Microstructure of LiCoO₂ with and without “AlPO₄” Nanoparticle Coating: Combined STEM and XPS Studies

Anjuli T. Appapillai, Azzam N. Mansour, Jaephil Cho, and Yang Shao-Horn*

Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, Naval Surface Warfare Center, Carderock Division, West Bethesda, Maryland 20817-5700, and Kumoh National Institute of Technology, Gumi, Republic of Korea

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Introduction

Lithium cobalt dioxide, LiCoO₂, is the most common positive electrode material used in lithium rechargeable batteries for portable electronics. LiCoO₂ adopts a layered structure having rhombohedral symmetry with space group R3m, which is described typically in a hexagonal cell setting with \( a_{\text{hex}} = 2.815 \) Å and \( c_{\text{hex}} = 14.05 \) Å.¹ The structure consists of layers of edge-sharing lithium and cobalt octahedra stacked alternatively between AB CA BC cubic-close-packed oxygen arrays. The theoretical capacity of LiCoO₂ is 274 mA h g⁻¹ for reversible extraction and insertion of one lithium per formula unit. However, cycling to voltages greater than 4.2 V (which corresponds to removal of ~0.5 Li per formula unit) has shown severe capacity loss.²,³ Two major causes have been proposed for the capacity fade: (1) structural instability²,⁴,⁵ (such as microcracks induced by dimensional changes as a function of Li content) and (2) the surface instability as a result of Li₂CO₃ reactivity with the electrolyte² (such as cobalt dissolution) of the LiCoO₂ crystals. Al substitution in LiCoO₂ has been shown to be particularly effective in improving capacity retention upon cycling by not only reducing changes in the lattice parameters of the layered LiCoO₂ structure⁶,⁷ but also decreasing cobalt dissolution.⁶ However, Al substitution reduces rechargeable capacities of Li₃AlCo₂O₆ as Al⁺³ in the layered structure is not electroactive. Recently, researchers have shown that application of a surface oxide or phosphate such as ZrO₂⁸ or Al₂O₃,⁸ AlO₃,⁸,¹⁰ TiO₂,⁸,¹¹ and AlPO₄¹² to LiCoO₂ particles can significantly improve the degree of capacity retention upon cycling to high voltages without loss in the reversible capacity. In particular, “AlPO₄”-coated LiCoO₂ as reported by Cho et al.¹²-¹⁹ has shown superior cycling performance.

¹ Corresponding author. E-mail: shaohorn@mit.edu.
² Massachusetts Institute of Technology.
³ Naval Surface Warfare Center.
⁴ Kumoh National Institute of Technology.


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relative to LiCoO$_2$ coated with other oxides. Specifically, the AlPO$_4$ coating has been shown to increase the initial reversible discharge capacity from 200 to 210 mA h g$^{-1}$ with a 4.8 V upper limit, and "AlPO$_4$"-coated LiCoO$_2$ electrodes retain $\sim$150 mA h g$^{-1}$ in capacity after 50 cycles. Moreover, "AlPO$_4$"-coated LiCoO$_2$ exhibits markedly improved thermal stability relative to uncoated LiCoO$_2$ and LiCoO$_2$ with oxide coating. In a charged state of 4.7 V, "AlPO$_4$"-coated LiCoO$_2$ increases the onset temperature for electrolyte oxidation from 187 to $\sim$220 °C, and reduces the overall heat evolution by a factor of 10.13

The mechanism of the improvement in cycling performance and thermal characteristics of lithium transition metal oxides with AlPO$_4$ and other oxides is not well-understood. Cho et al. have first proposed that increasing the fracture toughness of the coating oxide (e.g., Al$_2$O$_3$ and ZrO$_2$) can suppress phase transitions by constraining active particles against lattice parameter changes associated with lithium removal and insertion, which would reduce stresses and structural damage within individual particles and improve capacity retention during cycling. This concept is further supported by Fey et al. using slow-scan cyclic voltammetry data with an upper voltage limit of 4.4 V, which show that the phase transition peaks are suppressed to varying degrees that are dependent on the coating material. However, Chen and Dahn have shown that coating does not suppress the changes in the lattice parameters of the layered structure upon lithium removal and insertion, and the enhancement in cycling performance is independent of fracture toughness of the coating. This argument is in good agreement with recent findings of Cho et al., where it is shown that suppression of lattice expansion is not necessary to obtain improved cycling performance of "AlPO$_4$"-coated LiCoO$_2$ in contrast to oxide coatings. Chen and Dahn have also shown that a heat treatment to 550 °C alone can improve the reversible capacity and capacity retention of Li$_x$CoO$_2$ electrodes when cycled to 4.5 V by reducing moisture-related, surface, chemical species. Although coating application typically involves a heat-treatment step, this explanation does not explain the difference in cycling performance of lithium cobalt oxide electrode materials with different coatings. The mechanism by which coating may influence thermal characteristics of Li$_x$CoO$_2$ is not known. Although Cho et al. have speculated that the superior thermal properties of "AlPO$_4$"-coated LiCoO$_2$ is attributed to the strong covalency of the PO$_4$ polyanions with the Al$^{3+}$ ions of the coating, ambiguity exists in the chemistry and microstructure of the AlPO$_4$ coating. Cho et al. and Kim et al. have shown that coating nanoparticles can react with bare LiCoO$_2$ during the heat-treatment step, which may lead to considerably different surface microstructure and chemistry from pristine coating particles. Therefore, it is important to reveal the surface microstructure of coated Li$_x$CoO$_2$ after the heat-treatment step, from which the mechanisms of cycling and thermal performance enhancement may be developed.

