



Phase Transition of Bare and Coated Li_xCoO_2 ($x = 0.4$ and 0.24) at 300°C

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The phase transitions of the bare and AlPO_4 -coated delithiated Li_xCoO_2 ($x = 0.4$ and 0.24) according to the coating concentration (thickness) after heat-treatment at 300°C was investigated using nuclear magnetic resonance and X-ray absorption spectra. It was found that the bare and coated Li_xCoO_2 predominantly decomposed into spinel $\text{Li}_x\text{Co}_2\text{O}_4$ or Co_3O_4 phases depending on the charging voltage. As the charging voltage was increased from 4.3 to 4.6 V, the bare and 1 wt % AlPO_4 -coated Li_xCoO_2 decomposed into the $\text{Li}_x\text{Co}_2\text{O}_4$ phase while the 2.4 wt % AlPO_4 -coated sample decomposed into the Co_3O_4 phase. The improvement in the thermal stability of the 2.4 wt % AlPO_4 -coated Li_xCoO_2 , compared to the bare and 1 wt % AlPO_4 -coated samples, could be explained by the dominant local formation of the Co_3O_4 phase over the $\text{Li}_x\text{Co}_2\text{O}_4$ phase.
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MacNeil and Dahn reported that the exothermic reaction of $\text{Li}_{0.5}\text{CoO}_2$ in the presence of sufficient solvent proceeded as a function of temperature as follows: $\text{Li}_{0.5}\text{CoO}_2 \rightarrow \frac{1}{2} \text{LiCoO}_2 + \frac{1}{6} \text{Co}_3\text{O}_4 \rightarrow \frac{1}{2} \text{LiCoO}_2 + \frac{1}{2} \text{CoO} \rightarrow \text{Co} + \frac{1}{4} \text{Li}_2\text{CO}_3$.¹ However, if there is a small amount of solvent present relative to the amount of $\text{Li}_{0.5}\text{CoO}_2$, the final reaction does not occur, at least at temperatures below 450°C . Baba et al. showed, by using high-temperature X-ray diffractometry (XRD), the phase transition of monoclinic $\text{Li}_{0.49}\text{CoO}_2$ ($C2/m$) to a spinel $\text{Li}_x\text{Co}_2\text{O}_4$ structure ($Fd3m$) at 220°C .² At 350°C , XRD showed a mixture of hexagonal LiCoO_2 and spinel Co_3O_4 ($Fd3m$) phases. This result is quite similar to that reported by Choi and Manthiram where the chemical delithiated $\text{Li}_{0.5}\text{CoO}_2$ showed a phase transition to spinel $\text{Li}_x\text{Co}_2\text{O}_4$ at 300°C .³

Lee et al. reported that the improvement in thermal stability of the highly delithiated $\text{Li}_{1-x}\text{NiO}_2$ on cobalt addition could be explained by local formation of Co_3O_4 phase around the cobalt ions in $\text{Li}_{1-x}\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$ at 300°C .⁴ Hence, this phase around the cobalt ions was relatively stable compared with the spinel Li_xNiO_2 structure at high temperature, and therefore depressed the decomposition of $\text{Li}_{1-x}\text{NiO}_2$ to a rock-salt phase.

In previous studies, Li-ion cells containing an AlPO_4 -coated LiCoO_2 cathode exhibited decreased heat generation, which in turn led to a lower cell surface temperature with increasing AlPO_4 coating thickness.⁵⁻⁷ For example, 1 wt % AlPO_4 -coated $\text{Li}_{0.24}\text{CoO}_2$ (coating thickness of ~ 15 -20 nm) showed a total heat generation of 35 J/g, while the total heat generation in the 2.4 wt % AlPO_4 -coated sample (coating thickness of ~ 200 nm) was 0.2 J/g. However, the origin of the improved thermal stability by the coating is not clearly understood. In this study, the phase transition of bare, 1, and 2.4 wt % AlPO_4 -coated Li_xCoO_2 ($x = 0.4$ and 0.24) after heat-treatment at 300°C was examined using ^{59}Co nuclear-magnetic resonance (NMR) and X-ray absorption spectroscopy (XAS).

