

Short communication

Surface and bulk structure investigation of fully delithiated bare and AlPO₄-coated Li_xCoO₂ ($x = 0$) cathode materials annealed between 200 and 400 °C

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Available online 27 June 2007

Abstract

The surface and bulk structure of the fully delithiated bare and AlPO₄-coated Li_xCoO₂ cathode materials ($x = 0$) between 200 and 400 °C were investigated using high resolution XRD, XAS (X-ray absorption spectroscopy), TEM, and solid-state NMR. Bare and coated CoO₂ cathodes showed different phase transformation between 200 and 400 °C. The bare samples exhibited only the O1-CoO₂ phase in the fully delithiated state, but the CoO₂ phase was converted to the Co₃O₄ phase at higher temperatures. On the other hand, the AlPO₄-coated Li_xCoO₂ at $x = 0$ showed a mixture of phases including the major O1-type CoO₂ and minor Co₃O₄ spinel phases in the fully delithiated state. When annealing temperatures increased from 200 to 400 °C, the bare samples showed a slow phase transition to Co₃O₄ and were completely transformed into the thermally stable Co₃O₄ spinel phase at 400 °C. The coated samples, however, were completely transformed into the spinel phase alone at 200 °C. We believe that the AlPO₄ coating layer accelerated the phase transition to the spinel phase at lower temperatures. TEM and XAS results showed that structural damages were mainly confined to the cathode particle surface, and this phenomenon was only observed in the bare samples.

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Keywords: Li_xCoO₂; AlPO₄ coating; Structure; Surface; Annealing temperature

1. Introduction

Generally, Li_xCoO₂ shows a monoclinic, H1-3 and O1-type structural transformation upon delithiation out to $x \sim 0$ at room temperature, and the XRD pattern of the completely delithiated LiCoO₂ is indexed to the hexagonal unit cell in the space group of *P3m1* (CdI₂ or O1-type) [1]. In contrast, at elevated temperatures, Li_xCoO₂ exhibits phase transitions to a spinel Co₃O₄, and CoO or Co at Li_xCoO₂ ($x = 0.5$) depending on the temperature [2]. MacNeil et al. reported that the reaction between Li_{0.5}CoO₂ and the electrolytes led to the formation of the Co₃O₄, CoO and Co phases at 400 °C. Similarly, chemically delithiated Li_{0.49}CoO₂ showed a phase transition to the spinel phases (Li_xCo₂O₄ or Co₃O₄) from the O3-type LiCoO₂ above 300 °C [3]. On the other hand, Lee et al. reported the phase transitions of

AlPO₄-coated delithiated Li_xCoO₂ ($x = 0.4$ and 0.24) with varying coating concentrations (thicknesses) after heat-treatment at 300 °C. As the charging voltage was increased from 4.3 to 4.6 V, the bare and 1 wt.% AlPO₄-coated Li_xCoO₂ decomposed into the Li_xCo₂O₄ phase while the 2.4 wt.% AlPO₄-coated sample decomposed into the Co₃O₄ phase [4]. On the other hand, spinel Li_xCo₂O₄, which has a cubic spinel phase with an *Fd3m* space group, transforms to the O3-type LiCoO₂ upon heating. Moreover, it was reported that the spinel Li_xCo₂O₄ phase was initially formed on the particle surface [5]. However, there are few structural investigations at temperatures above 4.6 V, i.e., $x = 0.24$ in Li_xCoO₂, and, to our best knowledge, the phase transformation of the cathode with variations in temperature in the fully delithiated state ($x = 0$ in Li_xCoO₂) has not been examined.

In this study, the structural changes of the bare and AlPO₄-coated Li_xCoO₂ cathodes ($x = 0$) materials annealed at 200, 300 and 400 °C were investigated using high resolution XRD, TEM, XAS and solid-state NMR.

