Effect of AlPO$_4$-Nanoparticle Coating Concentration on High-Cutoff-Voltage Electrochemical Performances in LiCoO$_2$

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AlPO$_4$ coating thickness on LiCoO$_2$ cathodes was controlled in the range on the order of 10-100 nm by changing the AlPO$_4$-nanoparticle concentration in the coating solution. The specific capacity and cycle-life performance of the coated cathodes had a strong correlation with the AlPO$_4$ coating concentration (thickness). The cycle-life performance of the 1.0 wt % AlPO$_4$-coated cathodes had the best cycling stability, showing 149 mAh/g capacity retention with 4.8 V charge cutoff by 50 cycles at 1 C (=140 mA/g) rate after precycles. However, the bare cathode showed zero capacity retention at the same condition after only 20 cycles. As the coating concentration was increased to 3.2 wt %, the amount of Co dissolution into the electrolyte decreased. In contrast, the 1.0 wt % AlPO$_4$-coated cathode showed the best cycling stability, possibly due to the suppression of Li diffusivity decay and the appropriate electronic conduction.
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Although LiCoO$_2$ cathode material has been used in most commercial Li-ion cells due to its high energy density and good electrochemical performance at an elevated temperature, several studies have been reported beyond 4.3 V to improve the electrochemical properties. Tukamoto *et al.* reported that the partial substitution of Co^{3+} by Mg^{2+} improved the electronic conductivity of the cathode.[1] However, Mg doping could not enhance the capacity retention of the cathode, and the specific capacity of Mg-doped LiCoO$_2$ was lower than that of the undoped LiCoO$_2$. Jang *et al.* proposed that anisotropic lattice distortion during Li intercalation and deintercalation propagated microfractures of the cathode, resulting in capacity loss.[2] Furthermore, they demonstrated that the transmission electron microscopy (TEM) results of the cycled LiAl$_{0.25}$Co$_{0.75}$O$_2$ showed a lower microfracture phenomenon and suggested that the substitution of Co^{3+} by Al^{3+} in LiAl$_{1-x}$Co$_x$O$_2$ could solve the problem of capacity fading. However, the specific capacity of the LiAl$_{1-x}$Co$_x$O$_2$ was lower.

Recently, Cho *et al.* reported a different approach by coating the cathode particle with metal oxides (Al$_2$O$_3$, ZrO$_2$, etc.) derived using the sol-gel method.[3-7] A metal-oxide coating improved both capacity retention and rate capability without sacrificing the specific capacity of the cathode. They proposed that the metal-oxide coating layer acted as a solid electrolyte with a low electronic conductivity but a reasonably high Li-ion conductivity in the Li-Al-O coating layer.[7] For example, the Li-ion conductivity of a 0.7 Li$_2$O-0.3 Al$_2$O$_3$ solid electrolyte is ~10^{-7} S/cm at room temperature.[8] Similar to this, ZrO$_2$- and TiO$_2$-coated LiCoO$_2$ showed an excellent capacity retention above the 4.6 V charge-cutoff voltages, possibly due to a decreased Co dissolution.[9,10]

Despite the superior electrochemical properties, the metal-oxide coating exposed a critical problem: it showed the thermal instability of the Li-ion cell during the 12 V overcharge tests. Recently, it was reported that an AlPO$_4$-nanoparticle coating on LiCoO$_2$ improved both the thermal stability and electrochemical performance of LiCoO$_2$ cathodes at high voltages ($\geq$4.3 V).[11-13] This paper reports the dependence of the AlPO$_4$-nanoparticle-coating concentration on the electrochemical properties in LiCoO$_2$ cathodes with high charge-cutoff voltages.

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Experimental

The concentration of the AlPO$_4$-nanoparticle solution to LiCoO$_2$ was varied to control the thickness of AlPO$_4$-nanoparticle coating. To prepare the AlPO$_4$-nanoparticle solution, Al(NO$_3$)$_3 \cdot$9H$_2$O and (NH$_4$)$_2$HPO$_4$ were slowly dissolved in distilled water until a white AlPO$_4$-nanoparticle suspension was observed. Subsequently, LiCoO$_2$ (with an average particle size of ~10 μm) was added to the coating solution and mixed thoroughly for 5 min. The slurry was dried in an oven at 120°C for 6 h and heat-treated in a furnace at 700°C for 5 h. The estimated concentration of AlPO$_4$ in the LiCoO$_2$ powders was varied from 1.0 to 3.2 wt %.

