LiCoO₂ cathode material has a hexagonal α-NaFeO₂ layered structure (R3m) based on a close-packed network of oxygen atoms with alternating lithium and cobalt planes. This material is mainly used as a cathode material in commercial Li-ion batteries as a result of its excellent electrochemical properties. However, it has been reported that LiCoO₂ exhibited abrupt capacity fading during cycling above 4.3 V. Recently, there has been a great deal of effort made on improving the electrochemical properties of LiCoO₂. Tukamoto and West reported that the substitution of a small amount of Co³⁺ by Mg²⁺ could improve the electronic conductivity of LiCoO₂. Jang et al. proposed that a microfracture in the cathode powders during cycling led capacity loss. Through transmission electron microscopy (TEM) studies, they showed that substitution of Co³⁺ by Al³⁺ in LiCoO₂ restrained the evolution of a microfracture in the powder, and reduced the capacity fading, compared to the unsubstituted LiCoO₂. However, the cation-substituted LiCoO₂ had a lower initial discharge capacity than LiCoO₂. Recently, Cho et al. reported that a metal-oxide coating by a sol-gel method significantly improved the electrochemical properties of LiCoO₂ without significant specific-capacity loss, and that the metal-oxide-coating layer acted as a solid electrolyte with a reasonably high Li-ion conductivity. Similarly, other groups reported that ZrO₂- and TiO₂-coated LiCoO₂ improved the capacity retention with high charge-cutoff voltages (>4.4 V). Recently, Chen and Dahn reported that the cycle-life performance of LiCoO₂ was improved by using a simple heat-treatment, due to the elimination of surface contamination on the cathode, for example, moisture, organic species, etc. However, we found that the thermal history of bare powders did not improve the electrochemical properties. The powder size in Ref. 13 is smaller than the conventional ~10 μm sized powders.

Until now, most studies on cathode materials have concentrated on improving the electrochemical properties. However, even metal-oxide-coated LiCoO₂ with an excellent electrochemical performance shows thermal instability at the overcharged state, which is similar to the bare LiCoO₂. This safety problem of Li-ion cells is mainly related to the exothermic thermal decomposition of the cathode, electrolyte, and anode. Among these, the exothermic reaction of the flammable electrolyte with the cathode material is a well-known trigger for thermal runaway. To enhance the safety of Li-ion cells, some studies on more stable electrolytes at overcharged states have been reported. Recently, it was reported that a novel AlPO₄-nanoparticle coating on the LiCoO₂ surface improved both the thermal stability and electrochemical properties of the LiCoO₂ cathodes at high cutoff voltages. TEM showed that a nanoscale layer (~20 nm) was coated homogeneously over the LiCoO₂ surface, and consisted of randomly-oriented AlPO₄ nanoparticles with an average diameter of ~3 nm. In addition, it was reported that the coating material affected the electrochemical and thermal behaviors of the coated LiCoO₂.

In this paper, the effect of annealing temperature of the AlPO₄-nanoparticle coating was examined from the viewpoint of the electrochemical properties of LiCoO₂ with various charge-cutoff voltages of 4.3, 4.6, and 4.8 V.

The electrochemical properties of AlPO₄-coated LiCoO₂ cathodes were found to be superior to those of bare cathodes at various charge-cutoff voltages (4.3, 4.6, and 4.8 V), and depended on the annealing temperature. The AlPO₄-coated cathodes annealed at 600 and 700°C retained a discharge capacity of ~150 mAh/g even with a 4.8 V charge-cutoff voltage (after 46 cycles at 1 C = 140 mA/g). The bare cathode showed zero capacity retention at the same condition after only 20 cycles. The enhanced electrochemical performance and rate capability in the coated cathodes were attributed to the inhibition of structural degradation during cycling. The AlPO₄-nanoparticle coating layer on the LiCoO₂ effectively suppressed cobalt dissolution and a nonuniform distribution of local strain in the cathode.

**Experimental**

Al(NO₃)₃·9H₂O and (NH₄)₂HPO₄ (3 and 1 g, respectively) were dissolved in distilled water until a white AlPO₄-nanoparticle suspension was observed. Subsequently, the LiCoO₂ powders (with an average size of ~10 μm) was slowly added to the coating solution, and mixed until the final viscosity of the slurry reached ~100 poise. The slurry was then dried in an oven for 6 h at 130°C, and annealed at 400, 600, and 700°C, respectively, for 5 h in air. To test the electrochemical properties of the cathodes, coin-type half cells (2016 size) were fabricated in an Ar-filled glove box. The assembly and preparation of the coin-type half cells are described elsewhere.

