Short communication

Structural changes of bare and AlPO$_4$-coated Li$_x$CoO$_2$ ($x = 0.24$ and 0.1) upon thermal annealing $\geq 200°C$

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Abstract

Structural changes of bare and AlPO$_4$-coated Li$_x$CoO$_2$ with a coating thickness of 20 and 200 nm are investigated at $x = 0.24$ and 0.1 after thermal annealing at 200, 300, and 400 °C using XRD and Co K-edge XANES (X-ray absorption near-edge structure) and EXAFS (extended X-ray absorption fine structure). Both the bare and coated cathodes exhibit faster phase transformation into spinel phases at lower annealing temperatures as x in Li$_x$CoO$_2$ is decreased. Bare Li$_x$CoO$_2$ cathodes exhibit phase transitions from Li$_x$Co$_2$O$_4$ to Co$_3$O$_4$ spinel as the annealing temperature is increased and the x is value decreased, which suggests a possible reaction according to $(1/2)$Li$_x$Co$_2$O$_4 \rightarrow x$Li$_2$CO$_3 + (1/3)$Co$_3$O$_4 + (2/3)$O$_2$. However, the coated cathodes sustain a Li$_x$Co$_2$O$_4$ phase even at 400 °C and $x = 0.1$. This indicates that the AlPO$_4$ coating layer suppresses the Li$_x$Co$_2$O$_4$ phase decomposition into Co$_3$O$_4$.
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1. Introduction

Cathode materials that determine the thermal safety of Li-ion cells self-accelerate oxygen generation from their lattices as a result of exothermic reactions with electrolytes at elevated temperatures. In particular, oxygen that is emitted from LiCoO$_2$ leads to the formation of Li$_x$Co$_2$O$_4$ or Co$_3$O$_4$ depending on the temperature and lithium content (x). Previous studies of phase transformations in Li$_x$CoO$_2$ have been limited to x values larger than 0.45. Choi et al. [1] reported that delithiated Li$_{0.5}$CoO$_2$ undergoes a phase transition to spinel Li$_x$Co$_2$O$_4$ at 300 °C, and that Li$_x$Co$_2$O$_4$ transforms to the Co$_3$O$_4$-type spinel phase above 400 °C [1]. They proposed that Li$_{0.5}$CoO$_2$ is disproportionated into LiCoO$_2$ and the Co$_3$O$_4$ phase above 400 °C according to the reaction Li$_{0.5}$CoO$_2 \rightarrow 12$LiCoO$_2 + 16$Co$_3$O$_4$.

Similar results to those discussed above were reported by MacNeil et al. [2]. They concluded that the exothermic reaction of Li$_{0.5}$CoO$_2$ in the presence of sufficient solvent proceeds as the temperature is increased, as follows: Li$_{0.5}$CoO$_2 \rightarrow 12$LiCoO$_2 + 16$Co$_3$O$_4 \rightarrow 12$LiCoO$_2 + 1$CoO $\rightarrow$ Co $+ 14$Li$_2$CO$_3$ [2]. If a small amount of solvent was present relative to the amount of Li$_{0.5}$CoO$_2$, the final reaction does not occur, at least at temperatures below 450 °C. Using high-temperature X-ray diffraction (XRD), Baba et al. [3] found that monoclinic Li$_{0.49}$CoO$_2$ ($C2/m$) transforms to a spinel Li$_x$Co$_2$O$_4$ structure ($Fd3m$) at 220 °C [3]. At 350 °C, XRD analysis revealed a mixture of hexagonal LiCoO$_2$ and spinel Co$_3$O$_4$ ($Fd3m$) phases. Recently, Lee et al. [4] compared the structural stability of bare and AlPO$_4$-coated cathodes, which had coating thicknesses of approximately 15 and 200 nm at $x = 0.4$ and 0.24 upon thermal annealing of the cathodes at a temperature of 300 °C using NMR and X-ray absorption spectroscopy [4]. They found that as the x value decreased from 0.4 to 0.24, the AlPO$_4$-coated cathode with a 200-nm coating

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exhibited dominant local formation of the Co_3O_4 phase over the $Li_xCo_2O_4$ phase compared with a bare cathode as well as that with a 20-nm coating.

