-1} is shown in Fig. 2. Typical cyclic voltammogram of HT-$LiCoO_2$ is also observed, which is characterized by three sets of well-defined current peaks [16]. The cyclic voltammogram displays the main lithium intercalation and deintercalation peaks near 3.9 V. Two high voltage peaks observed above 4 V result from phase transition between ordered and disordered lithium ion arrangements in the CoO_2 framework.

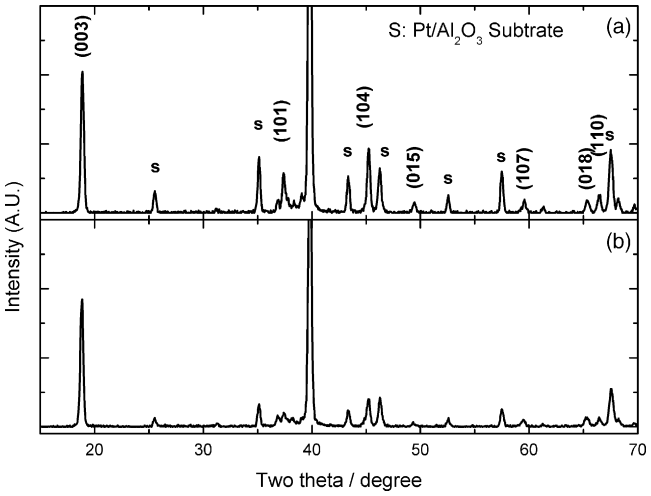

Fig. 1. XRD patterns for (a) $LiCoO_2$ and (b) $LiMn_2O_4$-coated $LiCoO_2$ film on Pt/Al_2O_3 substrate.

Differential scanning calorimetry (DSC) test were carried out in order to investigate the thermal stability of the film electrodes. Unlike the XRD and CV results, DSC result of $LiMn_2O_4$-coated $LiCoO_2$ film electrode is quite different from that of $LiCoO_2$ film electrode. Fig. 3 shows DSC scans of charged cathodes containing $LiCoO_2$ and $LiMn_2O_4$-coated $LiCoO_2$. For the pure $LiCoO_2$ cathode, the decomposition reaction appears to initiate at around 170 °C, followed by development of intense exothermic peak in the temperature range of 180–200 °C. This is consistent with the earlier report by Zhang et al. [17]. The overall heat generation under the exothermic peaks is a direct indication of the reactivity between the active materials and the electrolyte. The thermal behavior of the $LiMn_2O_4$-coated $LiCoO_2$ is quite different from that for $LiCoO_2$. The DSC scan of the $LiMn_2O_4$-coated $LiCoO_2$ shows increase of the peak temperature and reduction of the exothermic peak compared to that of the $LiCoO_2$, which indicates that $LiMn_2O_4$-coated $LiCoO_2$ shows the good thermal stability of the cathode and reduction of the heat amount of the reaction.

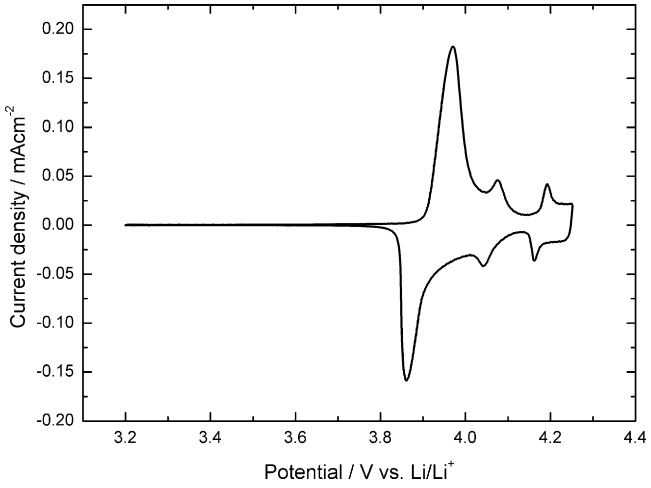

Fig. 2. Cyclic voltammograms for $LiMn_2O_4$-coated $LiCoO_2$ film annealed at various temperature at a scan rate of 0.1 mV s^{-1}.