It is hypothesized that the addition of a coating to the Li$_x$CoO$_2$ surface can modify the reactivity between active particles and the electrolyte, which can strongly influence its cycling performance and thermal characteristics. In this study, we focus on the following questions: (1) what is the microstructure of "AlPO$_4$"-coated LiCoO$_2$, particularly the coating microstructure; (2) how does its microstructure yield improved cycling and thermal stability; (3) how do lithium ions diffuse through the coating layer; and (4) why does the AlPO$_4$ coating chemistry yield superior cycling performance and thermal properties relative to other oxide coating materials. This work employs energy-dispersive X-ray spectroscopy (EDX) in a scanning transmission electron microscope (STEM) to obtain the distribution of Co, O, Al, and P on the micrometer- and nanometer-scale of the "AlPO$_4$"-coated LiCoO$_2$ powder sample, and uses X-ray photoelectron spectroscopy to analyze the chemical environments of C, Al, P, Co, O, and Li in order to provide new insights to the phases present on the surfaces of the active particles. In this paper, we show, for the first time, AlPO$_4$ is absent from the surfaces of the "AlPO$_4$"-coated LiCoO$_2$ particles. Li$_3$PO$_4$ and LiCo$_{1-y}$Al$_y$O$_2$ with relatively high Al substitution levels are detected on active particles. The mechanism by which the coating microstructure of "AlPO$_4$"-coated LiCoO$_2$ can lead to enhancement in cycle life and thermal stability relative to those of a uncoated LiCoO$_2$ sample is discussed.

**Experimental Section**

Bare LiCoO$_2$ and "AlPO$_4$"-coated LiCoO$_2$ powder samples were prepared as described previously. Bare LiCoO$_2$ was prepared from stoichiometric amounts of Co$_3$O$_4$ and Li$_2$CO$_3$ at 1000 °C for 4 h in an oxygen stream. An AlPO$_4$ nanoparticle solution was prepared by slowly dissolving Al(NO$_3$)$_3$·9H$_2$O and (NH$_4$)$_2$HPO$_4$ in distilled water until a white AlPO$_4$ nanoparticle suspension was observed. The AlPO$_4$ nanoparticles with particle sizes in the range of 5–10 nm were amorphous, as determined by X-ray diffraction (XRD). Bare LiCoO$_2$ was added to this suspension and mixed thoroughly for 5 min. The slurry was dried in an oven at 120 °C for 6 h and heat-treated at 700 °C for 5 h, from which the "AlPO$_4$"-coated LiCoO$_2$ was obtained. The weight fraction of AlPO$_4$ on LiCoO$_2$ is 1% after firing at 700 °C, as determined by inductively coupled plasma–mass spectroscopy (ICP–MS) (ICPS-1000IV, Shimadzu).

The reversible capacities and electrochemical activity of bare LiCoO$_2$ and "AlPO$_4$"-coated LiCoO$_2$ composite electrodes were measured in 2016 coin cells. Composite electrodes were prepared from electrode slurry, which was comprised of active material powder, poly vinylidene fluoride (PVDF), and Super P carbon black in an 80:10:10 weight ratio in N-methyl pyrrolidone (NMP) solution. The slurry was cast onto Al foil and dried under a vacuum at room temperature overnight, and subsequently dried under a vacuum at

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120 °C for 8–10 h. Fifteen millimeter diameter electrode disks were punched and redried under a vacuum at 120 °C for 30 min before being kept in an argon-filled glovebox. Coin cells were constructed inside the glovebox using a lithium metal foil as the negative electrode and the composite positive electrode separated by two polypropylene microporous separators (Celgard). The electrolyte used was 1 M LiPF$_6$ in a 1:1 weight ratio ethylene carbonate (EC): dimethyl carbonate (DMC) solvent (Merck or LithChem International). Assembled coin cells were allowed to soak overnight and then began electrochemical testing on a Solartron 1470 battery testing unit. Galvanostatic charging and discharging was performed at a C/50 rate (5.48 mAg) to measure the voltage profiles of bare LiCoO$_2$ and “AlPO$_4$”-coated LiCoO$_2$ close to thermodynamic equilibrium. In addition, cycling performance of these samples was compared at a C/5 rate between voltage limits of 3.0 and 4.7 V vs Li for 30 cycles after the first cycle measured at a C/10 rate.

The particle morphology and surface microstructure of bare LiCoO$_2$ and “AlPO$_4$”-coated LiCoO$_2$ powder samples, which were sprinkled onto silver paint on an aluminum stub, were examined and imaged on a JEOL 6320FV field-emission scanning electron microscope (SEM). In addition, transmission electron microscopy (TEM) was used to examine the cross-sectional microstructure of the coating layer on “AlPO$_4$”-coated LiCoO$_2$. TEM samples were prepared by embedding the “AlPO$_4$”-coated LiCoO$_2$ powder in a clear epoxy resin and then microtoming slices of 30 nm thickness. These cross-sections were examined on a JEOL 2010 transmission electron microscope under an accelerating voltage of 200 kV.

Powder XRD patterns of “AlPO$_4$”-coated LiCoO$_2$ samples were collected on a PANalytical X’Pert Pro X-ray diffractometer with CoK$_\alpha$ radiation. Data were collected between 10 and 140° of 2ϕ, at a scan rate of 0.167°/min. The lattice parameters were determined using the HighScore Plus software package.

Elemental distributions of Co, Al, P, and O in “AlPO$_4$”-coated LiCoO$_2$ particles that were fractured in liquid nitrogen were collected using EDX spectroscopy in a VG HB603 STEM at room temperature, using a beam voltage of 250 kV and a beam diameter of ~2 nm. Data collection times ranged from 3 to 10 min, depending on signal intensity for a given sample area.