In the present study, the temperature range of the structural investigation is extended to 400 °C while that of x in Li_xCoO_2 is set between 0.24 and 0.1 using bare and $AlPO_4$-coated cathodes with thicknesses ranging approximately from 20 to 200 nm.

2. Experimental methods

The $LiCoO_2$ used in this study had lattice constants of $a = 2.816 \pm 0.004$ Å and $c = 14.034 \pm 0.043$ Å, and a Brunauer, Emmett, and Teller (BET) surface area of $0.5 \, m^2 \, g^{-1}$. $AlPO_4$-coated samples with a coating thickness of approximately 20 nm were prepared via the mixing and firing of 100 g of $LiCoO_2$ powder and precipitated $AlPO_4$ nanoparticles obtained from 1 g of $Al(NO_3)_3 \cdot 9H_2O$ and 0.38 g of $(NH_4)_2HPO_4$ previously dissolved in distilled water. $AlPO_4$-coated samples with a coating thickness of ~200 nm were prepared via the mixing and firing of 100 g of $LiCoO_2$ powder and precipitated $AlPO_4$ nanoparticles obtained from 10 g of $Al(NO_3)_3 \cdot 9H_2O$ and 3.8 g of $(NH_4)_2HPO_4$. Details of the coating method have been described in the literatures [5,6]. The charged electrode samples were prepared in a 2016R-type coin cell using Li metal as the negative (anode) electrode. The electrodes were prepared by combining 3 wt.% each of Super P carbon black and polyvinylidene fluoride (PVDF) with 94 wt.% $LiCoO_2$ powders. 1 M of $LiPF_6$ in ethylene carbonate (EC)/diethyl carbonate (DEC) (33:67 vol.%) electrolyte (Cheil Industries, Korea) served as the electrolyte, and a polypropylene separator was used. The cells were initially charged to either 4.4 or 4.7 V (which corresponded to $x = 0.24$ and 0.1 in Li_xCoO_2, respectively), with a current of 0.15 mA. They were then stabilized at these voltages for 2 h in a constant-voltage mode. The charged coin cells were transferred to an argon-filled glove box, and the cathode electrodes were removed and scratched in order to collect the cathode composite soaked with the electrolyte. They were then transferred into aluminium sample pans for sealing. The sealed sample pan was heated to 300 °C at a rate of 5 °C min^{-1} and then held at this temperature for 30 min. This process was followed by slow cooling to room temperature.

A Co K-edge X-ray absorption spectroscopic study of the thermal phase transition of bare and $AlPO_4$-coated $LiCoO_2$ samples was carried out on the BL7C (Electrochemistry) beamline at the Pohang Light Source (PLS), 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 about 30%. The incident X-ray intensity was monitored using ionization chambers filled with pure nitrogen. The spectroscopic data was collected in transmittance mode. Energy calibration was made using a standard Co metal foil.

3. Results and discussion

Fig. 1 shows the XRD patterns of bare and coated Li_xCoO_2 samples with ~20 and ~200 nm coatings at $x = 0.24$ before and after annealing between 200 and 400 °C. Upon thermal annealing at 200 °C, the two sets of peaks (0 0 6)/(1 0 2) and (0 1 8)/(1 1 0) merge into single peaks, which indicates a gradual structural change from Li_xCoO_2 to spinel phases. Unlike bare and coated cathodes annealed at 200 °C, the samples annealed at 300 and 400 °C have fully merged (0 0 6)/(1 0 2) and (0 1 8)/(1 1 0) peaks, which signifies a smaller c/a ratio, and in turn, the formation of a cubic spinel phase. There are two spinel phases, namely, $Li_xCo_2O_4$ and Co_3O_4 that cannot be easily distinguished from each other. When, however, the peak intensity of the (3 1 1) peak is larger than that of the (1 1 1) peak, a predominant formation of Co_3O_4 over the $Li_xCo_2O_4$ phase can be expected. Accordingly, XRD patterns of bare and coated cath-