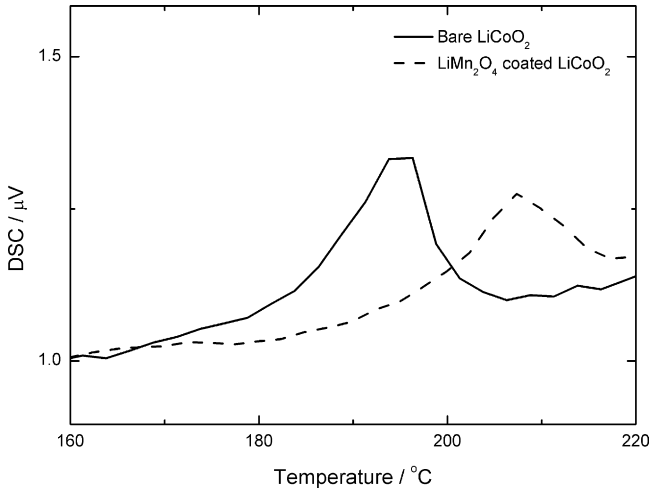

Fig. 3. DSC scans of charged cathodes containing bare and $LiMn_2O_4$-coated $LiCoO_2$. All the samples were equilibrated at 4.3 V before the DSC experiments.

Auger electron spectroscopy (AES) was carried out to examine the distribution of Mn atoms near the film surface. Fig. 4 shows concentration profiles of $LiMn_2O_4$-coated $LiCoO_2$ film by the AES analysis. The concentration profiles clearly show that the Mn atoms are distributed only at the film surface region. It is reasonable that the relatively low firing temperature of 400 °C limits diffusion of Mn ions inside the $LiCoO_2$ film resulting in the formation of a thin-film solid solution ($LiCo_xMn_{2-x}O_4$) at the surface region.

Fig. 5 shows normalized Mn $L_{II,III}$-edge X-ray absorption spectra of $LiMn_2O_4$ and $LiMn_2O_4$-coated $LiCoO_2$ film using total electron yield mode that is surface sensitive (within ~50 Å). Because of the electric-dipole-allowed $2p \rightarrow 3d$ transition, the absorption peaks for the metal $L_{II,III}$-edge XAS are relatively intense and are very sensitive to the oxidation state, spin state, and bond covalency. The electronic structure of the Mn ions in the surface of $LiMn_2O_4$-coated $LiCoO_2$ film can be investigated qualitatively through peak features in the XAS spectra. There are two main peaks of L_{III} and L_{II} edges which are due to electronic

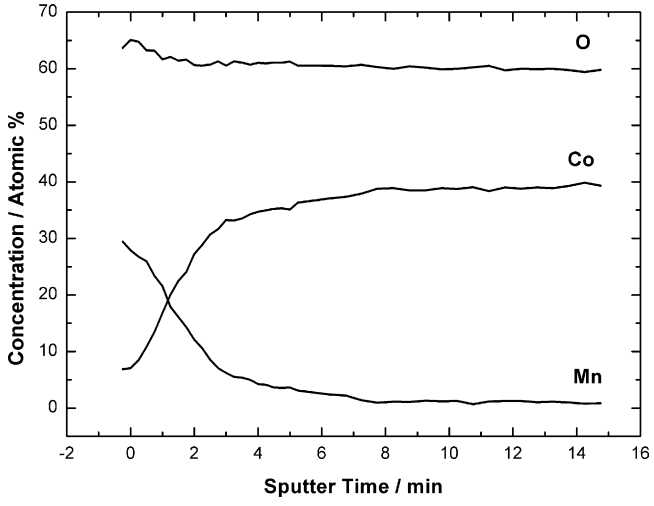

Fig. 4. Concentration profiles of $LiMn_2O_4$-coated $LiCoO_2$ film by the AES analysis.