Experimental

Spinel $\text{Li}_x\text{Co}_2\text{O}_4$ was prepared by the solid-state reaction of Co_3O_4 and LiOH at 400°C for 9 days in air. This method was quite similar to that reported by Shao-Horn et al.⁸ The XRD pattern of the prepared $\text{Li}_x\text{Co}_2\text{O}_4$ powders showed a mixture of major $\text{Li}_x\text{Co}_2\text{O}_4$ spinel and minor hexagonal LiCoO_2 phases. $\text{Li}_x\text{Co}_2\text{O}_4$ showed lattice constants $a = 0.7993$ nm with a space group $Fd3m$.

The LiCoO_2 used in these experiments had lattice constants of $a = 2.816 \pm 0.004$ Å and $c = 14.034 \pm 0.043$ Å, and a Brunauer, Emmett, Teller (BET) surface area of 0.5 m²/g. The charged elec-

trode samples were prepared in a 2016R coin-type cell using Li metal as the anode electrode. The electrodes were prepared by combining 3% each by mass of Super P carbon black and polyvinylidene fluoride (PVDF) with 94% LiCoO_2 powders. A 1 M LiPF_6 in ethylene carbonate (EC)/diethyl carbonate (DEC) (33:67 vol %) electrolyte (Cheil Industries, Korea) was used as the electrolyte, and a polypropylene separator was used. The cells were initially charged to either 4.35 or 4.6 V, with a current of 0.15 mA, and were stabilized at these voltages for 2 h at a constant voltage mode. The charged coin cells were transferred to an argon-filled glove box, and the cathode electrodes detached from the coin cells were scratched in order to collect the soaked cathode composite with the electrolyte, which was followed by being transferred into Al sample pans for sealing. The sealed sample pan was then heated to 300°C at a rate of $5^\circ\text{C}/\text{min}$ and was maintained at this temperature for 30 min, which was followed by slow cooling to room temperature. Our previous differential scanning calorimetry (DSC) study of the bare and coated cathodes showed that the electrolyte was decomposed around 150°C .⁶

The ^{59}Co magic angle spinning (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 ^{59}Co resonance frequency. A sample spinning speed of 32 kHz was used. The spectra were referenced to an external 1 M $\text{K}_3[\text{Co}(\text{CN})_6]$ aqueous solution for ^{59}Co 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 ^{59}Co NMR spectra. The isotropic chemical shifts were identified by varying the sample spinning rates.

The Co K-edge XAS study for the thermal phase transition of the bare and AlPO_4 -coated LiCoO_2 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(111) 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 $\sim 30\%$. The incident X-ray intensity was monitored using pure nitrogen gas-filled ionization chambers. The spectroscopic data was collected in transmittance mode. Energy calibration was made using standard Co metal foil. The data reduction of the experimental spectra was performed using the extended X-ray absorption fine structure (EXAFS) standard procedure reported previously.

Results and Discussion

^{59}Co MAS NMR studies were carried out to examine the local environment of cobalt atoms for Co_3O_4 , LiCoO_2 , and $\text{Li}_x\text{Co}_2\text{O}_4$. As

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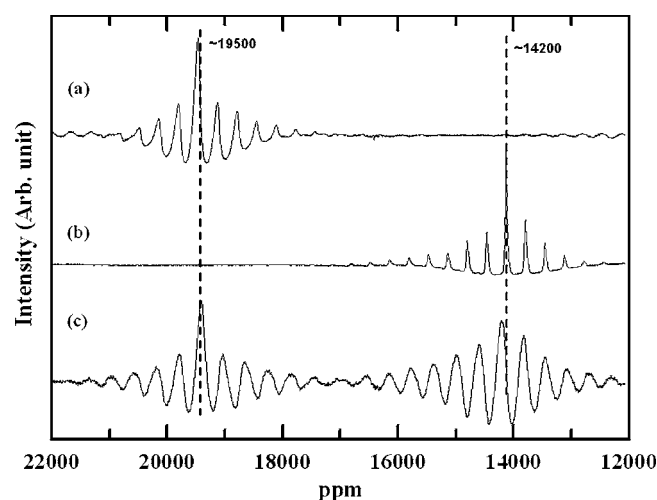