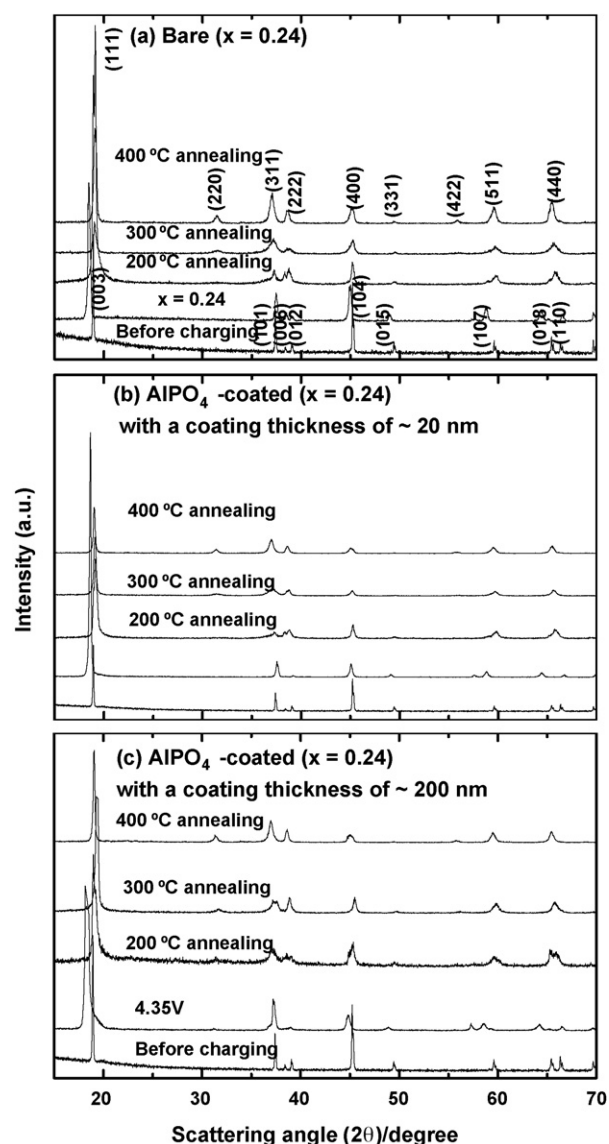Fig. 1. XRD patterns of bare and $AlPO_4$-coated Li_xCoO_2 ($x = 0.24$) with coating thicknesses of ~20 and ~200 nm after annealing at 200, 300 and 400 °C.

odes at $x = 0.24$ show the main formation of the $Li_xCo_2O_4$ phase. In addition, an increasing (2 0 0) peak at $\sim 32°$ is indicative of the development of a Co_3O_4-type spinel phase.

Based on a study by Choi [1], the $Li_{0.5}Co_2O_4$ phase becomes oxygen-deficient, i.e., $LiCo_2O_{4-\delta}$ and starts to lose additional oxygen upon further heating above 200 °C, resulting in the formation of a mixture of $LiCoO_2$ and Co_3O_4. In this case, however when the x value is 0.24, the cathodes annealed at 300 and 400 °C do not show evidence of the formation of a hexagonal layered $LiCoO_2$ phase; instead, the dominant formation of $Li_xCo_2O_4$ spinel phases occurs at 400 °C.

When the x value is 0.1, the XRD patterns of the cathodes differ from those at $x = 0.24$ (Fig. 2). At 200 °C, peak broadening is more developed and the two sets of peaks (0 0 6)/(1 0 2) and (0 1 8)/(1 1 0) are completely merged into single peaks, indicating a complete transformation into the spinel phases. Specifically, as the fraction of Co^{4+} ions increases in the lattice, phase transformation into the spinel phase becomes prevalent. At 300 °C, the peak intensity of (3 1 1) is larger than that of (1 1 1) in the coated sample, showing the preferential formation of $Li_xCo_2O_4$ over Co_3O_4. At 400 °C, however, all peaks indicate the dominant formation of the Co_3O_4 spinel phase.