The electrolyte used was 1 M LiPF$_6$ with ethylene carbonate/diethyl carbonate/ethyl-methyl carbonate (EC/DEC/EMC) (30:30:40 vol %). The cycle-life tests of the coin-type half-cells (with a Li-metal anode) were performed using different charge-cutoff voltages of 4.6 and 4.8 V. The cycle-life tests were proceeded by charging and discharging at 0.1 C rate for the first two cycles, followed by a cycle at 0.2 C rate, a cycle at 0.5 C rate, and finally at 1 C (=140 mA/g) rate for the other cycles. For the galvanostatic intermittent titration technique (GITT),[14,15] the Li/LiCoO$_2$ test cells were allowed to reach the equilibrium states after each incremental charge step using a constant current. (The test cells were precycled for each cycle at the rate of 0.1, 0.2, 0.5, and 1 C between 4.4 and 3 V.) Co dissolution of the bare and coated LiCoO$_2$ cathodes was measured by inductively coupled plasma-atomic emission spectroscopy (ICP-AES), and the electrolytes were obtained from the cycled cells using a centrifugal separation method. The lattice constants were characterized by X-ray diffraction (M18XHF-SRC, MAC Science) using Cu Kα radiation in the 2θ range of 15-70°.

Results and Discussion

Figure 1a shows the TEM image of 3.2 wt % AlPO$_4$-coated LiCoO$_2$ cathode material with a coating thickness on the order of ~100 nm. The selected area diffraction (SAD) pattern of the AlPO$_4$ coating layer shows a mixture phase of the amorphous and partially crystallized AlPO$_4$ phases (Fig. 1b). The TEM image of the 1.0 wt % AlPO$_4$-coated cathode shows that the AlPO$_4$ nanoparticles are embedded in the amorphous matrix, with its coating thickness on the order of ~10 nm, as shown in Fig. 1c. The SAD pattern of the 1.0 wt % AlPO$_4$ coating layer shows obvious crystalline spots and ring patterns (Fig. 1d). However, the formation of a new nanocrystal phase is different from the isolated AlPO$_4$ nanoparticles, exhibiting
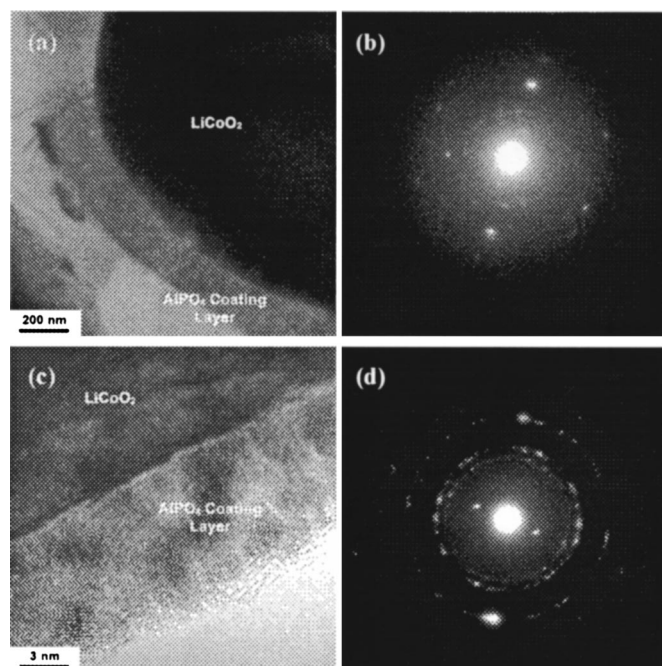
Figure 1. (a) TEM bright-field image of the 3.2 wt % AlPO$_4$-coated LiCoO$_2$ and (b) the SAD pattern of the coating layer. (c) High-resolution TEM image of the 1.0 wt % AlPO$_4$-coated LiCoO$_2$ showing the AlPO$_4$ nanoparticles and (d) the SAD pattern of the coating layer.