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2. Experimental

LiCoO₂ powders with an average particle size of 10 μm were prepared by a direct reaction between LiOH·H₂O and Co₃O₄ (average particle size of 5 μm) at 1000 °C for 4 h under an oxygen atmosphere. An inductively coupled plasma (ICP) analysis showed that the Li content in Li_xCoO₂ was 1.01. To prepare the AlPO₄ coating on the cathode, the appropriate amounts of Al nitrate and (NH₄)₂HPO₄ such that the weight ratio of AlPO₄ to LiCoO₂ was 8:92 were dissolved in distilled water and mixed with LiCoO₂ powders. More detailed procedures are described elsewhere [6]. A pouch-type Li-ion cell standard capacity with 20 mAh was used in order to get fully delithiated Li_xCoO₂ cathodes ($x=0$). Either the AlPO₄ nanoparticle-coated LiCoO₂ or the bare LiCoO₂ was used as the cathode and the anode material was synthetic graphite. The electrolyte used consisted of 1.03 M LiPF₆ that also contained ethylene carbonate/diethylene carbonate/ethyl-methyl carbonate (EC/DEC/EMC: 3/3/4 vol.%) (Cheil Ind. Korea). The fresh Li-ion cell was charged to 5 V at a constant current and was maintained at this voltage for 2 h in constant voltage mode. The results of an ICP–MS analysis of the cathodes showed no trace of Li in the cathode. After completing a 5 V charge, the cathodes extracted from the cell were hermetically sealed in Al sample pans and then the temperature was varied from 200–300 to 400 °C in an oven and these various temperatures were maintained for 1 h.

The ⁵⁹Co MAS NMR measurements were carried out at room temperature on a Bruker DSX 400 NMR spectrometer with a 9.4 T magnet. For MAS NMR experiments, a 2.5 mm CP–MAS probe was used with a zirconia rotor at 96.85 MHz for the ⁵⁹Co resonance frequency. A sample spinning speed of 32 kHz was used. The spectra were referenced to an external 1 M K₃[Co(CN)₆] aqueous solution for ⁵⁹Co NMR. A 90° pulse length of 1 μs, a repetition delay of 1 s, and a spectral width of 1 MHz were used for the ⁵⁹Co NMR spectra. The isotropic chemical shifts were identified by varying the sample spinning rates.

The Co K-edge X-ray absorption spectroscopic study for the thermal phase transition of the bare and AlPO₄-coated Li_xCoO₂ were carried out on the BL7C (Electrochemistry) beamline at the Pohang Light Source (PLS), which is a third generation synchrotron radiation source, in the 2.5 GeV storage ring with a ring current of 120–170 mA. A Si(1 1 1) double crystal monochromator was used to monochromatize the X-ray photon energy. Higher order harmonic contaminations were eliminated by detuning the monochromator in order to reduce the incident X-ray intensity by ~30%. The incident X-ray intensity was monitored using pure nitrogen gas-filled ionization chambers. The spectroscopic data was collected in transmittance mode. The energy calibration was made using standard Co metal foil.

3. Results and discussion

Fig. 1 shows the XRD patterns of the samples after the annealing of the fully delithiated bare samples. The sample showed a mixed phase of O1-CoO₂ and CoOOH, due to a reaction of CoO₂ with water in air which likely occurred when the CoO₂

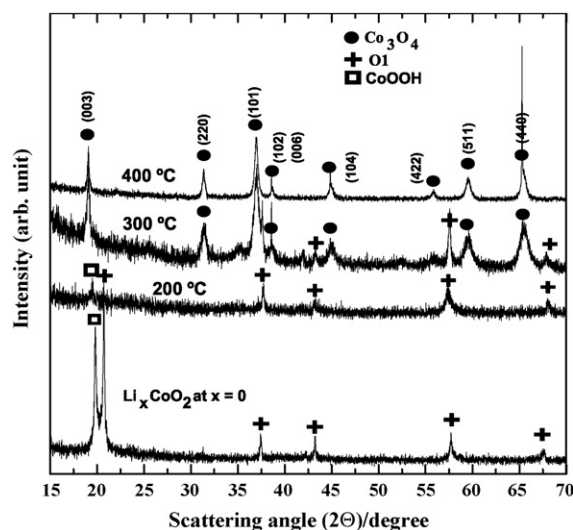


Fig. 1. XRD patterns of the bare Li_xCoO₂ cathodes ($x=0$) annealed at different temperatures: 200, 300 and 400 °C.

