Surface and bulk structure investigation of fully delithiated bare and AlPO4-coated Li\textsubscript{x}CoO\textsubscript{2} (x = 0) cathode materials annealed between 200 and 400 °C

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Abstract

The surface and bulk structure of the fully delithiated bare and AlPO\textsubscript{4}-coated Li\textsubscript{x}CoO\textsubscript{2} 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 CoO\textsubscript{2} cathodes showed different phase transformation between 200 and 400 °C. The bare samples exhibited only the O1-CoO\textsubscript{2} phase in the fully delithiated state, but the CoO\textsubscript{2} phase was converted to the Co\textsubscript{3}O\textsubscript{4} phase at higher temperatures. On the other hand, the AlPO\textsubscript{4}-coated Li\textsubscript{x}CoO\textsubscript{2} at x = 0 showed a mixture of phases including the major O1-type CoO\textsubscript{2} and minor Co\textsubscript{3}O\textsubscript{4} 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 Co\textsubscript{3}O\textsubscript{4} and were completely transformed into the thermally stable Co\textsubscript{3}O\textsubscript{4} spinel phase at 400 °C. The coated samples, however, were completely transformed into the spinel phase alone at 200 °C. We believe that the AlPO\textsubscript{4} 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.

Keywords: Li\textsubscript{x}CoO\textsubscript{2}; AlPO\textsubscript{4} coating; Structure; Surface; Annealing temperature

1. Introduction

Generally, Li\textsubscript{i}CoO\textsubscript{2} shows a monoclinic, H1-3 and O1-type structural transformation upon delithiation out to x ≈ 0 at room temperature, and the XRD pattern of the completely delithiated LiCoO\textsubscript{2} is indexed to the hexagonal unit cell in the space group of P3\textsubscript{m}1 (CdI\textsubscript{2} or O1-type) \[1\]. In contrast, at elevated temperatures, Li\textsubscript{i}CoO\textsubscript{2} exhibits phase transitions to a spinel Co\textsubscript{3}O\textsubscript{4}, and CoO or Co at Li\textsubscript{i}CoO\textsubscript{2} (x = 0.5) depending on the temperature \[2\]. MacNeil et al. reported that the reaction between Li\textsubscript{i.5}CoO\textsubscript{2} and the electrolytes led to the formation of the Co\textsubscript{3}O\textsubscript{4}, CoO and Co phases at 400 °C. Similarly, chemically delithiated Li\textsubscript{i.49}CoO\textsubscript{2} showed a phase transition to the spinel phases (Li\textsubscript{i}Co\textsubscript{2}O\textsubscript{4} or Co\textsubscript{3}O\textsubscript{4}) from the O3-type LiCoO\textsubscript{2} above 300 °C \[3\]. On the other hand, Lee et al. reported the phase transitions of AlPO\textsubscript{4}-coated delithiated Li\textsubscript{i}CoO\textsubscript{2} (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.% AlPO\textsubscript{4}-coated Li\textsubscript{i}CoO\textsubscript{2} decomposed into the Li\textsubscript{i}Co\textsubscript{2}O\textsubscript{4} phase while the 2.4 wt.% AlPO\textsubscript{4}-coated sample decomposed into the Co\textsubscript{3}O\textsubscript{4} phase \[4\]. On the other hand, spinel Li\textsubscript{i}Co\textsubscript{2}O\textsubscript{4}, which has a cubic spinel phase with an Fd\textsubscript{3}m space group, transforms to the O3-type LiCoO\textsubscript{2} upon heating. Moreover, it was reported that the spinel Li\textsubscript{i}Co\textsubscript{2}O\textsubscript{4} 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\textsubscript{i}CoO\textsubscript{2}, and, to our best knowledge, the phase transformation of the cathode with variations in temperature in the fully delithiated state (x = 0 in Li\textsubscript{i}CoO\textsubscript{2}) has not been examined.

In this study, the structural changes of the bare and AlPO\textsubscript{4}-coated Li\textsubscript{i}CoO\textsubscript{2} cathodes (x = 0) materials annealed at 200, 300 and 400 °C were investigated using high resolution XRD, TEM, XAS and solid-state NMR.
2. Experimental

LiCoO$_2$ powders with an average particle size of 10 µm were prepared by a direct reaction between LiOH·H$_2$O and Co$_3$O$_4$ (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$_x$CoO$_2$ was 1.01. To prepare the AlPO$_4$ coating on the cathode, the appropriate amounts of Al nitrate and (NH$_4$)$_2$HPO$_4$ such that the weight ratio of AlPO$_4$ to LiCoO$_2$ was 8:92 were dissolved in distilled water and mixed with LiCoO$_2$ 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$_x$CoO$_2$ cathodes ($x=0$). Either the AlPO$_4$ nanoparticle-coated LiCoO$_2$ or the bare LiCoO$_2$ was used as the cathode and the anode material was synthetic graphite. The electrolyte used consisted of 1.03 M LiPF$_6$ 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 $^{59}$Co 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 K$_3$[Co(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 X-ray absorption spectroscopic study for the thermal phase transition of the bare and AlPO$_4$-coated Li$_x$CoO$_2$ 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(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-CoO$_2$ and CoOOH, due to a reaction of CoO$_2$ with water in air which likely occurred when the CoO$_2$ powder was air-exposed for 3 h during the XRD experiments. It has been reported that CoO$_2$ is very sensitive to air and transforms into the CoOOH phase upon air-exposure [1]. At 200°C, a fully delithiated Li$_x$CoO$_2$ cathode, i.e., O1-type CoO$_2$, was maintained, indicating that CoO$_2$ was not fully decomposed into other phases. At 300°C, the formation of the Co$_3$O$_4$ phase was due to an oxygen loss from the CoO$_2$ phase, according to the following reaction: $3\text{CoO}_2 \rightarrow \text{Co}_3\text{O}_4 + \text{O}_2$. In addition, the increased intensity of the Co$_3$O$_4$ spinel phase at 400°C showed a similar trend to that observed in Li$_{0.5}$CoO$_2$ heat-treated above 400°C [7].