Figure 2. Plots of charge and discharge curves of the bare LiCoO$_2$ and 1.0, 2.5, and 3.2 wt % AlPO$_4$-coated LiCoO$_2$ cathodes at the rate of 0.1 C (=14 mA/g) with charge-cutoff voltages of 4.6 and 4.8 V. (The discharge-cutoff voltage of the cathodes in Li/LiCoO$_2$ was fixed at 3 V.)

an orthorhombic tridymite structure ($P2_12_12_1$). This suggests that AlPO$_4$ may react with Li and even Co from the LiCoO$_2$ during the 700°C annealing[16] and transform into a new phase with an intrinsic stress in the nanoscale-coating layer. While the TEM results confirm that the AlPO$_4$ coating is continuous along the particle surface, the coating thickness is varied depending on the morphology of the LiCoO$_2$ particle, with some occasional formation of AlPO$_4$ lumps.

Figures 2 and 3 show the voltage profiles and cycle-life performances of the bare and AlPO$_4$-coated cathodes with a different AlPO$_4$ concentration (thickness) at 4.6 and 4.8 V. The discharge-capacity values of the coated cathodes depend on the charge-cutoff voltage. Surprisingly, the discharge capacity of the bare cathode decreases with increasing charge-cutoff voltage from 4.6 to 4.8 V, which is in contrast to the coated cathodes. The initial discharge capacities of the 1.0, 2.5, and 3.2 wt % AlPO$_4$-coated cathodes at 4.8 V charge cutoff increase to 233, 234, and 228 mAh/g from 209, 215, and 207 mAh/g at the 4.6 V charge cutoff, respectively, while that of the bare cathode decreases to 200 from 213 mAh/g. The interesting behavior of the high charge capacities from the 2.5 wt % AlPO$_4$-coated cathodes (Fig. 2) needs to be clarified. Figure 3 also demonstrates that the 2.5 and 3.2 wt % AlPO$_4$-coated cathodes have larger capacity drops as the C rate is increased from 0.1 to 1 C. For instance, the 2.5 and 3.2 wt % AlPO$_4$-coated LiCoO$_2$ shows ~65 and ~63 mAh/g capacity drops at the 4.8 V charge-cutoff voltage, respectively, as the C rate increases from 0.1 to 1 C, while the 1.0 wt % AlPO$_4$-coated LiCoO$_2$ shows an ~44 mAh/g capacity drop.

The capacity retention of the bare and 1.0, 2.5, and 3.2 wt % AlPO$_4$-coated cathodes with the 4.6 and 4.8 V charge-cutoff voltages (3 V discharge-cutoff voltage) after 50 cycles at 1 C rate after the precycles are summarized in Fig. 4. Even though the capacity retention of the coated cathodes is superior to that of the bare cathode, which shows a zero capacity retention after only 20 cycles with a high charge-cutoff voltage, those of the 2.5 and 3.2 wt % AlPO$_4$-coated cathodes are inferior to those of the 1.0 wt % AlPO$_4$-coated cathodes. For example, the capacity retention from the 2.5 and 3.2 wt % AlPO$_4$-coated cathodes at the 4.8 V charge cutoff decreases to 122 and 104 mAh/g, respectively, compared to
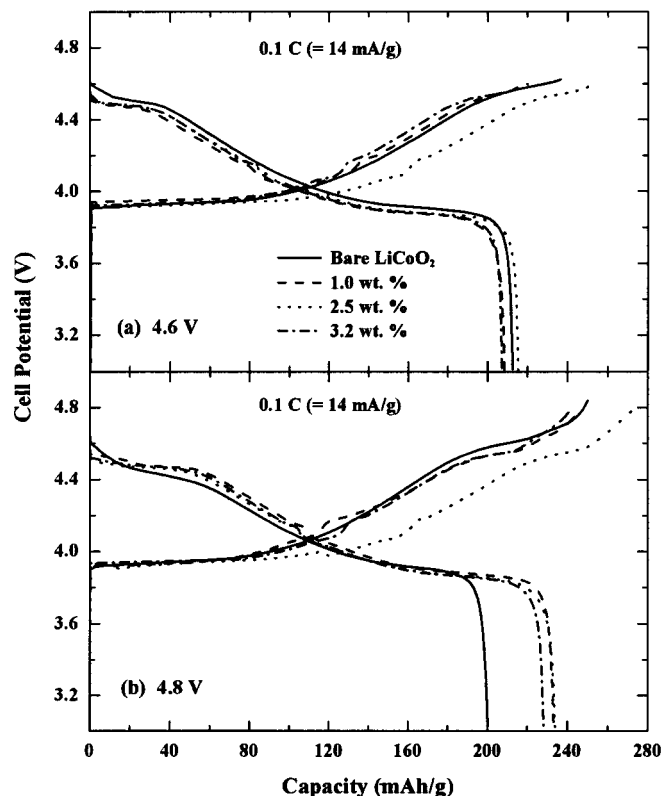
the 149 mAh/g for the 1.0 wt % AlPO$_4$-coated cathode after 50 cycles.