Surface chemical compositions of bare LiCoO$_2$ and “AlPO$_4$”-coated LiCoO$_2$ were measured using X-ray photoelectron spectroscopy on a Physical Electronics model 5400 X-ray photoelectron spectrometer. The data were collected at room temperature, using a non-monochromatic Al K$_\alpha$ (1486.6 eV) X-ray source, with an angle of 45° between the analyzer and the X-ray source. The samples were mounted onto a gold-coated sample holder with the aid of electrically conducting tabs and placed into the introduction chamber, which was evacuated using roughing and turbomolecular pumps, for about 10–15 min before being transferred into the analysis chamber of the XPS instrument. Data collection proceeded when the analysis chamber pressure reached 2 × 10$^{-8}$ Torr. The size of the analysis area was set to a 1.1 mm diameter spot. Survey spectra were collected at a low resolution using an analyzer pass energy of 89.45 eV, increment of 0.5 eV/step, and integration interval of 50 ms/step. The final spectrum consists of the average of 20 cycles. Multiplex spectra of various photoemission lines were collected at medium resolution using analyzer pass energy of 35.75 eV, increment of 0.2 eV/step, and an integration interval of 50 ms/step. Data collection intervals were approximately 37 min for survey spectra and ~100–200 min for each set of multiplex spectra depending on sample composition. The linearity of the spectrometer energy scale was calibrated using the Au 4f7/2 and Cu 2p$_{3/2}$ photoemission lines. The measured binding energies for these two lines were 83.93 and 932.59 eV, respectively, which compare well with the established values of 84.00 and 932.66 eV. The measured binding energies are shifted by ~0.07 eV with respect to the established values. To compensate for this small shift and sample charging effects, all spectra were calibrated with the C 1s photoemission peak for adventitious hydrocarbons at 284.6 eV. Curve fit analysis of the photoemission lines was done using a combined Gaussian–Lorentzian line shape, except in the case of the Co 2p$_{3/2}$ line where an asymmetric line shape was used, after subtracting a Shirley type background. For overall surface composition analysis, the atomic ratios of the relevant elements were determined from multiplex spectra using the integrated areas after subtracting the satellite contributions and a Shirley-type background and using the relative sensitivity factors provided by Physical Electronics for our spectrometer. The relative sensitivity factors for Li 1s, C 1s, O 1s, Co 2p$_{3/2}$, Al 2s, P 2p, and Na 1s photoemission lines were given as 0.028, 0.312, 0.733, 2.113, 0.256, 0.525, and 1.102. It should be noted that the X-ray source and collection angle of 45° used in this experiment yield a sampling depth of ~5 nm for the O 1s photoemission line.

To identify the nature of the bonding environment on the coated LiCoO$_2$, we used aluminum phosphate (AlPO$_4$), layered O$_3$ LiAl$_{0.1}$Co$_{0.9}$O$_2$, lithium carbonate (Li$_2$CO$_3$), gamma lithium phosphate ($\gamma$-Li$_3$PO$_4$), and layered O$_3$ lithium aluminum oxide (LiAlO$_2$) as reference samples for the XPS studies. The X-ray powder diffraction patterns of these reference samples are shown in the Supporting Information (Figure S1).

**Results and Discussion**

**Electrochemical Characterization.** The galvanostatic voltage profiles of lithium coin cells having bare LiCoO$_2$ and “AlPO$_4$”-coated LiCoO$_2$ electrodes are compared in Figure 1a. The “AlPO$_4$”-coated LiCoO$_2$ shows a voltage plateau at ~3.93 V, characteristic of the insulator–metal transition,28 a particular feature at ~4.15 V, characteristic of monoclinic distortion associated with lithium and vacancy ordering,29 and two distinct plateaus at ~4.53 and ~4.62 V, corresponding to the transitions from the O3 to the H1–3 phase, and the H1–3 to the O1 phase, respectively.30 The voltages at which these plateaus occurred were reproducible to an accuracy of 0.01 V. In contrast, the voltage profile of bare LiCoO$_2$ is rather smooth, where the insulator–metal transition at ~3.93 V and the monoclinic transition at ~4.15 V were not found. These observations are in agreement with those of bare LiCoO$_2$ and “AlPO$_4$”-coated LiCoO$_2$ reported by Cho et al.15 Levassuer et al. have reported that lithium overstoichiometry in LiCoO$_2$ having Li:Co ratios greater than 1.05 can suppress these phase transitions characteristic of stoichiometric LiCoO$_3$.31 Therefore, it is hypothesized that the bare LiCoO$_2$ sample is lithium overstoichiometric, whereas the “AlPO$_4$”-coated LiCoO$_2$ sample largely consists of stoichiometric LiCoO$_2$, which will be further discussed in the context of XPS data in later sections. Moreover, it is


noted that “AlPO₄”-coated LiCoO₂ exhibits higher voltages of approximately 0.02 V upon charge and discharge relative to the bare LiCoO₂ as shown in Figure 1a. As Al substitution in LiCoO₂ has been shown to increase the equilibrium voltage for lithium insertion and removal, it is postulated that a very small amount of Al substitution (5 at %) in LiCoO₂ (down to 100 nm from the particle surface) will result in the bulk of the “AlPO₄”-coated LiCoO₂ sample. This speculation is in good agreement with previous findings in that heating a mixture of 5 wt % Al₂O₃ nanoparticles and 95 wt % LiCoO₂ at 700 °C results in considerable Al substitution (5 at %) in LiCoO₂ (down to 100 nm from the particle surface).

Discharge capacities of bare LiCoO₂ and “AlPO₄”-coated LiCoO₂ upon cycling are compared in Figure 1b and have been shown to be repeatable within 10 mA h g⁻¹. After 30 cycles between the voltage limits of 3.0 and 4.7 V, the coated sample maintained 78.5% capacity retention compared to its first cycle, whereas the bare sample retained only 42.6% of its first-cycle capacity. The improvement in the capacity retention of “AlPO₄”-coated LiCoO₂ is in good agreement with previous studies. In addition, it should be noted that impedance growth was much reduced in the lithium cells of cycled “AlPO₄”-coated LiCoO₂ relative to those of cycled bare electrodes (see the Supporting Information, Figure S2). Previous studies have suggested that capacity loss is attributed to impedance growth during cycling to high voltage. Moreover, “AlPO₄”-coated LiCoO₂ electrodes in this study were shown to exhibit much better capacity retention relative to “ZrO₂”-coated LiCoO₂ electrodes upon cycling to 4.7 V. This difference is not understood. It is speculated that “AlPO₄”-coated and “ZrO₂”-coated LiCoO₂ samples might have very different surface microstructures, which may strongly influence the cycling characteristics.