The electrolyte used was 1 M LiPF₆ with ethylene carbonate/diethyl carbonate/ethyl-methyl carbonate (EC/DEC/EMC: 30/30/40 vol %). Cycling tests of the coin-type half cells (with a Li-metal anode) were performed with charge-cutoff voltages of 4.3, 4.6, and 4.8 V (with a fixed discharge-cutoff voltage of 3 V). The tests were proceeded by charging and discharging at 0.1 C for the first and second cycles, 0.2 C for the third cycle, 0.5 C for the fourth cycle, and finally at 1 C (=140 mA/g) for the remaining cycles. For the galvanostatic intermittent titration technique (GITT), the test cells were allowed to reach their equilibrium states after each incremental charge step using a constant current of 0.1 C by allowing an open-circuit period of 10 h. The cells for the diffusivity measurements were precycled for each cycle at 0.1, 0.2, 0.5, and 1 C between 4.4 and 3 V. To measure cobalt dissolution from the bare and coated LiCoO₂ cathodes, the electrolyte in the cycled cells was collected by a centrifugal separation method, and the amount of dissolved Co in the electrolyte was measured by inductively coupled plasma-atomic emission spectroscopy (ICP-AES).
The lattice constants and local strains were characterized by X-ray diffraction (XRD) using Cu Kα radiation.

Results and Discussion

Figure 1 shows a TEM bright-field image of the AlPO₄-coated LiCoO₂ annealed at 400°C. Energy-dispersive X-ray spectroscopy (EDS) confirms the presence of Al and P in the nanoscale-coating layer. The arrows indicate the interface between the AlPO₄ nanoscale-coating layer and LiCoO₂.

Figure 2 shows the ex situ XRD patterns of the bare and coated LiCoO₂ at different charge voltages up to 4.7 V. Van der Ven et al. proposed that a stage-two phase (H1-3) exists at x = 0.16 (~4.6 V) in LiₓCoO₂. Chen et al. experimentally confirmed the presence of a H1-3 phase in the Al₂O₃-coated LiCoO₂. Similarly, the phase transition from O3 to H1-3 is confirmed between 4.5 and 4.6 V. However, only the bare LiCoO₂ shows a minor peak corresponding to the O1 phase, not the AlPO₄-coated cathode. In addition, at the 4.6 V-charged state, an unidentified peak, which was first mentioned by Chen et al., is observed at ~19.1°. They suggested that other staging phases may exist during the phase transition from O3 to H1-3. However, more systematic studies are needed to confirm the effect of the AlPO₄ coating on the phase transitions.

The annealing temperature has an influence on the electrochemical properties of the coated LiCoO₂ upon cycling. Figure 3 shows the initial charge and discharge curves of the bare and AlPO₄-coated LiCoO₂ cathodes with various charge-cutoff voltages of 4.3, 4.6, and 4.8 V. The discharge-cutoff voltage in Li/LiCoO₂ was fixed at 3 V. Although the 400°C annealed cathodes have a relatively low initial discharge capacity, they also show good capacity retention, compared with the bare ones. It is clear that the coated cathodes with various charge-cutoff voltages show superior cycle-life performance to the bare ones after 50 cycles.

The lithium diffusivities of the cathodes after the pre-cycles were measured by GITT. As shown in Fig. 5, the 600 and 700°C annealed cathodes effectively prevent the degradation of Li diffusivities during the cycles, in comparison to the bare and 400°C annealed cathode. To test the rate capability of the cathodes, Li-ion cells (graphite/
LiCoO₂) using the bare, 400 and 700°C annealed cathodes were fabricated and cycled between 4.2 and 2.75 V with a discharge rate from 0.2 to 2 C.

Figure 6. Rate capabilities of the coin-type Li-ion cells (with a graphite anode) using the bare and AlPO₄-coated LiCoO₂ cathodes. The discharge rate was 0.2, 1, or 2 C, while the charging rate was fixed at 1 C between 4.2 and 2.75 V.