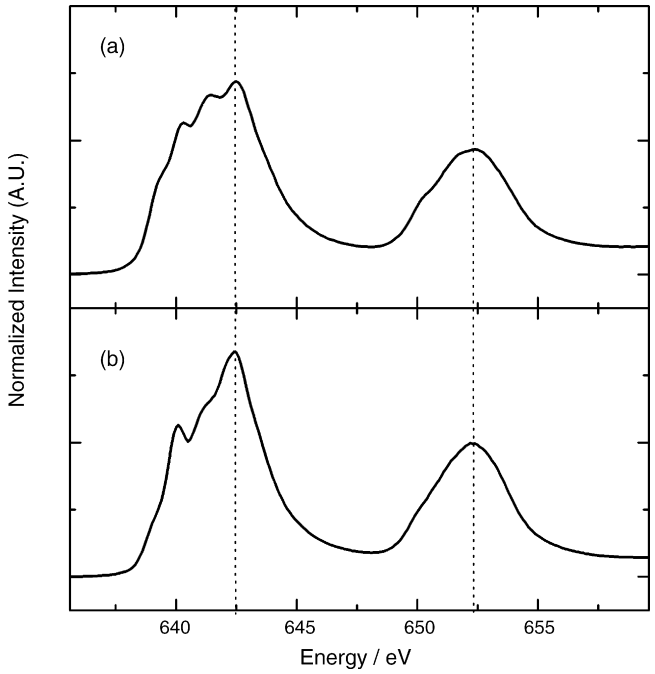

Fig. 5. Normalized Mn $L_{II,III}$-edge X-ray absorption spectra of (a) $LiMn_2O_4$ and (b) $LiMn_2O_4$-coated $LiCoO_2$ film.

transitions of Mn $2p_{3/2}$ and $2p_{1/2}$ core electrons, split by the spin–orbit interaction of the Mn 2p core level, to an unoccupied 3d level hybridized with oxygen 2p orbital, respectively. The Mn $L_{II,III}$-edge XAS spectrum of $LiMn_2O_4$-coated $LiCoO_2$ film is slightly different from that of $LiMn_2O_4$. Based on the earlier soft XAS results of $Li_{1-x}Mn_2O_4$ during charge [18], it is clear that the oxidation state of Mn ions at the surface of $LiMn_2O_4$-coated $LiCoO_2$ film is slightly higher than 3.5, which suggests that the structure at the surface of $LiMn_2O_4$-coated $LiCoO_2$ film is a spinel $LiCo_xMn_{2-x}O_4$. In order to make a clear comparison, we reproduce the Mn L-edge XAS spectra of $Li_{1-x}Mn_2O_4$ during charge in Fig. 6.

Fig. 7 shows normalized O K-edge X-ray absorption spectra of $LiMn_2O_4$ and $LiMn_2O_4$-coated $LiCoO_2$ film. The spectrum of $LiMn_2O_4$ shows intense absorption peaks (A and B) at ~530 and ~532 eV and broad higher energy peaks (C and D) above 535 eV. The first intense pre-edge peaks (A and B) corresponds to the transition of oxygen 1s electron to the hybridized state of Mn 3d and oxygen 2p orbitals, whereas the broad higher energy peaks correspond to the transitions to hybridized states of oxygen 2p and Mn 4sp orbitals. Although the oxygen $1s \rightarrow$ Mn 3d transition is forbidden by the electric-dipole approximation, the appearance of the absorption peak is caused by the hybridization of Mn 3d and oxygen 2p orbitals. In this case, the first structure at 531 eV is assigned to a superposition of majority (spin-up) e_g and minority (spin-down) t_{2g} bands. On the other hand, the second structure at 533 eV is attributed to a band of minority e_g character. The peak features in the spectrum of $LiMn_2O_4$-coated $LiCoO_2$ film is very similar to that of $LiMn_2O_4$ suggesting that the surface coating layer has spinel $LiMn_2O_4$-based structure. It is observed that the pre-edge peaks (A and B) of $LiMn_2O_4$-coated $LiCoO_2$ film slightly shifted to the higher energy, which