**Microstructure Characterization—SEM and TEM Imaging.** SEM secondary electron images of bare LiCoO₂ and “AlPO₄”-coated LiCoO₂ particles are compared in images a and b in Figure 2. The rounded morphology of bare LiCoO₂ particles is in good agreement with the hypothesis that bare LiCoO₂ is lithium overstoichiometric, as stoichiometric LiCoO₂ produced at high temperatures such as 1000 °C are typically platelike. The surface of the bare LiCoO₂ particle appears to be fairly smooth, whereas most of the surface of “AlPO₄”-coated LiCoO₂ particles is rough. A fractured particle from the “AlPO₄”-coated LiCoO₂ sample shown in Figure 2c appears to suggest that (1) each particle is a single crystal and (2) a large number of small pits exist at the edge of what appear to be the basal (003)hex planes in comparison to the crystal surfaces parallel to the (003)hex planes. To gain further insight on the microstructure of “AlPO₄”-coated LiCoO₂, we performed TEM studies of micromet “AlPO₄”-coated LiCoO₂ particles, where more than 15 different particles were examined to provide a representative picture of the microstructure. Typical cross-sectional TEM images of an “AlPO₄”-coated LiCoO₂ particle or crystal are shown in Figure 3, where reveals the microstructure of the outer edge of the particle. The coating layer appeared to cover most of the particle surface but it was found that the thickness was not uniform on the micrometer-scale with a thickness variation of 10–100 nm. This observation is repeatable over a number of particle cross-sections with intact surfaces that were studied. This observation is also consistent with the pitted surface found in the SEM images (Figure 2b). At the nanometer scale, an ~10 nm surface layer is clearly visible (Figure 3), which is in good agreement with previous findings.

**Powder X-ray Diffraction Measurements.** X-ray powder diffraction analyses showed that bare LiCoO₂ was single-phase, which can be indexed to the O₃ layered structure with space group R3̄m. Although the O₃ layered phase was the major phase in the “AlPO₄”-coated LiCoO₂ sample, orthorhombic Li₃PO₄ in the γ-phase, which can form at temperatures above 500 °C, was detected as a minor phase, as shown in the X-ray powder diffraction data in Figure 4. Evidence for the presence of AlPO₄ was not found in the diffraction data. The volume fraction of Li₃PO₄ is less than

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In the “AlPO₄”-coated LiCoO₂ sample, 1% in the “AlPO₄”-coated LiCoO₂ sample. Although the reactivity between LiCoO₂ and AlPO₄ thin films was found recently by Kim et al., this result revealed the first evidence of Li₃PO₄ formation in the “AlPO₄”-coated LiCoO₂ samples. It is believed that the AlPO₄ coating nanoparticles reacted with excess lithium in bare LiCoO₂ particles to form Li₃PO₄ on the particle surface and rendered stoichiometric LiCoO₂ in the bulk during the heat treatment at 700 °C. Upon Li₃PO₄ formation, remaining Al³⁺ may form LiAlO₂ or LiCo₁₋ₓAlₓO₂ with high levels of Al substitution on the particle surface and diffuse into the particle interior to form LiCo₁₋ₓAlₓO₂ solid solutions with small amounts of Al substitution.

Table 1. Results of XPS Quantitative Analysis of Overall Surface Composition of Bare and Coated LiCoO₂

<table>
<thead>
<tr>
<th>element</th>
<th>bare LiCoO₂</th>
<th>“AlPO₄”-coated LiCoO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>lithium (Li 1s)</td>
<td>18.6</td>
<td>18.3</td>
</tr>
<tr>
<td>cobalt (Co 2p²ο₂)</td>
<td>15.9</td>
<td>6.2</td>
</tr>
<tr>
<td>oxygen (O 1s)</td>
<td>50.5</td>
<td>50.3</td>
</tr>
<tr>
<td>ionically bonded</td>
<td>27.0</td>
<td>15.6</td>
</tr>
<tr>
<td>covalently bonded</td>
<td>23.5</td>
<td>34.7</td>
</tr>
<tr>
<td>aluminum (Al 2s)</td>
<td>0</td>
<td>6.7</td>
</tr>
<tr>
<td>phosphorus (P 2p)</td>
<td>0</td>
<td>2.5</td>
</tr>
<tr>
<td>carbon (C 1s)</td>
<td>13.6</td>
<td>14.1</td>
</tr>
<tr>
<td>adventitious</td>
<td>11.0</td>
<td>12.5</td>
</tr>
<tr>
<td>oxidized</td>
<td>2.6</td>
<td>1.6</td>
</tr>
<tr>
<td>Na 1s</td>
<td>1.4</td>
<td>1.9</td>
</tr>
<tr>
<td>Li:Co ratio</td>
<td>1.17</td>
<td>2.96</td>
</tr>
<tr>
<td>Al:P ratio</td>
<td>N/A</td>
<td>2.73</td>
</tr>
</tbody>
</table>

* Quantitative analysis was performed using high-resolution spectra of the photoemission lines listed in the table using CasaXPS software. Both peaks measured for O 1s were included in the analysis for each sample. Other elements consisted of a single peak for analysis. Satellite contributions were removed, and curve fitting analysis was used to eliminate interference between the Co 3p and Li 1s peaks.

Table 2. XRD Lattice Parameters and c₆hex/a₆hex Ratio of Bare LiCoO₂ and “AlPO₄”-Coated LiCoO₂ Reveal Negligible Differences between the Two Samples: Lattice Parameters Were Determined Using the HighScore Plus Software Package

<table>
<thead>
<tr>
<th></th>
<th>bare LiCoO₂</th>
<th>“AlPO₄”-coated LiCoO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>a₆hex (Å)</td>
<td>2.8152</td>
<td>2.8151</td>
</tr>
<tr>
<td>c₆hex (Å)</td>
<td>14.0374</td>
<td>14.0430</td>
</tr>
<tr>
<td>c₆hex/a₆hex</td>
<td>4.986</td>
<td>4.988</td>
</tr>
</tbody>
</table>

It is believed that the AlPO₄ coating nanoparticles reacted with excess lithium in bare LiCoO₂ particles to form Li₃PO₄ on the particle surface and rendered stoichiometric LiCoO₂ in the bulk during the heat treatment at 700 °C. Upon Li₃PO₄ formation, remaining Al³⁺ may form LiAlO₂ or LiCo₁₋ₓAlₓO₂ with high levels of Al substitution on the particle surface and diffuse into the particle interior to form LiCo₁₋ₓAlₓO₂ solid solutions with small amounts of Al substitution.