powder was air-exposed for 3 h during the XRD experiments. It has been reported that CoO₂ is very sensitive to air and transforms into the CoOOH phase upon air-exposure [1]. At 200 °C, a fully delithiated Li_xCoO₂ cathode, i.e., O1-type CoO₂, was maintained, indicating that CoO₂ was not fully decomposed into other phases. At 300 °C, the formation of the Co₃O₄ phase was due to an oxygen loss from the CoO₂ phase, according to the following reaction: 3CoO₂ → Co₃O₄ + O₂↑. In addition, the increased intensity of the Co₃O₄ spinel phase at 400 °C showed a similar trend to that observed in Li_{0.5}CoO₂ heat-treated above 400 °C [7].

Unlike the bare cathode, the AlPO₄-coated cathodes showed a different set of phase transitions with respect to increasing temperatures, as shown in Fig. 2. At $x=0$, the O1-CoO₂ phase was the major phase with the Co₃O₄ spinel phase occurring as a minor phase, but the latter phase was completely absent from the bare sample. The AlPO₄ coating was believed to play a major

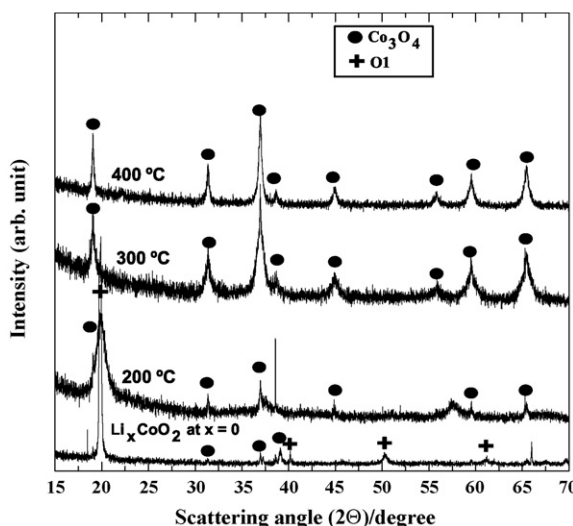


Fig. 2. XRD patterns of the AlPO₄-coated Li_xCoO₂ electrodes ($x=0$) annealed at different temperatures: 200, 300 and 400 °C.

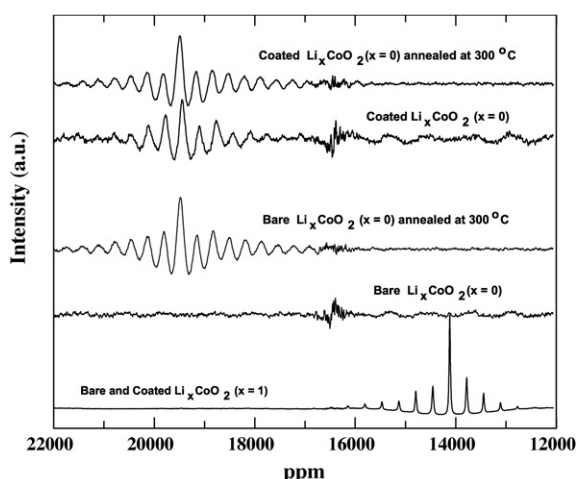


Fig. 3. ^{59}Co MAS NMR spectra of the bare and AlPO_4 -coated Li_xCoO_2 ($x=1$ and 0) and annealed at 400°C .

role in the early decomposition of the CoO_2 phase into the Co_3O_4 phase at 5 V. Upon increasing temperature from 200 to 300°C , the CoO_2 phase completely disappeared and only Co_3O_4 spinel peaks grew. This type of spinel phase was expected to be rather disordered because it was obtained through cationic migrations occurring at low temperature, which contrasted with the spinel phases that were directly synthesized at high temperature.