The better capacity retention of the coated cathodes than the bare ones at the high charge-cutoff voltages can be attributed to the structural integrity of the LiCoO$_2$ at the high voltage. For example, the fresh cells were charged to 4.6 and 4.8 V, and were carefully disassembled to measure the amount of Co dissolution into the electrolyte. Figure 5a shows the Co dissolution of the bare and 1.0, 2.5, and 3.2 wt % AlPO$_4$-coated samples at the initial charging. The amount of Co dissolution of the bare sample increases as the charge-cutoff voltage is increased. However, the AlPO$_4$-coated cathodes show much smaller amounts of Co dissolution. In addition, the amount of Co dissolution reduces as the coating concentration is increased. Likewise, the amounts of Co dissolution after 50 cycles (Fig. 5b) in the bare and coated cathodes at 4.6 and 4.8 V show the coating effect on Co dissolution more clearly.

It was reported that both the anisotropic lattice distortion and Co dissolution strongly correlated with the cycle-life performance. Jang *et al.* reported that upon cycling with a 4.4 V or higher charge cutoff, the increased anisotropic lattice distortion along the *c* axis raised the cell resistance and the capacity loss.[17] Similarly, Amatucci *et al.* reported that the capacity loss was attributed to electromechanical milling between the particles arising from the anisotropic lattice distortion, which enhanced the Co dissolution.[18] In relation to the Co dissolution, Fig. 6 shows the lattice constants *c* and the *c/a* ratio of the coated cathodes (at the discharged state of 3 V) after cycles which change less than those of the bare cathode. During cycles, the surface of bare cathode gets damaged due to Co dissolution, and Li intercalation/deintercalation through this structurally damaged region becomes difficult. On the contrary, the coating layer suppresses Co dissolution. Thus, the surface region of LiCoO$_2$ cathode may be less damaged compared with that of bare cathode. As a result of this
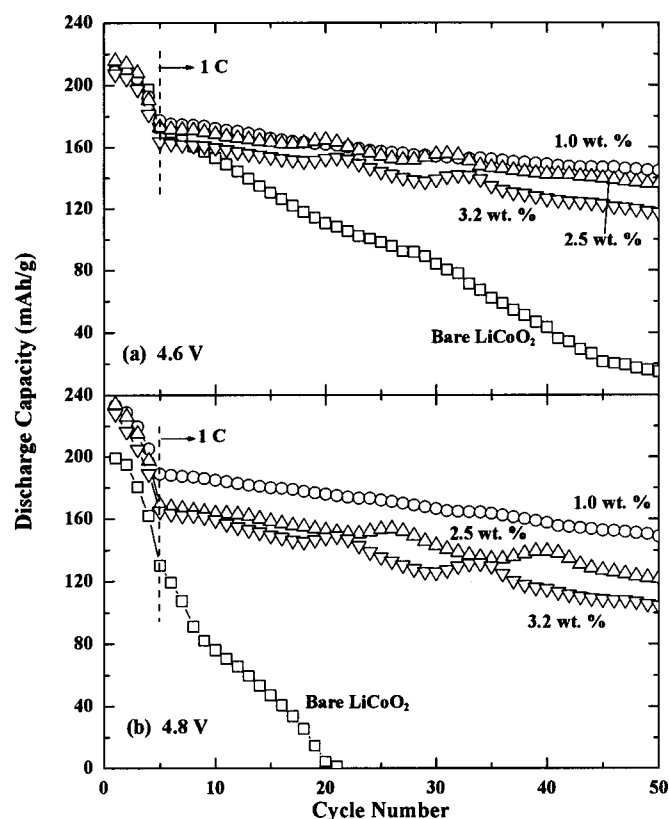
Figure 3. Cycle-life performance of the bare and 1.0, 2.5, and 3.2 wt % AlPO$_4$-coated LiCoO$_2$ cathodes at 0.1 C rate for the first two cycles, the third cycle at 0.2 C rate, the fourth cycle at 0.5 C rate, and finally at 1 C (=140 mA/g) rate for the rest of cycles with charge-cutoff voltages of 4.6 and 4.8 V.