The lattice parameters of the O₃ layered structure in the bare LiCoO₂ and “AlPO₄”-coated LiCoO₂ samples are compared in Table 2. No significant difference was found between these samples. This observation is consistent with previous findings in that although lithium overstoichiometry leads to different voltage profiles, there is no correlation between lattice parameters and lithium overstoichiometry.

STEM EDX Measurements of “AlPO₄”-Coated LiCoO₂. A bright-field STEM image and EDX elemental maps of Co, Al, P, and O collected from one particle are shown in Figure 5. Al and P maps clearly reveal that these two
elements are not distributed uniformly over the whole particle. In addition, the intensities of Al and P do not show co-incident regions of high or low intensity, as would be expected if they occurred in a 1:1 atomic ratio of Al:P as in AlPO₄. Moreover, the intensity of Co signals increases from particle edge to particle center, which is expected from the increasing thickness toward the center under the transmitted electron beam. However, the aluminum signal appears strong and well-defined at the particle edge, which indicates that Al is not substituted uniformly in the “AlPO₄”-coated LiCoO₂ and is segregated on the particle surface in a thin layer. These observations indicate the formation of Al-rich regions and P-rich regions on the particle surface. A bright-field STEM image and EDX maps of another particle in Figure 6 clearly reveals the distinct separation of Al-rich regions and P-rich regions in the surface layer. It is interesting to note that Co was not detected in the Al-rich and P-rich regions. In addition, a thin white line was noted in the Al map, which may suggest the formation of a thin shell of O₃ layered LiCo₁₋₆Al₂O₅ solid solution with high Al substitution levels. Moreover, the O signals corresponded closely to the same region as the P signals, indicating the presence of a compound containing both elements as in Li₃PO₄. The observations are in good agreement with the formation of Li₃PO₄ as revealed by XRD (Figure 4). Therefore, combined X-ray diffraction and STEM EDX data suggest that reactions between AlPO₄ nanoparticles and bare LiCoO₂ during the heat-treatment step lead to formation of Al-rich regions, namely, LiCo₁₋₆Al₂O₅ with high Al content, and P-rich regions, namely, Li₃PO₄ on the particle surface.

XPS Measurements of Bare LiCoO₂ and “AlPO₄”-Coated LiCoO₂. Surface Chemical Compositions. The surface chemical compositions of bare LiCoO₂ and “AlPO₄”-coated LiCoO₂ are compared in Table 1. The bare LiCoO₂ sample was found to have a surface composition of Li₁₉Co₁₉O₅₈. The intensity of Co signals increases from particle edge to particle center, which is expected from the increasing thickness toward the center under the transmitted electron beam. However, the aluminum signal appears strong and well-defined at the particle edge, which indicates that Al is not substituted uniformly in the “AlPO₄”-coated LiCoO₂ and is segregated on the particle surface in a thin layer. These observations indicate the formation of Al-rich regions and P-rich regions on the particle surface. A bright-field STEM image and EDX maps of another particle in Figure 6 clearly reveals the distinct separation of Al-rich regions and P-rich regions in the surface layer. It is interesting to note that Co was not detected in the Al-rich and P-rich regions. In addition, a thin white line was noted in the Al map, which may suggest the formation of a thin shell of O₃ layered LiCo₁₋₆Al₂O₅ solid solution with high Al substitution levels. Moreover, the O signals corresponded closely to the same region as the P signals, indicating the presence of a compound containing both elements as in Li₃PO₄. The observations are in good agreement with the formation of Li₃PO₄ as revealed by XRD (Figure 4). Therefore, combined X-ray diffraction and STEM EDX data suggest that reactions between AlPO₄ nanoparticles and bare LiCoO₂ during the heat-treatment step lead to formation of Al-rich regions, namely, LiCo₁₋₆Al₂O₅ with high Al content, and P-rich regions, namely, Li₃PO₄ on the particle surface.
The oxidized C detected in both samples is in the form of Li$_2$CO$_3$. It should be noted that all the Li-containing samples examined in this study (Figure 7) exhibit the C 1s peak characteristic of Li$_2$CO$_3$. Therefore, it is believed that the presence of Li$_2$CO$_3$ on the particle surface results from surface reactions with CO$_2$ in air. It is also possible that a small fraction of this signal is due to Na$_2$CO$_3$ species, as indicated by a small Na signal in the survey spectrum. It was found that bare LiCoO$_2$ has significantly more surface Li$_2$CO$_3$ in comparison to “AlPO$_4$”-coated LiCoO$_2$. Quantitative comparison of C 1s peaks of carbonate species with the hydrocarbon calibration peaks revealed that the amount of carbonate species was reduced by about 70% for the coated LiCoO$_2$ compared to bare LiCoO$_2$.

The Al 2p and P 2p photoemission peaks were found for “AlPO$_4$”-coated LiCoO$_2$ but not for bare LiCoO$_2$, as expected. Here, we examine the binding environment of Al and P. As shown in Figure 8a, the Al 2p peak occurs at 73.3 eV. This peak position considerably differs from the Al 2p peak at 75.0 eV of the reference AlPO$_4$ sample used in this study. The oxidation states of Al and P on the coated LiCoO$_2$ surface are similar to those of P in Li$_3$PO$_4$ and Al in LiAlO$_2$. Dashed lines indicate peak positions in the coated LiCoO$_2$ sample.

