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Nanoscale Control of Cathode Materials for the Enhanced Cycle-Life Performances

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Metal-phosphate-coated $LiCoO_2$ cathode materials were studied for the electrochemical properties. Al-P-O-coated $LiCoO_2$ exhibited the best cycle-life performance among the examined metal-phosphate-coated $LiCoO_2$. To investigate the nanostructural effect of $AlPO_4$-coating layer, three different phases of $AlPO_4$ nanoparticles were synthesized. The $LiCoO_2$ thin-film cathodes coated with amorphous $AlPO_4$ followed by annealing showed the best cycle-life performance, and effectively suppressed the degradation of Li^+-diffusion kinetics during cycling.

Keywords: Li-battery, $LiCoO_2$, metal phosphates, nanoscale coating

1. INTRODUCTION

$LiCoO_2$ is an attractive cathode material for lithium-ion batteries due to its high energy density and superior electrochemical properties. Generally, Li_xCoO_2 cathode exhibits a cell voltage of ~4.2 V having a charge capacity of ~140 mAh/g.[1-4] However, significant capacity fading occurs during cycling, which is attributed to structural distortions,[1-3] cobalt dissolution,[4] oxygen loss,[5] and the formation of electrically-resistive surface film.[6] This could be resolved by the nanoscale control of the interface, which has been shown to effectively enhance the electrochemical properties of $LiCoO_2$, and to successfully inhibit the initial capacity loss and cobalt dissolution in $LiCoO_2$.[7]

Metal-oxide coating has been shown to enhance the electrochemical properties and cycle-life performance of the $LiCoO_2$ cathode.[8-12] Despite the improved performance, metal-oxide-coated $LiCoO_2$ has exhibited thermal instability. Recently, it was reported that a nanoscale coating of $AlPO_4$ nanoparticles on $LiCoO_2$ powders improved thermal stability as well as electrochemical performance at high cutoff voltages, as compared with bare and other surface-modified $LiCoO_2$.[13-17]

2. EXPERIMENTAL SECTION

To synthesize the metal-phosphate-nanoparticle solution, metal nitrate ($Al(NO_3)_3 \cdot 9H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, $Sr(NO_3)_2$, or $Ce(NO_3)_3 \cdot 6H_2O$) with ammonium phosphate ($(NH_4)_2HPO_4$) was dissolved in distilled water with constant stirring. Then, $LiCoO_2$ powders were poured into the coating solution and mechanically stirred to achieve a coating of nanoparticles. The $LiCoO_2$ was then dried at 120°C for 6 h, and annealed at various temperatures ranging from 400°C to 900°C for 5 h.[17]

$LiCoO_2$ thin films were deposited on $SiO_2/Si(100)$ substrates using magnetron sputtering, and annealed at 700°C for 2 h. Three-phase $AlPO_4$ nanoparticles (amorphous, tridymite, or cristobalite) were coated on the prepared $LiCoO_2$ thin films by spin coating. Subsequently, these coated thin films (and uncoated film) were annealed at 400°C.[18]

3. RESULTS AND DISCUSSION

The cycle-life performances corresponding to the optimum condition for each metal-phosphate-coated $LiCoO_2$ are shown in Fig. 1. The metal-phosphate-coated $LiCoO_2$ powders (except the Ce-P-O-coated $LiCoO_2$) show better cycle-life performance than bare $LiCoO_2$. The Al-P-O-coated $LiCoO_2$ exhibits superior initial rate property and capacity retention among those, while the rate property of the Fe-P-O-coated $LiCoO_2$ (particularly with a charge-cutoff voltage of 4.6 V is poor. However, the Fe-P-O-coated $LiCoO_2$ shows stable capacity retention compared with the Al-P-O-coated $LiCoO_2$. The Sr-P-O-coated $LiCoO_2$ also exhibits poor initial rate properties, but its capacity retention is better than that of the bare $LiCoO_2$. The Ce-P-O-coated $LiCoO_2$ shows cycle-life performance similar to that of the bare $LiCoO_2$. The apparent initial rate properties of the coated cathode might