To obtain detailed information on the structure of 400 °C samples, Rietveld analyses were performed on the bare and the coated samples with thicknesses of approximately 200 nm after thermal annealing at 400 °C. The results for samples with $x = 0.24$ and 0.1 after annealing at 400 °C are given in Table 1. The lattice constant a used for the fitting of $Li_xCo_2O_4$ is 7.992 (JCPDS no. 82-0343) while that for Co_3O_4 is 8.085 (JCPDS no. 78-1970). At $x = 0.24$, the Li contents estimated from the ICP-MS and Rietveld results are similar; the result shows that the $Li_xCo_2O_4$-type spinel phase is dominant. At $x = 0.1$, however, the bare sample shows complete transformation into the Co_3O_4-type spinel, which suggests the possible reaction of $(1/2)Li_xCo_2O_4 \rightarrow xLi_2CO_3 + (1/3)Co_3O_4 + (2/3)O_2$. MacNeil et al. [2] reported the possible formation of Li_2CO_3. $Li_{0.5}CoO_2$ was found to be transformed into $LiCoO_2$ and Co_3O_4 phases according to the following reaction: $6Li_{0.5}CoO_2 \rightarrow 3LiCoO_2 + Co_3O_4 + O_2$. Accordingly, the incongruous result, compared with that presented here, is related to the amount of lithium in Li_xCoO_2.

Cathode decomposition starts on the particle surface and propagates into the core of the particle with increasing temperature. Hence, random nucleation, which is initiated at the
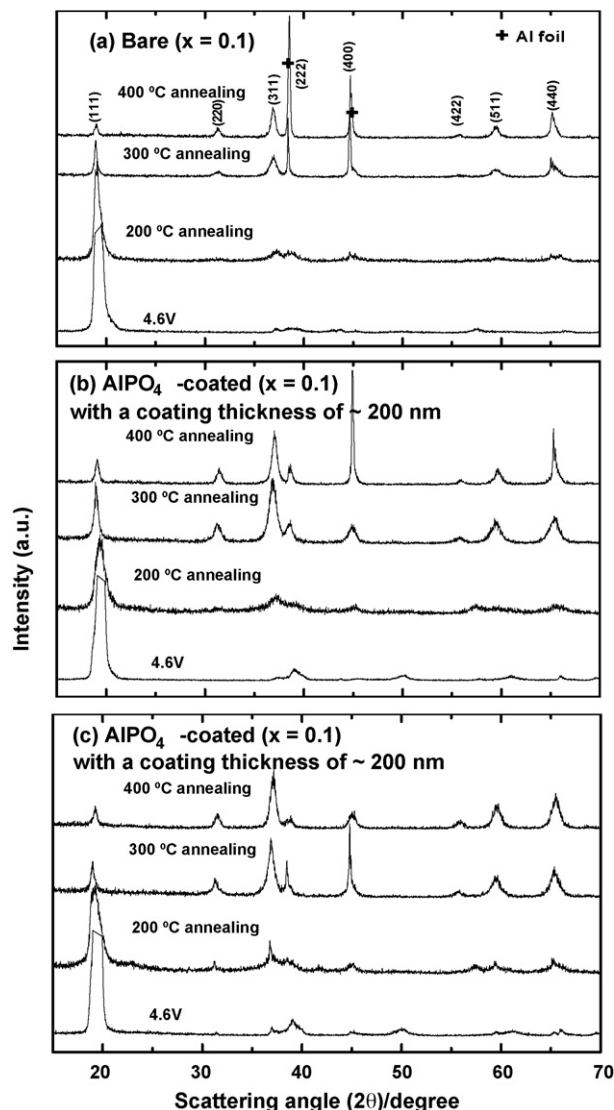