![Figure 8](image1.png)

**Figure 8.** XPS spectra of the (a) Al 2p and (b) P 2p photoemission lines for “AlPO$_4$”-coated LiCoO$_2$ and pure AlPO$_4$. The large shifts to lower binding energy for the coated LiCoO$_2$ relative to the reference AlPO$_4$ for both spectra indicate that the aluminum and phosphorus are not present as AlPO$_4$ in the surface coating. The oxidation states of Al and P on the coated LiCoO$_2$ surface are similar to those of P in Li$_3$PO$_4$ and Al in LiAlO$_2$. Dashed lines indicate peak positions in the coated LiCoO$_2$ sample.

The O 1s photoemission lines from bare LiCoO$_2$ and “AlPO$_4$”-coated LiCoO$_2$ samples show two peaks, as shown in Figure 9. The coated LiCoO$_2$ photoemission peak at 531.13 eV is distinctly different from that of the reference AlPO$_4$ sample at 532.22 eV. Dashed lines indicate the peak positions in the coated LiCoO$_2$ sample.

![Figure 9](image2.png)

**Figure 9.** XPS spectra of the O 1s photoemission line for bare and coated LiCoO$_2$, in comparison with some reference compounds. The coated LiCoO$_2$ photoemission peak at 531.13 eV is distinctly different from that of the reference AlPO$_4$ sample at 532.22 eV. Dashed lines indicate the peak positions in the coated LiCoO$_2$ sample.

AlPO$_4$ thin film. This difference further confirms that the AlPO$_4$ phase is absent from the particle surface of “AlPO$_4$”-coated LiCoO$_2$. Given a resolution of 0.05 eV for our XPS data, the Al 2p peak found in the “AlPO$_4$”-coated LiCoO$_2$ is comparable to that of the reference LiAlO$_2$ sample having an Al 2p peak at 73.4 eV but is higher than that of the reference Al-substituted LiCoO$_2$-$\text{LiAl}_0.1\text{Co}_0.9\text{O}_2$ sample (72.4 eV). This result is in good agreement with the view that the surface of the coating layer may contain Al-substituted LiCoO$_2$ with substitution levels that are much higher than that of Li$_3$PO$_4$. The P 2p photoemission peak at 133.2 eV for “AlPO$_4$”-coated LiCoO$_2$ is considerably different from that of the reference AlPO$_4$ at 134.4 eV but agrees very well with that of the reference Li$_3$PO$_4$ sample at 133.2 eV, as shown in Figure 8b. This result is consistent with the detection of orthorhombic Li$_3$PO$_4$ on the surface of “AlPO$_4$”-coated LiCoO$_2$ as revealed by X-ray powder diffraction data. Therefore, these comparative studies of Al 2p and P 2p binding energies confirm previous STEM EDX data that the coating layer contains no AlPO$_4$.

The O 1s photoemission lines from bare LiCoO$_2$ and “AlPO$_4$”-coated LiCoO$_2$ samples show two peaks, as shown in Figure 9. The lower-binding-energy peak at 528.9 eV for bare LiCoO$_2$ and 529.4 eV for “AlPO$_4$”-coated LiCoO$_2$ can be attributed to the O$_2^-$ ions in the O$_3$ layered structure. It is speculated that the higher binding energy of O 1s line for “AlPO$_4$”-coated LiCoO$_2$ is attributed to Al substitution in LiCoO$_2$ on the particle surface, which makes the cobalt–oxygen bonds more covalent and shifts the O 1s peak to higher binding energy relative to bare LiCoO$_2$. Dupin et al. have shown that a LiCoO$_2$ sample prepared at 900 °C shows the O1s peak at 529.1 eV (with hydrocarbon calibration to the same energy as that used in this study). The slight shifts in the binding energy of O 1s of bare LiCoO$_2$ relative to bare LiCoO$_2$.

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that of Dupin et al.\textsuperscript{41} are not well-understood. The presence of Li$_3$PO$_4$ and LiCo$_{1-y}$Al$_y$O$_2$ (with high levels of Al substitution) phases in the surface layer can lead to shifts of the O 1s peak at ~529 eV to higher energy, as shown in Figure 9. The higher-binding-energy peaks of bare LiCoO$_2$ and “AlPO$_4$”,-coated LiCoO$_2$ occur at 531.2 and 531.1 eV, respectively. This peak in the “AlPO$_4$”,-coated LiCoO$_2$ sample can be attributed to the presence of Li$_3$PO$_4$ on the surface, as the Li$_3$PO$_4$ sample shows an O 1s peak at 531.1 eV. However, it is difficult to speculate the physical origin of this peak for the bare sample. Assuming all non-HC carbon peak is carbonate species, about 33.734% of this higher binding energy peak of O 1s results from carbonate species on the surface of bare LiCoO$_2$ particles, and other components such as surface defects have to be considered. Dupin et al. have suggested that such a peak might result from surface defects associated with oxygen oxidation greater than O$^{2-}$ ions\textsuperscript{41,42} and more covalent Co–O bonds\textsuperscript{43} on the LiCoO$_2$ particle surface. Moreover, it should be noted that reference AlPO$_4$ shows an O 1s peak at 532.2 eV that is considerably different from the observed O 1s signals of “AlPO$_4$”,-coated LiCoO$_2$, which further confirms that AlPO$_4$ is not present on the coated particle surface.

The Co 2p peaks for bare LiCoO$_2$ reveal a 2p$_{1/2}$ peak and a 2p$_{3/2}$ peak at 779.6 and 794.8 eV, respectively, as shown in Figure 10. Shakeup satellite peaks for each line are located at 10 eV higher relative to the main peak. These peak positions correspond well with those of Co$^{3+}$ (779.6 and 794.8 eV) as reported by Dupin et al.\textsuperscript{42} “AlPO$_4$”,-coated LiCoO$_2$ shows 2p$_{1/2}$ and 2p$_{3/2}$ peaks with a shift of 0.4 eV toward higher binding energy relative to those of bare LiCoO$_2$ and LiCo$_{0.9}$Al$_{0.1}$O$_2$. The nature of this energy difference observed in the “AlPO$_4$”,-coated LiCoO$_2$ sample is not understood, which may result from a dissimilar bonding environment of Co$^{3+}$ in pyramidal sites induced by lithium-overstoichiometry\textsuperscript{42} in the bare LiCoO$_2$ and LiCo$_{0.9}$Al$_{0.1}$O$_2$ nanocomposite.