Figure 5. Plots of the Co dissolution in the bare and 1.0, 2.5, and 3.2 wt % AlPO$_4$-coated LiCoO$_2$ before and after cycling. In order to measure the amount of Co dissolution prior to cycling, each cell was initially charged to 4.6 or 4.8 V at the rate of 0.1 C (=14 mA/g).

suppression, the values of the 1.0, 2.5, and 3.2 wt % AlPO$_4$-coated samples are superimposed over each other at the charge-cutoff voltages after 50 cycles.

Although the anisotropic lattice distortion along the *c* axis (at 3 V) and Co dissolution are suppressed by the AlPO$_4$ coating, lower capacity retention (Fig. 4) is shown with increasing the coating con-
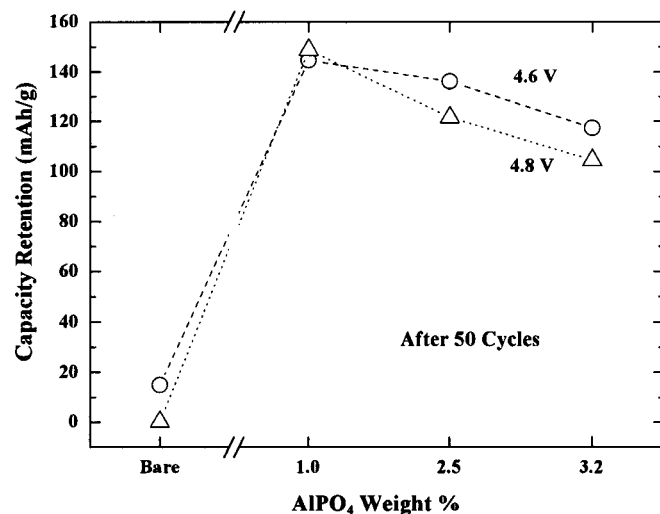

Figure 4. Plots of the capacity retention of the bare and 1.0, 2.5, and 3.2 wt % AlPO$_4$-coated LiCoO$_2$ cathodes at charge-cutoff voltages of 4.6 and 4.8 V (after 50 cycles).
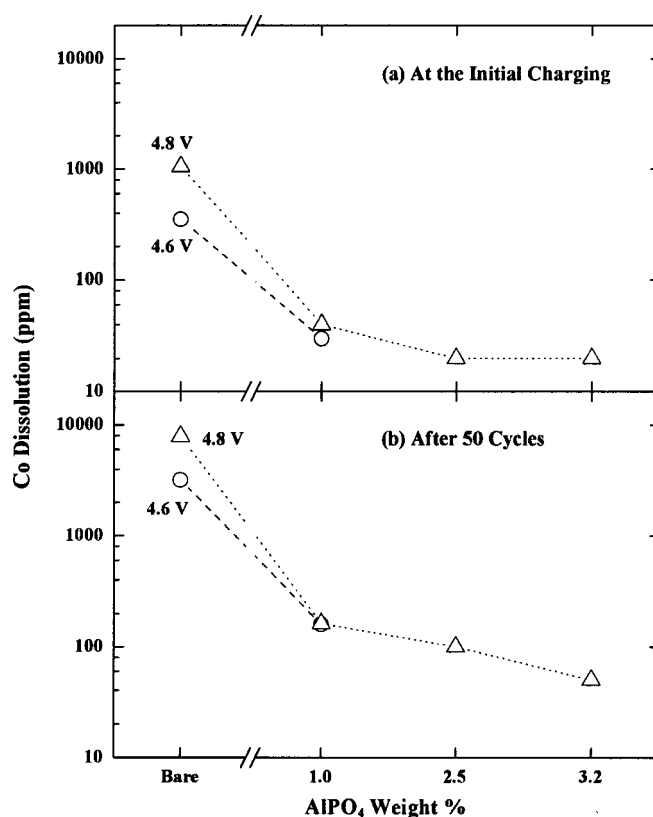
centration. To explain these, the Li diffusivities are measured using GITT after four precycles (between 4.4 and 3 V). As shown in Fig. 7, the Li diffusivity is the highest with the 1.0 wt % AlPO$_4$ coating, which decreases as the concentration (thickness) of the AlPO$_4$ coating layer is increased.