Figure 1. ^{59}Co MAS-NMR spectra of (a) Co_3O_4 , (b) layered LiCoO_2 , and (c) $\text{Li}_x\text{Co}_2\text{O}_4$.

shown in Fig. 1a, the ^{59}Co NMR spectrum of Co_3O_4 contains a single resonance at around 19,500 ppm. It is known that Co_3O_4 has a normal spinel structure where diamagnetic Co^{3+} ions are located at the octahedral sites, and paramagnetic Co^{2+} ions are located at the tetrahedral sites.⁹ In order to observe the signal of the Co^{2+} ions at the tetrahedral sites, the ^{59}Co NMR experiments need to be performed far below room temperature.¹⁰ 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 are as likely to come from the dipolar coupling to the unpaired electrons on the Co^{2+} spins as from the quadrupolar interaction. The ^{59}Co NMR spectrum of LiCoO_2 shows a single resonance with spinning sidebands at around 14,200 ppm, as shown in Fig. 1b. This cobalt should be assigned to Co^{3+} of octahedral sites in layered structure as expected. For the $\text{Li}_x\text{Co}_2\text{O}_4$, two NMR resonances with spinning sidebands are observed as shown in Fig. 1c. The resonance at around 19,500 ppm was assigned to the Co^{3+} of the spinel structure, and the other around 14,200 ppm was assigned to the Co^{3+} of the layered structure. Therefore, the prepared $\text{Li}_x\text{Co}_2\text{O}_4$ is comprised of both spinel and layered lithium cobalt oxides. However, because the experiments were performed at room temperature, it is difficult to determine if the signal at $\sim 19,500$ ppm originated from either Co_3O_4 or $\text{Li}_x\text{Co}_2\text{O}_4$.

Figure 2 shows that the ^{59}Co NMR spectra of Li_xCoO_2 ($x = 0.4$) are shown with variant coating concentrations after charging to 4.35 V and being heated at 300°C. As shown in Fig. 2, the spectra of all samples showed a strong resonance at around 14,200 ppm from the Co^{3+} in the layered structure. For the 2.4 wt % AlPO_4 -coated sample, there was an additional resonance at around 19,500 ppm, which was assigned to the Co^{3+} of the spinel structure. Figure 3 shows the ^{59}Co NMR spectra of the Li_xCoO_2 ($x = 0.24$) with various coating concentrations after being charged to 4.6 V, which was followed by heat-treatment at 300°C. The results are similar to those shown in Fig. 2. However, an additional resonance at around 19,500 ppm was observed for the coated samples of both the 2.4 wt % and 1 wt % AlPO_4 -coated Li_xCoO_2 , and the relative intensity increased for the 2.4 wt % AlPO_4 -coated Li_xCoO_2 compared with the 1 wt % AlPO_4 -coated one. This indicates that fractions of the Co_3O_4 or $\text{Li}_x\text{Co}_2\text{O}_4$ phase increased with increasing coating concentration and a cutoff voltage. XAS analysis was carried out to examine the structural changes of the samples in detail.

Figure 4 shows the normalized Co K-edge X-ray absorption near edge structure (XANES) features for the bare and AlPO_4 -coated Li_xCoO_2 , in addition to those annealed at 300°C after being charged