Fig. 2. XRD patterns of bare and $AlPO_4$-coated Li_xCoO_2 ($x = 0.1$) with coating thicknesses of ~ 20 and ~ 200 nm after annealing at 200, 300, and 400 °C.

edges and surface cracks in the particle, occurs. Nuclei of $Li_xCo_2O_4$ and Co_3O_4 form with the release of oxygen, and these phases continue to grow into the particles with increasing temperature [2]. When, however, a thermally stable coating layer exists on the particle surface, its decomposition reactions

Table 1
Rietveld and ICP-MS analyses results of bare and $AlPO_4$-coated Li_xCoO_2 after annealing at 400 °C ($x = 0.24$ and 0.1)

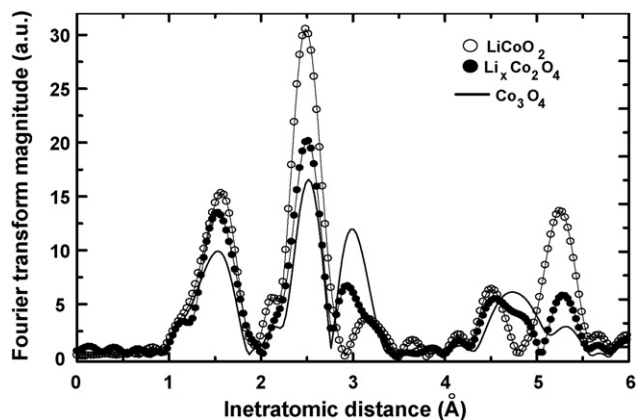| Sample	Lattice constant (a)	Calculated Li content	Calculated composition	Li content (ICP-MS)
$x = 0.24$				
Bare	8.0345(6)	0.25	$Li_{0.25}Co_{0.75}Co_2O_4$	0.241
Coated (~ 20 nm)	8.0238(7)	0.22	$Li_{0.22}Co_{0.78}Co_2O_4$	0.237
Coated (~ 200 nm)	8.0249(7)	0.23	$Li_{0.23}Co_{0.77}Co_2O_4$	0.244
$x = 0.1$				
Bare	8.0345(6)	0	Co_3O_4	0.01
Coated (~ 20 nm)	8.0238(7)	0.05	$Li_{0.05}Co_{0.95}Co_2O_4$	0.07
Coated (~ 200 nm)	8.0249(7)	0.09	$Li_{0.09}Co_{0.91}Co_2O_4$	0.08

Fig. 3. Fourier transform (FT) magnitudes of Co K-edge $k3$-weighted EXAFS spectra for bare $LiCoO_2$ and reference cobalt oxides ($Li_xCo_2O_4$ and Co_3O_4).

can be retarded or suppressed. Indeed, an $AlPO_4$ coating layer suppresses $Li_xCo_2O_4$ decomposition into Li_2CO_3 and Co_3O_4 phases, as shown in Figs. 1 and 2. This may be attributed to the strong P=O bond (bond energy = 5.64 eV), which is very resistant to chemical attack [7,8]. High thermal stability of the $AlPO_4$ nanoparticle layer can be attributed to the strong covalency of the PO_4 polyanions with the Al^{3+} ions in $AlPO_4$ [8].

Fig. 3 shows the Fourier transform (FT) magnitudes of the Co K-edge $k3$-weighted EXAFS spectra for the bare and reference cobalt oxides ($Li_xCo_2O_4$ and Co_3O_4) (the spectra of the coated samples are identical to those of the bare sample). The FT peak

variations are due to a static disorder in the atomic distribution of six-coordinated oxygen and cobalt ions. For the bare and $AlPO_4$-coated $LiCoO_2$ sample, the first FT peak (A) at ~1.6 Å corresponds to six Co–O bonds while the second FT peak (B) at ~2.5 Å denotes six, edge-shared, CoO_6 octahedra. For the spinel $Li_xCo_2O_4$ and Co_3O_4 phases, a new FT peak (C) is generated at ~3.0 Å, and corresponds to corner-shared CoO_6 octahedra. The third FT peak (C) intensity of Co_3O_4 is larger than that of $Li_xCo_2O_4$, as the latter includes Li ions in the corner-shared O_h site. Therefore, the relative intensity can be a criterion for determining the phase transition to Co_3O_4 or $Li_xCo_2O_4$.