Here the diffusion of Li through the LiCoO$_2$ particles with AlPO$_4$ nanoscale-coating layer needs to be considered. A previous study on the Al$_2$O$_3$-coated LiCoO$_2$ thin film reported that the surface region of the LiCoO$_2$ reacted with Al$_2$O$_3$ during charge/discharge, forming a Li-Al-O solid-solution phase on the surface.[7] It is possible that a thick, nonconducting Li-Al-O layer increases the interfacial resistance in the powder geometry, which deteriorates the cycle-life performance. The independence of the Al$_2$O$_3$ thickness on the electrochemical properties in the thin-film geometry indicated that the oxide coating layer acted as a solid electrolyte with a low electronic conductivity and a reasonably high Li-ion conductivity. In the case of the AlPO$_4$-coated cathodes, the formation of a Li-Al-P-O solid-solution coating layer is expected during the cycles. As the coating thickness is increased, the reaction of Li may become slower and less efficient due to the limited electronic conduction among the particles. (The studies of Li diffusivities in the AlPO$_4$-coated cathodes are underway as a function of cycle number.) There is an optimum condition (as shown in Fig. 3) that shows the most enhanced electrochemical properties because the appropriate coating layer can suppress both Co dissolution and the lattice distortion (at the discharged state), and does not hinder Li diffusion much with the appropriate electronic conduction.

Figure 8 compares the voltage profiles and cycling stability of the bare and 1.0 and 3.2 wt % AlPO$_4$-coated LiCoO$_2$ in the coin-type Li-ion cells (with a carbon anode) between 4.3 and 3 V at the rate of 1 C (=140 mA/g). The 1.0 wt % AlPO$_4$-coated cathode
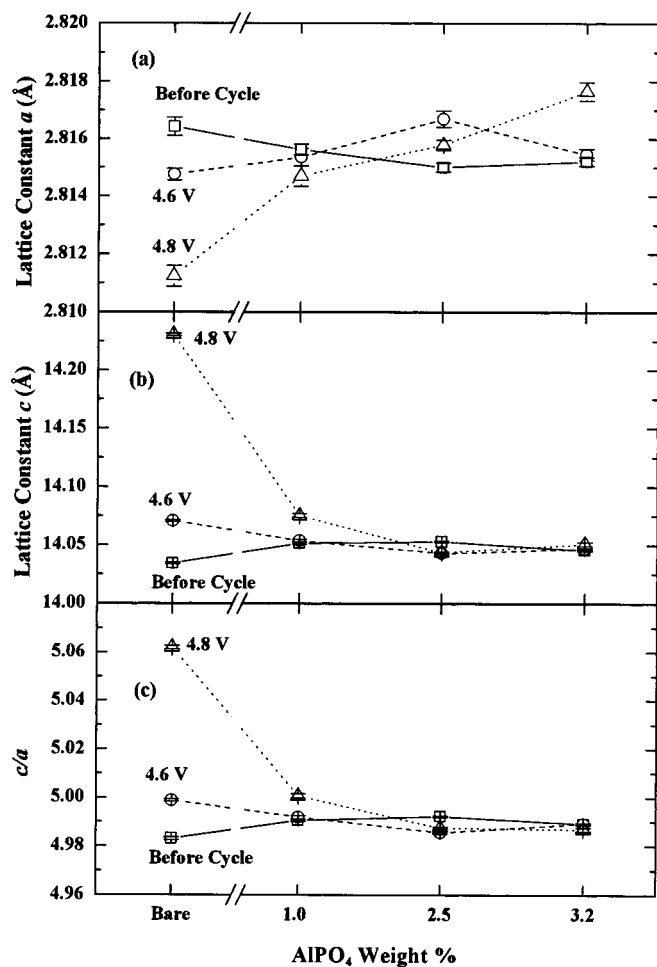
Figure 6. Plots of (a) and (b) showing the lattice constants a and c, and (c) the c/a ratio (all at 3 V) in the bare $LiCoO_2$, and 1.0, 2.5, and 3.2 wt % $AlPO_4$-coated cathodes, before cycling and after 50 cycles with charge-cutoff voltages of 4.6 and 4.8 V.
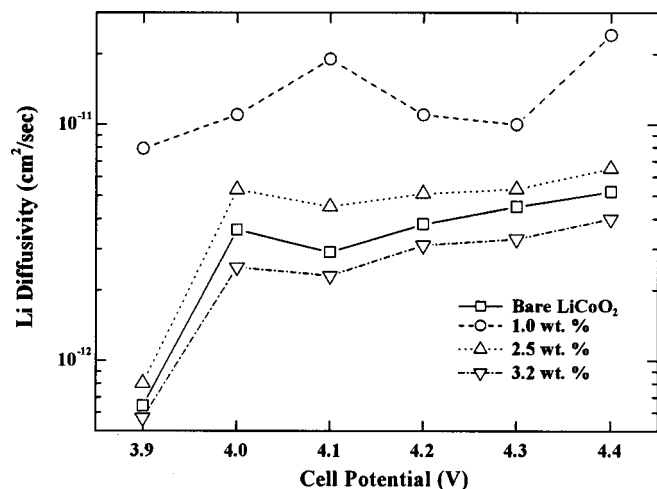