^{59}Co MAS NMR studies were carried out to investigate the local environment of the cobalt atoms for the bare and AlPO_4 -coated Li_xCoO_2 cathodes with $x=0$ and subsequent annealing at 300°C , as shown in Fig. 3. The ^{59}Co NMR spectrum of the bare $\text{Li}_{1.01}\text{CoO}_2$ showed a typical single resonance with spinning sidebands around 14,200 ppm due to the Co^{3+} in the octahedral sites being in a layered structure, as expected. Because of the inherent difficulties with conventional NMR systems, we were unable to find the peak corresponding to CoO_2 in our spectrum for the bare Li_xCoO_2 at $x=0$, since it only contained paramagnetic Co^{4+} , which is expected to show very broad ^{59}Co NMR lines due to a shortened spin–spin relaxation time (T_2). Heat treatment of the Li_xCoO_2 at 300°C gave a single resonance at $\sim 19,500$ ppm, which is in good agreement with previous work [3]. At room temperature, the single resonance of Co_3O_4 assigned to Co^{3+} at the octahedral sites was observed. The large spinning sidebands seen in the Co spectra were as likely to originate from the dipolar coupling to the unpaired electrons on the Co^{2+} spins as from quadrupolar interactions. The ^{59}Co NMR spectra of the AlPO_4 -coated Li_xCoO_2 at $x=0$ and annealed at 300°C are also shown in Fig. 3. Opposite of the bare Li_xCoO_2 at $x=0$, the spectra of this sample at $x=0$ exhibited a resonance around 19,500 ppm, which was assigned to the Co^{3+} of the Co_3O_4 spinel at the octahedral sites. This result was in accordance with the XRD results.

Fig. 4 shows the normalized Co K-edge XANES (X-ray absorption near edge structure) features for the bare and AlPO_4 -coated Li_xCoO_2 ($x=0$) annealed at 300°C in addition to the reference Co_3O_4 .

A pre-edge peak (1s–3d transition, denoted by peak A), shoulder peaks (ligand to metal charge transfer process, peak B1 and

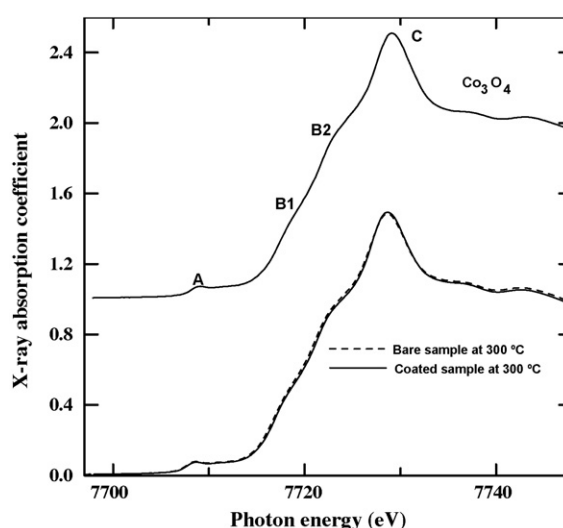


Fig. 4. Normalized Co K-edge XANES features for the reference Co_3O_4 and the bare and coated sample heat-treated at 300°C .

B2) and a white line (1s–4p transition, peak C) are characteristic peak features for the spinel Co_3O_4 structure. Based on the pre-edge peak position and the shoulder peak features, the XANES spectra for the annealed samples of the bare and AlPO_4 -coated samples were identical to that of the Co_3O_4 spinel phase, indicating the bulk structure of the bare samples at higher temperatures is quite similar to that of the coated samples.