Fig. 4 gives a comparison of the FT magnitudes of Co K-edge $k3$-weighted EXAFS spectra for bare and $AlPO_4$-coated Li_xCoO_2 cathodes, where the x value is 0.24. These samples were annealed at 200 and 400 °C, respectively. In particular, the second peak feature (B) variation is closely related to the decrease in the number of edge-shared CoO_6 octahedra and the atomic mixing between the Li and Co sites by the thermal heating [4]. Thermal annealing leads to the generation of a new FT peak at ~3.0 Å, with respect to the FT features without the thermal annealing (see Fig. 3). For the samples annealed at 200 °C, the relative peak intensities of B to C are similar, indicating the presence of the $Li_xCo_2O_4$-type spinel phase. After thermal annealing at 400 °C, however, it is possible to observe a decrease in peak C intensity in the order of the coated sample of ~200 nm, the coated sample of ~20 nm, and the bare sample. This behaviour suggests predominant formation of the Co_3O_4 phase from decomposition of the $Li_xCo_2O_4$ phase. Furthermore,
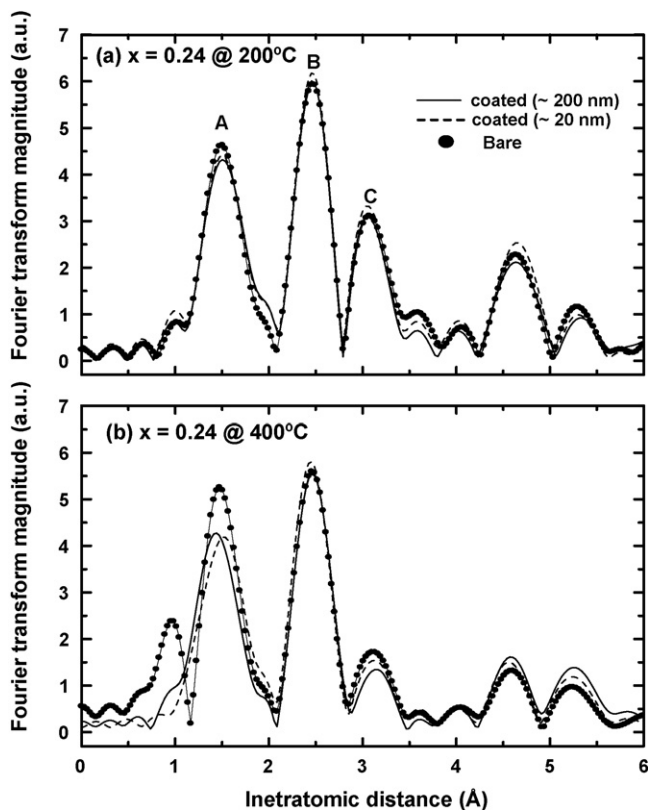