Figure 7. GITT measurements of the Li diffusivities at the various charge voltages in the bare and 1.0, 2.5, and 3.2 wt % $AlPO_4$-coated $LiCoO_2$. The test cells (with a Li-metal anode) were precycled at the rate of 0.1, 0.2, 0.5, and 1 C (=140 mA/g) for each cycle.
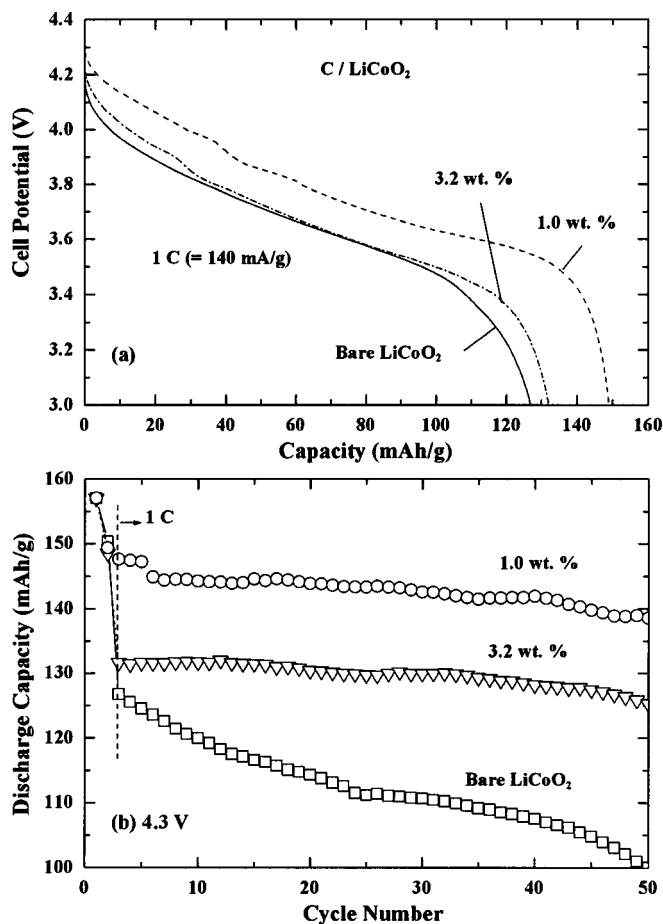

Figure 8. (a) Voltage profiles of the bare and 1.0 and 3.2 wt % $AlPO_4$-coated $LiCoO_2$ in the coin-type Li-ion cells (C/$LiCoO_2$) at the third cycle, and (b) cycle-life performance of the same cathode between 4.3 and 3 V at 0.2 C rate for the first cycle, 0.5 C rate for the second cycle, and at 1 C rate thereafter.

shows a much-improved voltage profile compared to those of the bare and 3.2 wt % $AlPO_4$-coated cathodes, which is consistent with the measured Li diffusivities. Moreover, the capacity retention of the 1.0 and 3.2 wt % $AlPO_4$-coated cathodes after 50 cycles at 1 C rate (after precycles) is superior to that of the bare cathode, showing 139 and 125 mAh/g, respectively.

Conclusions

Using the $AlPO_4$-nanoparticle coating on $LiCoO_2$ with a thickness ranging on the order of 10-100 nm, the specific capacity and cycle-life performance of the coated cathodes exhibited strong correlation with the coating concentration. The 1.0 wt % $AlPO_4$-coated cathodes showed the best capacity retention (149 mAh/g) with a 4.8 V charge cutoff after 50 cycles at 1 C rate after the precycles, while the bare cathode showed zero capacity retention under the same conditions after only 20 cycles. The amount of Co dissolution reduced as the coating concentration increased. However, the decreased capacity retention with the increasing $AlPO_4$ coating concentration is possibly due to the low Li diffusivity and poor electronic conduction.

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