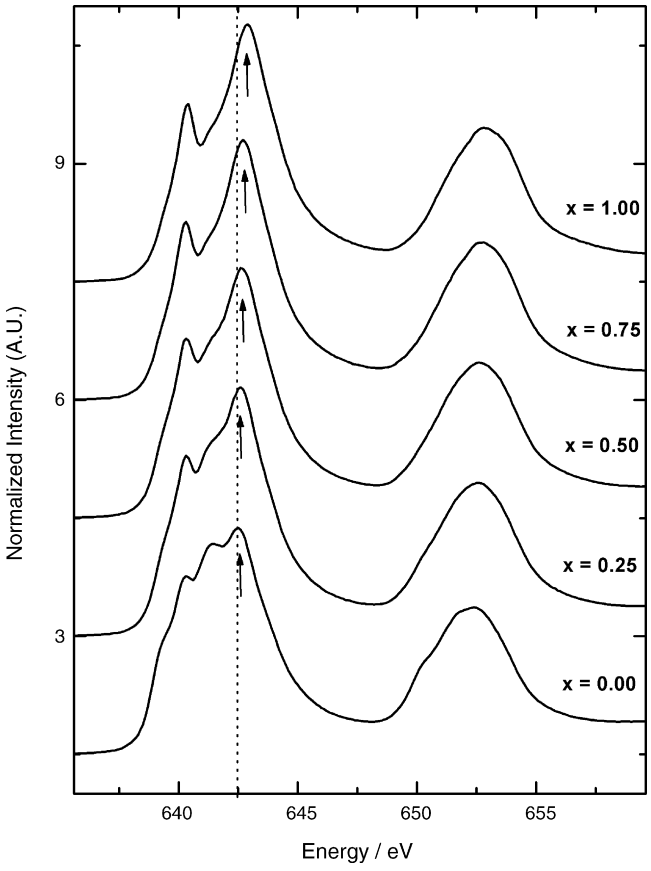

Fig. 6. Normalized Mn $L_{II,III}$-edge X-ray absorption spectra of $Li_{1-x}Mn_2O_4$ system with respect to the x value.

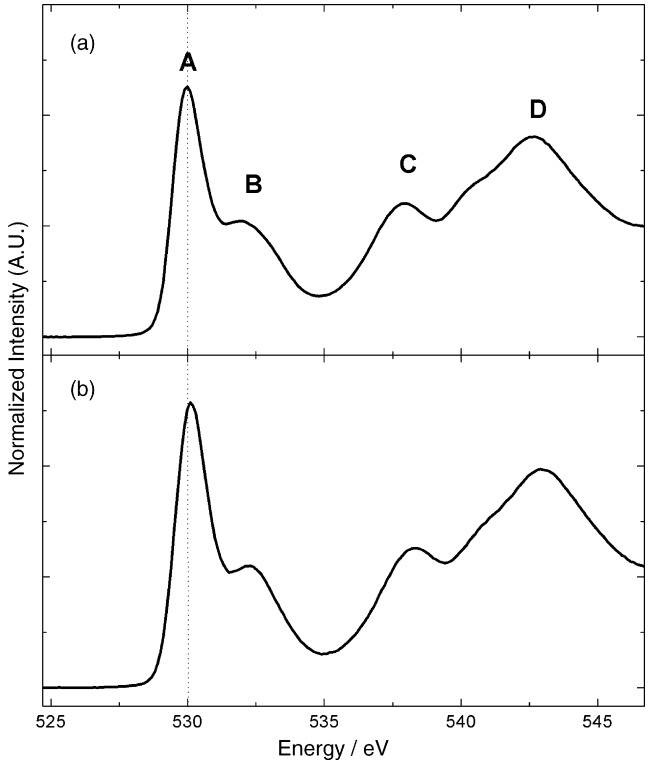

Fig. 7. Normalized O K-edge X-ray absorption spectra of (a) $LiMn_2O_4$ and (b) $LiMn_2O_4$-coated $LiCoO_2$ film.