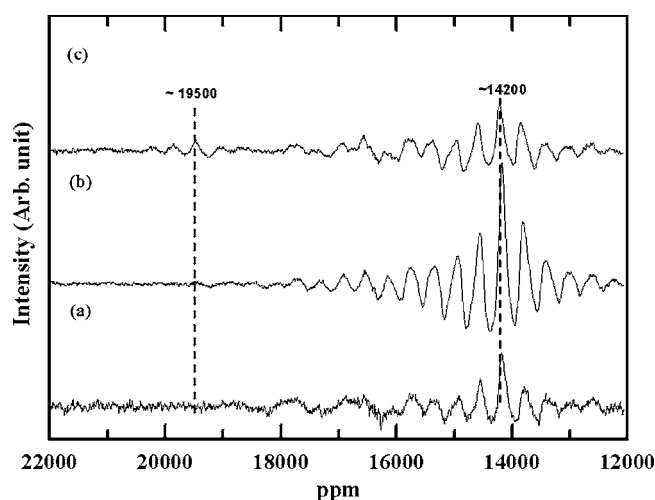


Figure 2. ^{59}Co MAS NMR spectra of (a) bare LiCoO_2 , (b) 1 wt % AlPO_4 -coated sample, and (c) 2.4 wt % AlPO_4 -coated sample after charging to 4.35 V ($x = 0.4$ in Li_xCoO_2) and annealed at 300°C.

to 4.35 V ($x = 0.4$ in Li_xCoO_2 , Fig. 4a) and 4.6 V ($x = 0.24$ in Li_xCoO_2 , Fig. 4b), respectively. Upon charging to 4.35 V, a pre-edge peak (1s to 3d transition, denoted by peak A), a shoulder peak (ligand-to-metal charge-transfer process, peak B), and a white line (1s to 4p transition, peak C) were dominantly shifted toward a higher energy region. The trivalent Co ion is partially oxidized to the tetravalent state, on charging the bare, 1 wt %, and 2.4 wt % AlPO_4 -coated LiCoO_2 . The peak feature corresponds to the typical XANES spectral variation for the layered LiCoO_2 under electrochemical Li-ion delithiation. After annealing at 300°C, the Co K-edge XANES spectra was changed noticeably with respect to the delithiated layered Li_xCoO_2 . The peak position of the pre-edge peak returned to the trivalent state of the Co ion. The shoulder peaks (peaks B₁ and B₂) gradually evolve, which is a characteristic peak feature for the spinel structure. The peak variation includes a possibility of phase transition from layered to cubic spinel phase. In this case, two types of spinel structure can be considered, Co_3O_4 and $\text{Li}_x\text{Co}_2\text{O}_4$. Based on the pre-edge peak position and the shoulder peak features, the XANES spectra for annealed samples of the bare and AlPO_4 -coated samples were similar to that of the $\text{Li}_x\text{Co}_2\text{O}_4$

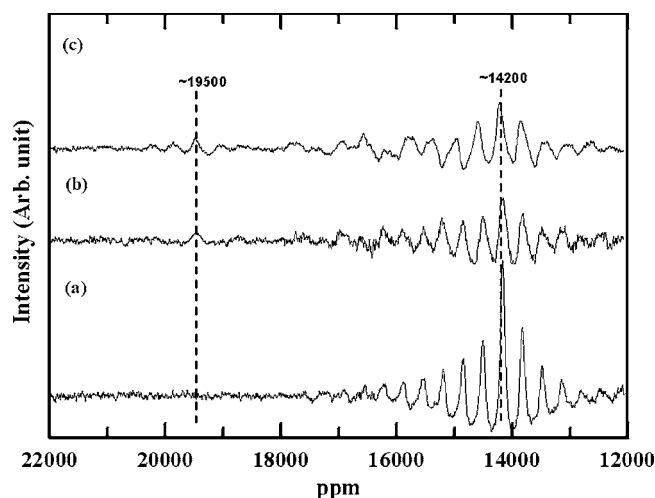


Figure 3. ^{59}Co MAS NMR spectra of (a) bare LiCoO_2 , (b) 1 wt % AlPO_4 -coated sample, and (c) 2.4 wt % AlPO_4 -coated sample after charging to 4.6 V ($x = 0.24$ in Li_xCoO_2) and annealed at 300°C.