In order to investigate the difference in surface structure of both bare and coated samples, TEM analysis of the samples annealed at 300°C was carried out at first. Fig. 5a shows a low magnification bright field TEM image of the bare Li_xCoO_2 ($x=0$) at 300°C . Without a coating, a non-uniform contrast near the edge of the particle resulting from structural defects or lattice strain indicated that the structure was severely damaged. The HREM image of Fig. 5b shows that the contrast near the edge is substantially different from the interior, and the transition is quite abrupt. This suggested that structural defects may be mainly confined to the edge of the particle, as can be seen from the magnified images of the regions labeled A and B shown in Fig. 5b. Indeed, the arrows in Fig. 5c, magnified image of region B of Fig. 5b denote the transition boundary from one structural image to another. The two such markedly different HRTEM structural images in Fig. 5c suggest either an abrupt difference in the sample thickness arising from particle surface roughness or the existence of a different crystal structure at the edge of the sample arising from an electrolyte reaction. It can be also observed that the particle surface was indeed quite rough on the microscopic scale, which indicated a chemical attack.

However, the AlPO_4 -coated sample annealed at 300°C clearly demonstrated evidence for a reduced structural damage of the coated sample as shown by the magnified image of the particle edge (Fig. 6).

The electron diffraction patterns shown in Fig. 7 were obtained from the fringes in the individual particles of the bare and AlPO_4 -coated cathode heated to 300°C . The appearance of the [1 1 0] zone in the diffraction patterns in Fig. 7(a and b) suggest that Li_xCoO_2 ($x=0$) particles have been converted to a

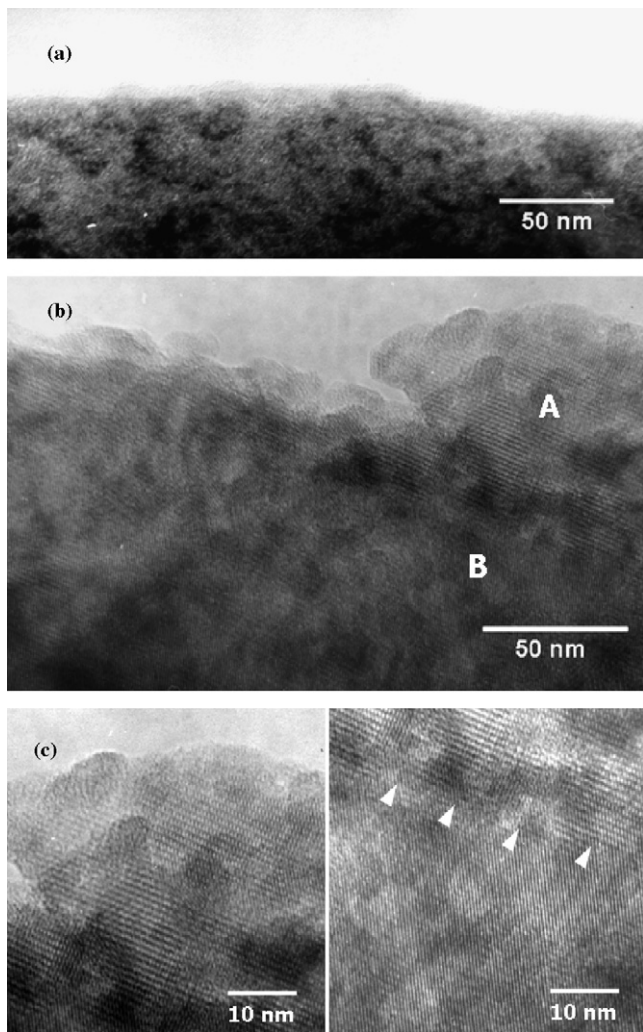


Fig. 5. (a) Bright field TEM image of the bare Li_xCoO_2 ($x=0$) cathode at 300 °C; (b) [1 1 0] zone HRTEM image of the bare Li_xCoO_2 ($x=0$) cathode at 300 °C; (c) magnified images of the regions of (b) (the arrows indicate the boundary at which the structural contrast is abruptly altered).