Dupin et al.\textsuperscript{41} have suggested that such a peak might result from contri-butions from other Li-containing phases present in the coating layer. For example, LiAlO$_2$ and Li$_3$PO$_4$ show a Li 1s peak at 54.7 and 54.9 eV, respectively. The value of the Li 1s peak position found for “AlPO$_4$”,-coated LiCoO$_2$ fell in between that of LiCoO$_2$ and that of LiAlO$_2$, which is in good agreement with the presence of a heavily Al-substituted LiCoO$_2$ phase present on the particle surface.

**Discussion**

**Proposed Microstructure for AlPO$_4$-Coated LiCoO$_2$.** Charge and discharge voltage profiles have suggested that bare LiCoO$_2$ is lithium-overstoichiometric and XPS analyses have revealed that this sample has a Li:Co atomic ratio of 1.14. The high Li:Co ratio, in part, is due to the presence of surface Li$_2$CO$_3$ contaminant. The bare LiCoO$_2$ sample was mixed with 1 wt % AlPO$_4$ nanoparticles and heat-treated at 700 °C to form “AlPO$_4$”,-coated LiCoO$_2$. In the “AlPO$_4$”,-coated LiCoO$_2$ sample, the bulk layered structure appears to be lithium-stoichiometric, as evidenced by the presence of insulator–metal, lithium-vacancy ordering, and O3 to H1–3 transitions, although a small level of Al (<10 at. %) may be substituted in bulk during the heat-treatment step.

Combined X-ray powder diffraction, STEM EDX, and XPS analyses of “AlPO$_4$”,-coated LiCoO$_2$ have shown that (1) AlPO$_4$ is absent on the coated particle surface; (2) Al-rich

LiAl$_{x}$Co$_{1-y}$O$_2$ (y is close to 1) and P-rich Li$_3$PO$_4$ regions are present on the surface; and (3) surface coverage of Al-rich regions (~10 nm) is high but the thickness is small relative to P-rich regions (~100 nm). The proposed microstructure for “AlPO$_4$”-coated LiCoO$_2$ is shown in Figure 12. X-ray powder diffraction analyses have confirmed that Li$_3$PO$_4$ has an orthorhombic structure in the γ phase. In this study, we propose that excess lithium in the form of Li$_2$CO$_3$ in bare LiCoO$_2$ reacts with AlPO$_4$ nanoparticles during the heat treatment at 700 °C and produces a rough or pitted surface microstructure along the edges of the layers.

**Implication of Coating Microstructure on Rate Capability and Cycling.** Li$_3$PO$_4$ is a lithium ion conductor, which would allow lithium diffusion through the coating during charge and discharge of “AlPO$_4$”-coated LiCoO$_2$. As it has a lithium ion conductivity of ~6 × 10^{-8} S/cm, a 100 nm Li$_3$PO$_4$ layer would result in an area specific resistance of ~170 Ω cm$^2$, which would lead to an electrode resistance of ~0.17 Ω for a typical porous electrode of 1000 cm$^2$/cm$^2$geo. Moreover, XPS data in this study suggest that the amount of Li$_2$CO$_3$ on the “AlPO$_4$”-coated LiCoO$_2$ particle surface is much lower than that on the bare LiCoO$_2$ (Figure 7). Li$_2$CO$_3$ is not known to conduct lithium in bulk and can be highly resistive to lithium transport between the liquid electrolyte and active particles. Therefore, the presence of Li$_3$PO$_4$ in the particle surface of “AlPO$_4$”-coated LiCoO$_2$ can lower resistance of lithium diffusion through the particle surface and reduce electrode polarization relative to bare LiCoO$_2$, which would lead to the improvement in rate capability. Al substitution in LiCoO$_2$ is shown to increase the lattice parameter $c_{\text{hex}}$ and interlayer spacing, and this structural change is believed to be responsible for enhanced lithium diffusion in bulk Li$_{1-x}$Al$_x$O$_2$ particles by Myung et al. However, as the amounts of Al substitution in the bulk of “AlPO$_4$”-coated LiCoO$_2$ particles are very small, the role of bulk Al substitution in enhancing the rate capability is believed to be minor.

We propose that surface LiAl$_{x}$Co$_{1-y}$O$_2$ (y is close to 1) and Li$_3$PO$_4$ particles of “AlPO$_4$”-coated LiCoO$_2$ can protect Li$_3$PO$_4$ from harmful interactions with the electrolyte and from attack by trace amounts of HF and reduce cobalt dissolution, which is believed to largely contribute to impedance growth upon cycling to high voltages. The protective nature of surface LiAl$_{x}$Co$_{1-y}$O$_2$ (y is close to 1) is supported by previous findings of Myung et al., which have shown that Al substitution of up to 30 at % can significantly reduce cobalt dissolution in the electrodes charged to 4.5 V. It is interesting to mention that Cho et al. have reported that “AlPO$_4$”-coated LiCoO$_2$ exhibits a considerably lower amount of cobalt dissolution and superior stability upon cycling to 4.8 V relative to “Al$_2$O$_3$”-coated LiCoO$_2$. It should be noted that the “Al$_2$O$_3$”-coated LiCoO$_2$ obtained from a heat treatment at 700 °C is shown to develop LiCoO$_2$ solid solutions (having y in the range of 0.05 to 0) near the particle surface. Superior capacity retention of “Al$_2$O$_3$”-coated LiCoO$_2$ to “AlPO$_4$”-coated LiCoO$_2$ may be attributed to (1) absence of cobalt-free surface particles to protect active Li$_3$PO$_4$ particles and (2) cobalt and aluminum dissolution from LiCoO$_2$→Al$_2$O$_3$ having low levels of Al substitution. Moreover, Pereira et al. have reported that removal of surface Li$_2$CO$_3$ from lithium overstoichiometric LiCoO$_2$ has been shown to lower electrode impedance and enhance cycling performance at room temperature. Reduction of surface Li$_2$CO$_3$ in the “AlPO$_4$”-coated LiCoO$_2$ may thus contribute to markedly improved cycling performance relative to bare “LiCoO$_2$”. Detailed studies are needed to elucidate the mechanism.