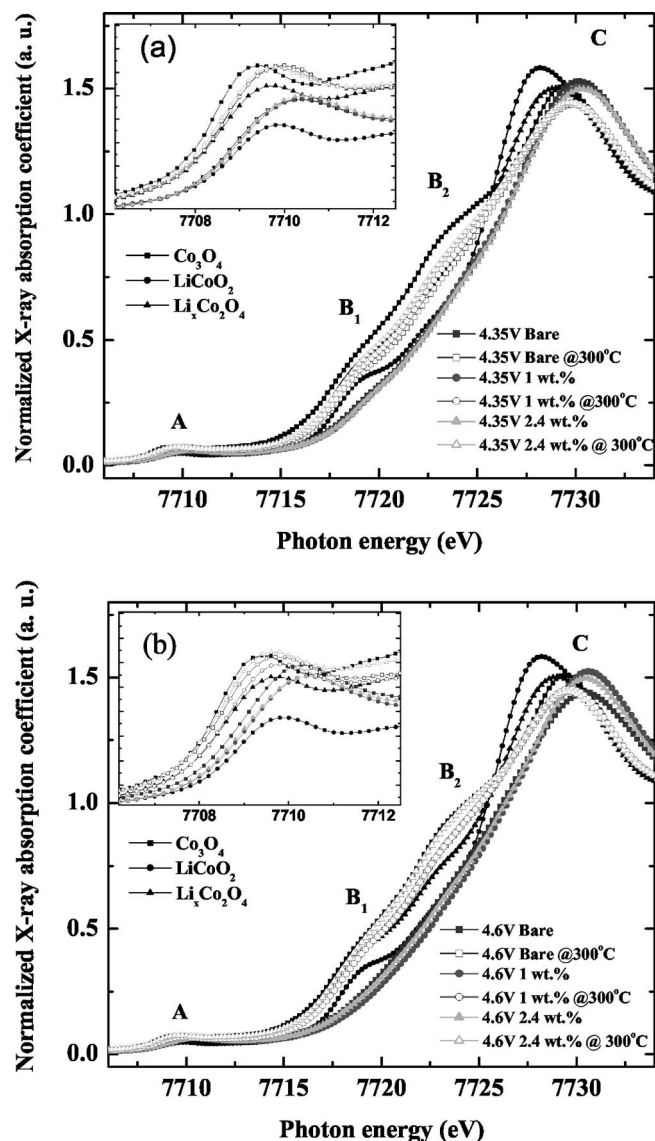


Figure 4. Normalized Co K-edge XANES features for the bare and 1 and 2.4 wt % AlPO_4 -coated Li_xCoO_2 annealed at 300°C after being charged to (a) 4.35 and (b) 4.6 V, respectively. An enlargement of peak A is shown as an insert.

structure rather than that of the Co_3O_4 structure. This means that the thermal annealing at 300°C leads to a phase transition from a layered to a $\text{Li}_x\text{Co}_2\text{O}_4$ structure in the less delithiated state, irrespective of the AlPO_4 coating. For the more delithiated Li_xCoO_2 charged to 4.6 V, the XANES spectra show a noticeably different spectral change. For the bare and 1 wt % AlPO_4 -coated sample, the peak features of the annealed samples were also similar to that of the spinel Li_xCoO_2 . However, the XANES feature of the 2.4 wt % AlPO_4 -coated sample showed a peak for Co_3O_4 , indicating an energy shift of peak A toward a much lower energy region and the dominant appearance of a shoulder feature of peak B_2 with respect to those of the bare and 1 wt % coating samples. Therefore, the coating on LiCoO_2 changes the local environment of cobalt ions effectively, even though some fraction of the original layered structure for the bare LiCoO_2 is retained after heating up to 300°C . This means that by coating, some portion of the layered LiCoO_2 is turned to a spinel structure, which can also be related to the charging voltage.