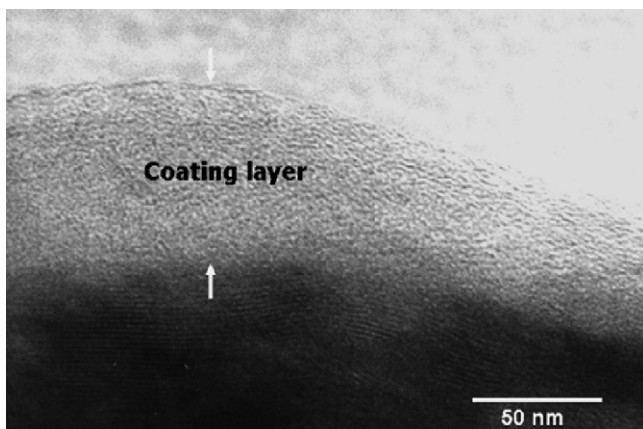


Fig. 6. TEM image of the AlPO_4 -coated Li_xCoO_2 cathode ($x=0$) at 300 °C which shows an intact coating layer.

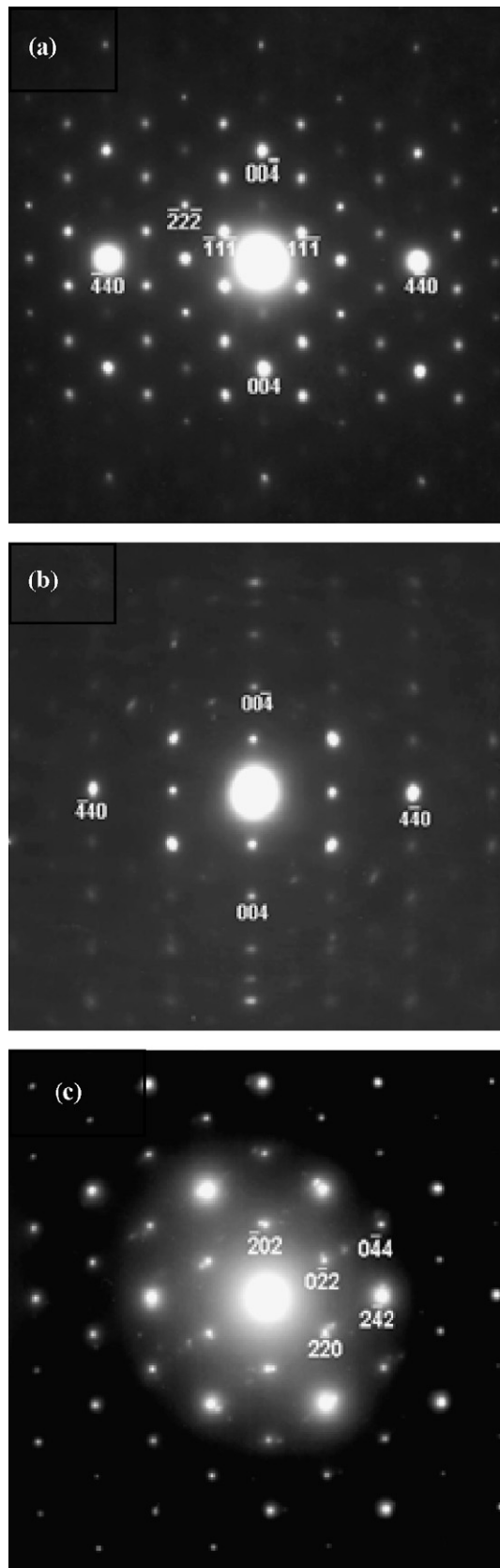


Fig. 7. Electron diffraction patterns: (a) [1 1 0] zone from the bare Li_xCoO_2 cathode ($x=0$) at 200 °C, retaining perfect spinel symmetry; (b) [1 1 0] zone from a structurally damaged particle from the bare Li_xCoO_2 cathode with $x=0$ at 300 °C; (c) [1 1 1] zone from the AlPO_4 -coated Li_xCoO_2 cathode with $x=0$ at 300 °C.