As shown in Fig. 4, the coated cathodes have excellent capacity retention compared to the bare ones at a high charge-cutoff voltage. The capacity retention after 46 cycles at a rate of 1 C is shown in Fig. 7. All the cathodes show relatively good capacity retention with a 4.3 V charge-cutoff voltage. As the cutoff voltage increases, the coated cathodes exhibit excellent capacity retention, but the bare cathode degrades rapidly. To understand the electrochemical performance enhancement by the AlPO₄ coating, the dissolution of cobalt from the cathodes was measured by ICP-AES, and a nonuniform distribution of local strain was obtained by XRD peak broadening.

Figure 8 shows the dissolution of cobalt from the cathodes at the initial charging and after 50 cycles, respectively. Initially, the bare and coated cathodes were charged to 4.3, 4.6, and 4.8 V, respectively, maintained at each voltage for 30 min, and disassembled in an Ar-filled glove box. As the charge voltage increases, the amount of Co dissolution from the bare cathode rapidly increases at the initial charging (Fig. 8a). The bare cathode charged to 4.8 V has a larger Co dissolution (by approximately two orders of magnitude) than that charged to 4.3 V. The AlPO₄-coated cathodes show suppressed Co dissolution. Furthermore, Co dissolution from the coated cathodes after 50 cycles, as shown in Fig. 8b, has very similar behavior to that at the initial charging. The cobalt dissolution from the coated cathodes is effectively suppressed by the AlPO₄-nanoparticle coating, and correlates with the enhanced electrochemical performance of cathodes with the high charge-cutoff voltages (>4.6 V).

Amatucci et al. proposed that the capacity decay in LiCoO₂ is coupled with cobalt and oxygen decomposition from LiCoO₂, thus inducing structural degradation. Therefore, variations in the lat-
tice constant \(c\) and the \(c/a\) ratio (at 3 V) are measured after 50 cycles with different charge-cutoff voltages (Fig. 9). The \(c\)-axis in the bare LiCoO\(_2\), after cycling expands as the charge-cutoff voltage increases, which is unlike the coated cathodes. A similar behavior is observed from the change in the \(c/a\) ratio (indicating structural degradation) on the bare and AlPO\(_4\)-coated LiCoO\(_2\) cathodes: the coated cathodes show much smaller changes in the \(c/a\) ratio than the bare ones. An AlPO\(_4\) nanoparticle coating may inhibit LiCoO\(_2\) from structural degradation during cycling, and can therefore improve the capacity retention over the bare cathodes.

To quantitatively estimate the structural degradation after cycling, the nonuniform distribution of local strain was obtained from the broadening of diffraction peaks, before and after cycling. Figure 10 shows the XRD patterns of the bare and AlPO\(_4\)-coated (600°C annealing) cathodes with a 4.6 V cutoff voltage. The peak widths \(\Delta k\) (full width at half-maximum, fwhm) were fitted for five selective peaks \((003), (101), (104), (015),\) and \((018)\) with a scattering vector \(k = (4\pi/\lambda)\sin \theta\) using a double-peak Lorentzian function for \(K\alpha_1\) and \(K\alpha_2\). Peak broadening may be associated with microstructural defects or a nonuniform distribution of local strain.\(^{28,29}\) To remove the instrumental broadening effect, a resolution function \(D_k\) obtained from Si crystals was subtracted after fitting each peak. The nonuniform distribution of local strain in the cathode is estimated from the slope of \(\Delta k\) vs. \(k\) plots (Fig. 11). The local strains of both the bare and coated cathodes prior to cycling have similar values of \(-0.04\%\). With the 4.6 V charge-cutoff, the local strain in the cycled-bare cathode increased by a factor of three, compared to the uncycled bare one. Local-strain analysis clearly demonstrates that the AlPO\(_4\)-nanoparticle coating successfully suppresses the structural degradation caused by Co dissolution, thereby preventing the capacity fading during cycling with high charge-cutoff voltages.

Conclusions

The annealing temperature significantly affected the electrochemical properties of the AlPO\(_4\) coated LiCoO\(_2\) cathodes. After
600 and 700°C annealing, the coated cathodes showed excellent electrochemical performance with high cutoff voltages (≈4.6 V). While 400°C annealed cathodes had a relatively low initial discharge capacity and a poor rate capability, they also exhibited good capacity retention after 50 cycles. Cobalt dissolution from the cathode and a nonuniform distribution of local strain were attributed to the suppressed structural degradation during cycling. More studies aimed at identifying the detailed mechanisms of enhanced electrochemical performance in the AlPO4-coated LiCoO2 are underway.

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