Fig. 4. FT magnitudes of Co K-edge $k3$-weighted EXAFS spectra for bare and $AlPO_4$-coated Li_xCoO_2 cathodes with coating thicknesses of ~20 and ~200 nm, where x value is 0.24 and annealing temperature is 200 and 400 °C.
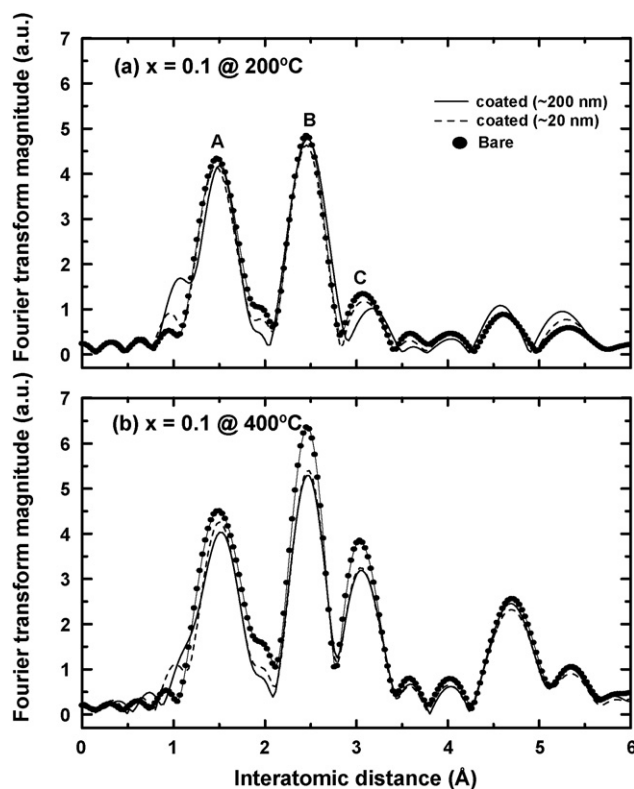

Fig. 5. FT magnitudes of Co K-edge $k3$-weighted EXAFS spectra for bare and $AlPO_4$-coated Li_xCoO_2 cathodes with coating thicknesses of ~20 and ~200 nm, where the x value is 0.1 and annealing temperature is 200 and 400 °C.

the thicker coating layer effectively suppresses phase transition to the Co_3O_4 phase.

For the $x = 0.1$ sample annealed at $200\,^{\circ}C$ (Fig. 5), similar behaviour to that with $x = 0.24$ is observed while the coated samples annealed at $400\,^{\circ}C$ show a similar relative peak intensity. This result indicates that while a coating thickness of $\sim20\,nm$ is adequate to minimize the phase transition from $Li_xCo_2O_4$ spinel to Co_3O_4 at $x = 0.24$, a coating thicker than $\sim20\,nm$ does not help to minimize the phase transition to the Co_3O_4 phase at $x = 0.1$. By contrast, the bare cathode shows Co_3O_4 as the dominant formation.

4. Conclusions

As the Li content x decreases in bare and coated Li_xCoO_2 cathodes, changes in their structures are significantly affected by the annealing temperature and the coating thickness. At lower temperatures ($200\,^{\circ}C$), phase transition of the layered Li_xCoO_2 phase to the $Li_xCo_2O_4$ spinel phase prevails in both the bare and coated samples. At temperatures greater than $200\,^{\circ}C$, however, the bare cathode transforms into the Co_3O_4 phase, while the coated cathodes maintain a $Li_xCo_2O_4$ phase. As a result, the coated cathodes have a more thermally stable structure compared with the bare cathode at higher temperatures, which leads to decreased oxygen generation from the cathode lattice.

References

[1] S. Choi, A. Manthiram, J. Electrochem. Soc. 149 (2002) A162.
[2] D.D. MacNeil, J.R. Dahn, J. Electrochem. Soc. 149 (2002) A912.
[3] Y. Baba, S. Okada, J.-I. Yamaki, Solid State Ionics 148 (2002) 311.
[4] Y. Lee, M.G. Kim, J. Kim, Y. Kim, J. Cho, J. Electrochem. Soc. 152 (2005) A1824.
[5] J. Cho, Y.-W. Kim, B. Kim, J.-G. Lee, B. Park, Angew. Chem. Int. Ed. 42 (2003) 1618.
[6] J. Cho, Electochim. Acta 48 (2003) 2807.
[7] S.W. Martin, Ph.D. Thesis, Purdue University, 1986.
[8] R.B. King (Ed.), Encyclopedia of Inorganic Chemistry, vol. 1, Wiley, New York, 1994, pp. 302–305.