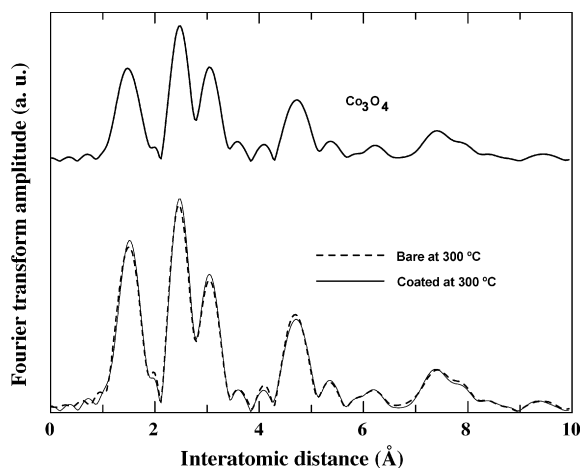


Fig. 8. Fourier transform (FT) magnitudes of the Co K-edge k^3 -weighted EXAFS spectra for the reference Co_3O_4 , bare and coated sample heat-treated at 300°C .

spinel structure during thermal annealing. The diffraction pattern in Fig. 7a shows perfect spinel symmetry in the $[1\ 1\ 0]$ zone. However, Fig. 7b shows a completely different pattern, which is largely due to the missing $\{1\ 1\ 1\}$ peaks and weak $\{1\ 1\ 3\}$ peaks, even though both patterns were identically indexed to the $[1\ 1\ 0]$ zone. In this particle, it appeared that the site disordering of Co and O within the lattice led to a change in the peak intensity, almost destroying the spinel symmetry.

On the other hand, all of the observed particles from the fringe in the AlPO_4 -coated sample at 300°C maintained the spinel symmetry, as shown in the $[1\ 1\ 1]$ zone of the electron diffraction pattern taken from one of the particles (Fig. 7c).

This suggested that the particle did not undergo extensive structural disorder, which differed from the bare sample. However, we cannot rule out the possibility that such a structural disorder of the spinel phase may be confined to the fringes of the particles in which a direct reaction with the electrolyte occurred. In order to verify the degree of the structural disorder, we carried out EXAFS (extended X-ray absorption fine structure) of the samples annealed at 300°C .

Fig. 8 shows the Fourier transform (FT) magnitudes of the Co K-edge k^3 -weighted EXAFS (extended X-ray absorption fine structure) for the reference Co_3O_4 and the bare and coated sam-

ple heat-treated at 300°C . For Co_3O_4 , the first FT peak at $\sim 1.6\ \text{\AA}$ corresponded to six Co–O bonds and the second FT at $\sim 2.5\ \text{\AA}$ represented a six edge-shared CoO_6 octahedra. The FT peak was generated at $\sim 3.0\ \text{\AA}$, which corresponded to corner-shared CoO_6 octahedra. As can be seen in Fig. 8, the main interatomic distances between Co and oxygen in both samples were almost identical to each other. This supported the evidence that the spinel structural disorder in the bare sample was only limited to the particle surfaces.

4. Conclusion

Bare and coated Li_xCoO_2 cathodes ($x=0$) showed different phase transformation paths during heating from 200 to 400°C . Bare cathodes showed a stepwise phase transition to the Co_3O_4 spinel phase from the O1-CoO_2 phase, turning into the Co_3O_4 phase at 400°C . On the other hand, the AlPO_4 -coated cathodes showed a mixed phase of Co_3O_4 and CoO_2 after completely removing Li from Li_xCoO_2 , but showed the complete Co_3O_4 spinel transition only at 200°C . The overall degree of structural disorder of the bare samples was quite similar to that of the coated samples after annealing, but the surface structures of the bare cathodes were shown to be severely damaged in contrast to the coated cathodes.

Acknowledgement

We are grateful to the authorities of the Pohang Light Source (PLS) for XAS and high resolution XRD measurements. This study was supported by ITRC project.

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