Figure 5 shows the Fourier transform (FT) magnitudes of the Co

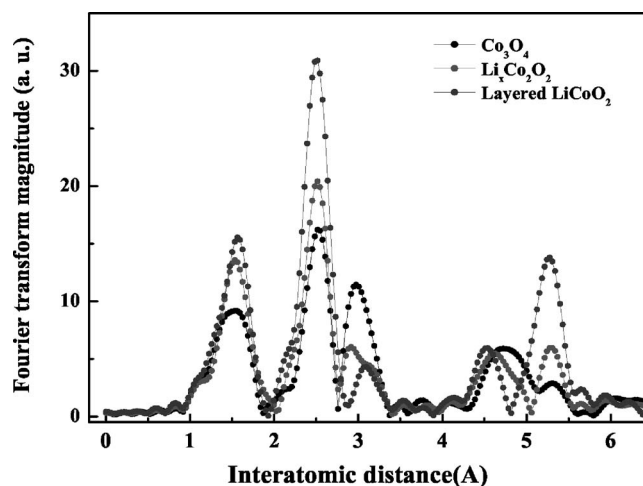


Figure 5. FT magnitudes of the Co K-edge k^3 -weighted EXAFS spectra for reference cobalt oxides such as Co_3O_4 , $\text{Li}_x\text{Co}_2\text{O}_4$, and layered LiCoO_2 .

K-edge k^3 -weighted EXAFS spectra for the reference cobalt oxides. For the layered bare and AlPO_4 -coated LiCoO_2 , the first FT peak at $\sim 1.6 \text{ \AA}$ corresponds to six Co-O bonds and the second FT at $\sim 2.5 \text{ \AA}$ means a six edge-shared CoO_6 octahedra. For the spinel $\text{Li}_x\text{Co}_2\text{O}_4$ structure, a new FT peak is generated at $\sim 3.0 \text{ \AA}$, which corresponds to a corner-shared CoO_6 octahedra. The relative intensity of the second and third FT peaks makes it possible to distinguish between Co_3O_4 and $\text{Li}_x\text{Co}_2\text{O}_4$. The third FT peak intensity of Co_3O_4 is larger than that of $\text{Li}_x\text{Co}_2\text{O}_4$ because the latter includes Li ions in the corner-shared O_h site. Therefore, the relative intensity can be a criterion determining the phase transition to Co_3O_4 or $\text{Li}_x\text{Co}_2\text{O}_4$.

Figure 6 shows a comparison of the FT magnitudes of Co K-edge k^3 -weighted EXAFS spectra for AlPO_4 - LiCoO_2 charged to 4.35 and 4.6 V and annealed at 300°C with those of bare LiCoO_2 . The FT peak feature varied effectively on annealing. Upon annealing at 300°C and after charging to 4.35 V, the first and second FT peak intensities decrease effectively. The FT peak variations were due to a static disorder in the atomic distribution of six-coordinated oxygen and cobalt ions. In particular, the second peak feature variation was closely related to the decrease in the number of edge-shared CoO_6 octahedra and the atomic mixing between Li and Co sites by the thermal heating. Thermal heating leads to the generation of a new

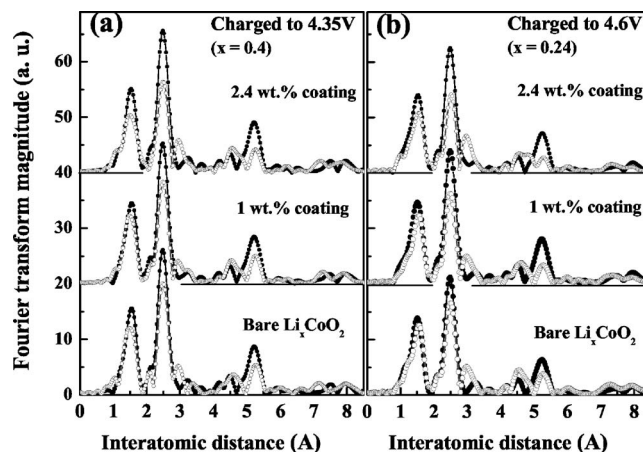


Figure 6. FT magnitudes of the Co K-edge k^3 -weighted EXAFS spectra for the bare and AlPO_4 - LiCoO_2 annealed at 300°C (O) after charging (●) to (a) 4.35 and (b) 4.6 V compared with those of bare Li_xCoO_2 .