could be attributed to Co-doping effect in the spinel $LiMn_2O_4$ structure.

4. Conclusions

The $LiMn_2O_4$-coated $LiCoO_2$ film electrode was successfully synthesized by ESD method. XRD and CV results showed that $LiMn_2O_4$-coated $LiCoO_2$ film electrode is very similar to conventional $LiCoO_2$ film electrode in terms of bulk structure and electrochemical property. However, DSC results revealed that $LiMn_2O_4$-coated $LiCoO_2$ film show better thermal stability than bare $LiCoO_2$ film. AES results showed that the Mn atoms are distributed only at the film surface region. From the observation of soft XAS spectra at the O K-edge and the Mn L-edge, it is concluded that the structure at the surface of $LiMn_2O_4$-coated $LiCoO_2$ film is spinel $LiCo_xMn_{2-x}O_4$.

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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, Prog. Batt. Solar Cells 9 (1991) 209.
[3] B. Wang, J.B. Bates, F.X. Hart, B.C. Sales, R.A. Zuhr, J.D. Robertson, J. Electrochem. Soc. 143 (1996) 3203.
[4] C. Chen, E.M. Kelder, M.J.G. Jak, J. Schoonman, Solid State Ionics 86–88 (1996) 1301.
[5] C. Chen, E.M. Kelder, P.J.J.M. van der Put, J. Schoonman, J. Mater. Chem. 6 (1996) 765.
[6] J. Cho, G.B. Kim, H.S. Lim, C.S. Kim, S.-I. Yoo, Electrochem. Solid State Lett. 2 (1999) 607.
[7] J. Cho, Y.J. Kim, T.J. Kim, B. Park, Chem. Mater. 13 (2001) 18.
[8] Y.J. Kim, T.J. Kim, J.W. Shin, B. Park, J. Cho, J. Electrochem. Soc. 149 (2002) A1337.
[9] A. Montoro, M. Abbate, J.M. Rosolen, J. Electrochem. Soc. 147 (2000) 1651.
[10] Y. Uchimoto, H. Sawada, T. Yao, J. Synchrotron. Rad. 8 (2001) 872.
[11] W.-S. Yoon, K.-B. Kim, M.-G. Kim, M.-K. Lee, H.-J. Shin, J.-M. Lee, J.-S. Lee, C.-H. Yo, J. Phys. Chem. B 106 (2002) 2526.
[12] F.M.F. de Groot, J. Electron Spectrosc. Relat. Phenom. 67 (1994) 529.
[13] W.-S. Yoon, S.-H. Ban, K.-K. Lee, K.-B. Kim, M.G. Kim, J.M. Lee, J. Power Sources 97–98 (2001) 282.
[14] T.N. Lee, M.H. Yoon, Y.S. Kim, H.G. Kim, Aust. J. Phys. 48 (1995) 321.
[15] H.J. Shin, Y. Chung, B. Kim, J. Synchrotron. Rad. 5 (1998) 648.
[16] I. Uchida, H. Saito, J. Electrochem. Soc. 142 (1995) L139.
[17] Z. Zhang, D. Fouchard, J.R. Rea, J. Power Sources 70 (1998) 16.
[18] W.-S. Yoon, K.Y. Chung, K.-H. Oh, K.-B. Kim, J. Power Sources 119 (2003) 706.