Unlike the bare cathode, the AlPO$_4$-coated cathodes showed a different set of phase transitions with respect to increasing temperatures, as shown in Fig. 2. At $x=0$, the O1-CoO$_2$ phase was the major phase with the Co$_3$O$_4$ spinel phase occurring as a minor phase, but the latter phase was completely absent from the bare sample. The AlPO$_4$ coating was believed to play a major
role in the early decomposition of the \text{CoO}_2 phase into the \text{Co}_3\text{O}_4 phase at 5 V. Upon increasing temperature from 200 to 300 °C, the \text{CoO}_2 phase completely disappeared and only \text{Co}_3\text{O}_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.

\text{Co}^\text{59} \text{MAS NMR} studies were carried out to investigate the local environment of the cobalt atoms for the bare and AlPO_4-coated Li_{1.01}\text{CoO}_2 cathodes with \text{x} = 0 and subsequent annealing at 300 °C, as shown in Fig. 3. The \text{Co}^\text{59} \text{NMR} spectrum of the bare Li_{1.01}\text{CoO}_2 showed a typical single resonance with spinning sidebands around 14,200 ppm due to the \text{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 \text{CoO}_2 in our spectrum for the bare Li_{1.01}\text{CoO}_2 at \text{x} = 0, since it only contained paramagnetic \text{Co}^{4+}, which is expected to show very broad \text{Co}^\text{59} \text{NMR} lines due to a shortened spin–spin relaxation time (T_2). Heat treatment of the Li_{1.01}\text{CoO}_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 \text{Co}_3\text{O}_4 assigned to \text{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 \text{Co}^{2+} spins as from quadrupolar interactions. The \text{Co}^\text{59} \text{NMR} spectra of the AlPO_4-coated Li_{1.01}\text{CoO}_2 at \text{x} = 0 and annealed at 300 °C are also shown in Fig. 3. Opposite of the bare Li_{1.01}\text{CoO}_2 at \text{x} = 0, the spectra of this sample at \text{x} = 0 exhibited a resonance around 19,500 ppm, which was assigned to the \text{Co}^{3+} of the \text{Co}_3\text{O}_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_{1.01}\text{CoO}_2 (\text{x} = 0 and 1) annealed at 300 °C in addition to the reference \text{Co}_3\text{O}_4.

A pre-edge peak (1s–3d transition, denoted by peak A), shoulder peaks (ligand to metal charge transfer process, peak B1 and B2) and a white line (1s–4p transition, peak C) are characteristic peak features for the spinel \text{Co}_3\text{O}_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 \text{Co}_3\text{O}_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_{1.01}\text{CoO}_2 (\text{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 also be 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_{1.01}\text{CoO}_2 (\text{x} = 0) particles have been converted to a...
Fig. 5. (a) Bright field TEM image of the bare Li$_x$CoO$_2$ ($x = 0$) cathode at 300 °C; (b) [1 1 0] zone HRTEM image of the bare Li$_x$CoO$_2$ ($x = 0$) 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$_x$CoO$_2$ 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$_x$CoO$_2$ cathode ($x = 0$) at 200 °C, retaining perfect spinel symmetry; (b) [1 1 0] zone from a structurally damaged particle from the bare Li$_x$CoO$_2$ cathode with $x = 0$ at 300 °C; (c) [1 1 1] zone from the AlPO$_4$-coated Li$_x$CoO$_2$ cathode with $x = 0$ 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 AlPO4-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 k³-weighted EXAFS spectra for the reference Co3O4, bare and coated sample heat-treated at 300 °C. For Co3O4, the first FT peak at ~1.6 Å corresponded to six Co–O bonds and the second FT at ~2.5 Å represented a six edge-shared CoO6 octahedra. The FT peak was generated at ~3.0 Å, which corresponded to corner-shared CoO6 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 Li₄CoO₂ cathodes (x = 0) showed different phase transformation paths during heating from 200 to 400 °C. Bare cathodes showed a stepwise phase transition to the Co3O4 spinel phase from the O1-CoO₂ phase, turning into the Co3O4 phase at 400 °C. On the other hand, the AlPO4-coated cathodes showed a mixed phase of Co3O4 and CoO2 after completely removing Li from Li₄CoO₂, but showed the complete Co3O4 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.

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References