FT peak at ~ 3.0 Å, with respect to the FT features without the thermal heating. The FT peak corresponds to the corner-shared Co atom by way of oxygen atoms. The distinct appearance of the FT peak presents that the Co ion in the layered octahedral site of the delithiated bare and $\text{AlPO}_4\text{-Li}_x\text{CoO}_2$ migrate into the Li vacant site on thermal heating. The weak FT peak intensity is similar to that of spinel $\text{Li}_x\text{Co}_2\text{O}_4$, meaning that the thermal heating of the delithiated bare and $\text{AlPO}_4\text{-LiCoO}_2$ prefers to decompose to $\text{Li}_x\text{Co}_2\text{O}_4$ rather than spinel Co_3O_4 .

Atomic migration leads to the coexistence of both edge-shared and corner-shared octahedral sites within the lattice and then results in the phase transition to a spinel $\text{Li}_x\text{Co}_2\text{O}_4$ structure by the atomic rearrangement at the annealing temperature. From the relative intensity of the third FT peak, a phase transition to $\text{Li}_x\text{Co}_2\text{O}_4$ structure can be more suppressed in the AlPO_4 -coated cathode than in the bare one.

Second, for charging to 4.6 V, it was observed that the degree of the phase transition was much more pronounced than in the case of charging to 4.35 V. In particular, the radial distribution function of the 2.4 wt % AlPO_4 -coated Li_xCoO_2 is characteristic of not only $\text{Li}_x\text{Co}_2\text{O}_4$ but Co_3O_4 . This is based on the relative FT intensity between the edge- and corner-sharing and the abrupt decrease of FT peak intensity at ~ 5.2 Å, corresponding to multiple scattering from $\text{Co} \leftrightarrow \text{Co} \leftrightarrow \text{Co}$ path. The latter is reasonable in that the multiple scattering path is preferable within the octahedral plane of the layered LiCoO_2 , which is known as the focusing effect.¹¹ Both the first FT peak intensity of oxygen ions and the second FT peak of edge-shared Co ions were decreased effectively by thermal annealing, compared with bare LiCoO_2 . The third FT peak of the corner-shared Co ion appeared to be dominant. The first FT peak feature is related to the decrease in the coordination number of oxygen, namely, oxygen vacancies. The inverse tendency of the second and third FT peak intensity shows the atomic migration of Co ions from the sites in the layered plane to the cavity site produced by the delithiation. As a result, the delithiated 2.4 wt % AlPO_4 -coated Li_xCoO_2 preferentially decomposes from a layered to Co_3O_4 structure. This is in contrast to the 1 wt % coated Li_xCoO_2 ($x = 0.24$), which tended to decompose to the $\text{Li}_x\text{Co}_2\text{O}_4$ phase. The DSC scans of the charged bare and coated samples at 4.6 V clearly showed the rapidly decreased exothermic peak area with increasing AlPO_4 coating thickness.⁵ The bare and the coated cathode with a thickness of 15-20 nm favorably decomposed into the $\text{Li}_x\text{Co}_2\text{O}_4$ phase, which is

similar to that reported in previous studies. The cathode with a coating thickness of ~ 200 nm transformed into Co_3O_4 phase. This indicates that the amount of oxygen generated from the exothermic reaction between the electrolyte and cathode reduced with increasing Co_3O_4 phase formation. Even though this study is only focused on the phase transition at 300°C, structural evolution studies of the bare and coated Li_xCoO_2 at different temperatures, such as 250, 350, and 400, are underway.

Conclusion

Increased AlPO_4 coating concentration led to a decreased phase transition to the $\text{Li}_x\text{Co}_2\text{O}_4$ spinel phase from the layered LiCoO_2 , resulting in the formation of the Co_3O_4 phase. The bare and 1 wt % AlPO_4 -coated Li_xCoO_2 tended to decompose to $\text{Li}_x\text{Co}_2\text{O}_4$ spinel while the 2.4 wt % AlPO_4 -coated sample decomposed to Co_3O_4 at 300°C. This result is similar to the $\text{Li}_{1-x}\text{NiO}_2$ cathode, which decomposed into the spinel $\text{Li}_x\text{Ni}_2\text{O}_4$ phase above 200°C.

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