Lithium removal from “AlPO$_4$”-coated LiCoO$_2$ leads to all phase transitions (insulator→metal, lithium and vacancy ordering, and O3 to H1–3 transitions) known to stoichiometric LiCoO$_2$. In contrast, these transitions are absent in the bare LiCoO$_2$. Although these phase transitions may lead to structural damage and capacity loss, particularly at extremely high current densities, it is believed that superior cycling characteristics of “AlPO$_4$”-coated LiCoO$_2$ to bare LiCoO$_2$ results largely from surface stability rather than structural stability upon cycling to high voltages.

**Implication of Coating Microstructure on Thermal Properties.** Highly delithiated Li$_{1-x}$CoO$_2$ with a large number of Co$^{4+}$ is thermodynamically unstable. It can release oxygen gas by thermal decomposition at relatively low temperatures, and react with liquid electrolyte to cause gas generation. “AlPO$_4$”-coated LiCoO$_2$ has exhibited superior thermal and safety characteristics upon overcharging and high-temperature storage at highly charged states in comparison to bare LiCoO$_2$ and “Al$_2$O$_3$”-coated LiCoO$_2$ samples. The notice-

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able difference in the thermal and safety characteristics of highly charged electrodes in the presence of electrolyte suggests that modification of particle surface microstructure can significantly alter the kinetics of reactions between active particles and electrolyte. Yu et al. have shown that LiP04 thin films can be stable up to 6 V vs Li under impedance measurements and some decomposition occurs (possibly decomposes to Li2P2O7) at 3.6 V vs Li from potentiodynamic measurements, where this discrepancy is not explained. It is hypothesized in this study that large potential gradients can develop in the Li3P04 regions on the surface of “AlPO4”-coated LiCoO2 particles upon overcharging and thus reduce the potential experienced by Li1CoO2 from which the decomposition of liquid electrolyte and gas generation are significantly decreased. The lack of a lithium-conducting solid electrolyte layer on the particle surface would result in high potentials at the interface between particle surface and liquid electrolyte upon overcharging. Therefore, it is postulated that the presence of electrochemically stable, lithium-conducting phases on the particle surface may significantly improve the thermal characteristics of Li1CoO2 at high voltages. This hypothesis is further supported by the fact that “AlPO4”-coated LiCoO2 exhibits much improved thermal characteristics in comparison to LiCoO2 with oxide coating materials, where Li-conducting phases are unlikely to form on the particle surface during the heat-treatment step. Although small amounts of Al substitution in LiCoO2 particles can effectively reduce cobalt dissolution and provide improved cycling performance, it is speculated that Li1AlCo2−xO2 solid solutions may not lower the kinetics of reactions with electrolyte relative to Li1CoO2 at low Li contents. Therefore, it is believed that complete surface coverage of LiCoO2 particles with a thin layer of lithium-conducting phases that are electrochemically stable at high voltages would lead to superior thermal characteristics relative to the “AlPO4”-coated LiCoO2 sample examined in this study, which consists of particles partially covered by Li1P04.

Very recently, Lee et al. have shown that “LiCoPO4”-coated LiCoO2 shows even better thermal characteristics relative to “AlPO4”-coated LiCoO2 particles during nail penetration tests at 4.4 V. Such improvement has been attributed to reduction in the amounts of surface Li2CO3 and LiOH in the “LiCoPO4”-coated LiCoO2 relative to “AlPO4”-coated LiCoO2. However, it is surprising to note that LiCoPO4 can suppress reactions with the electrolyte upon cycling to high voltages (close to ~5 V) or during overcharging, as recent findings have shown that lithium removal from olivine LiCoPO4 leads to significant electrolyte decomposition, which results in capacity loss during cycling.

Further microstructural studies are needed to reveal the physical nature of particle surface of “LiCoPO4”-coated LiCoO2.

**Conclusions**

In this study, it is proposed that surface microstructure of active particles plays an important role in the cycling and thermal characteristics of lithium batteries, particularly upon cycling to high voltages. Superior cycling and thermal properties of “AlPO4”-coated LiCoO2 to bare LiCoO2 is attributed largely to a difference in the surface microstructure rather than structural instability. Combined STEM EDX and XPS studies have revealed that AlPO4 does not exist in the “AlPO4”-coated LiCoO2 sample treated with a 700 °C heating step. The surface of “AlPO4”-coated LiCoO2 consists of a LiPO4 phase and a LiAl3Co1−xO2 phase with high levels of aluminum. It is proposed that both phases can significantly reduce Co dissolution and impedance growth during cycling to high voltages, which leads to superior cycling performance relative to bare LiCoO2. XPS studies have shown that the amount of surface Li2CO3 is much smaller on the “AlPO4”-coated LiCoO2 particles. Moreover, having Li-conducting phases such as Li3PO4 and LiAl3Co1−xO2 on the particle surface instead of Li-blocking Li2CO3 can reduce resistance to lithium diffusion at the particle—electrolyte interface, which may lead to enhanced rate capability. Furthermore, it is postulated that the presence of electrochemically stable, lithium-conducting phases on the particle surface may reduce the potential experienced by Li1CoO2 and significantly improve the thermal characteristics of Li1CoO2 at high voltages. Last, this study shows the importance of understanding the surface microstructure of electrode materials in order to design and develop lithium batteries with cycling and thermal properties that can meet the demands of portable and transportation applications.

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**Supporting Information Available:** X-ray diffraction patterns for reference compounds; voltage profiles (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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