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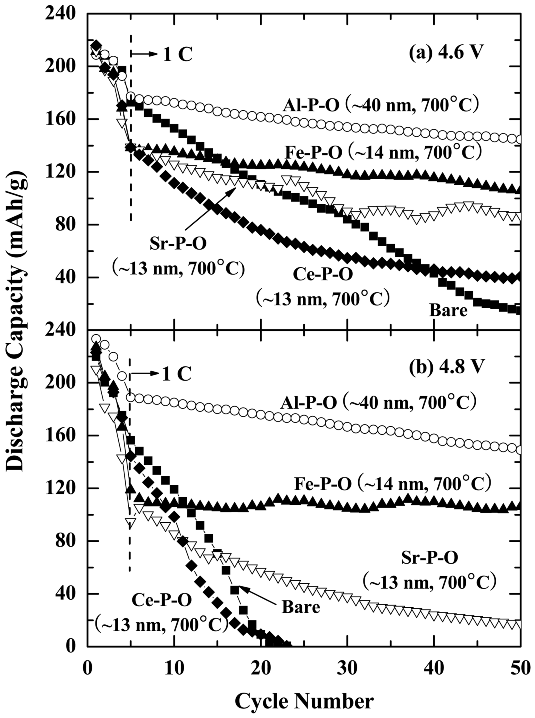

Fig. 1. Cycle-life performance of the metal-phosphate-coated $LiCoO_2$ cathodes under the optimized coating conditions. (Reprinted with permission from B. Park.[16] Copyright 2006, Elsevier.)

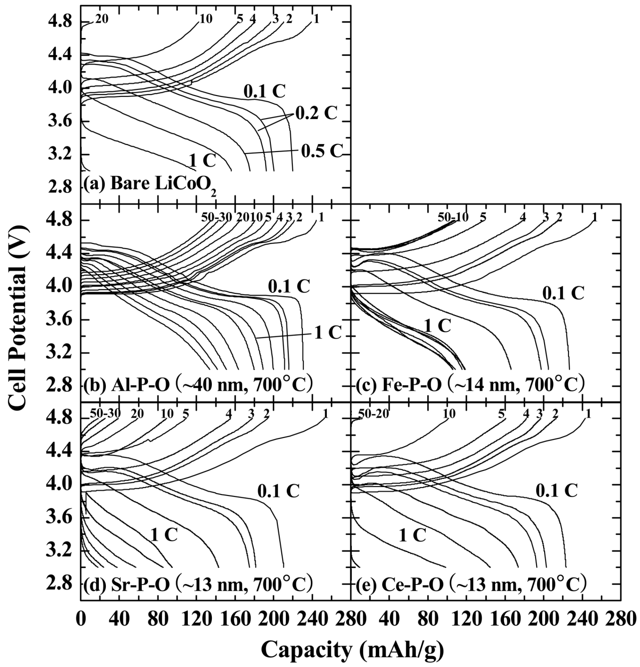

Fig. 2. Plots of discharge profiles of metal-phosphate-coated $LiCoO_2$ in coin-type half cells between 4.8 and 3.0 V. (Reprinted with permission from B. Park.[16] Copyright 2006, Elsevier.)

be different from the actual initial rate properties, due to the insufficient formation of solid electrolyte during the initial few cycles.[19]

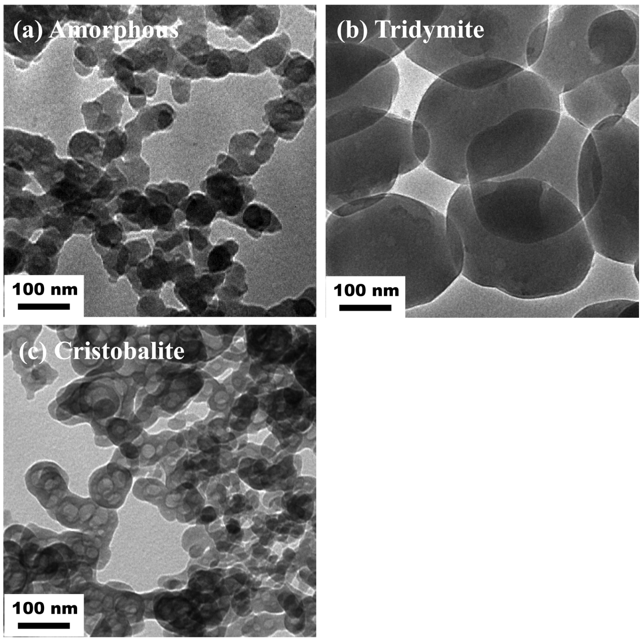

Fig. 3. TEM images of $AlPO_4$ nanoparticles with (a) amorphous, (b) tridymite, and (c) cristobalite phases. (Reproduced with permission from B. Park.[17] Copyright 2006, The Electrochemical Society.)

In Fig. 2, plateau regions can be clearly seen in the voltage profiles of the Al-P-O-coated cathode. The voltages at the initial few discharge stages of the Fe-P-O-, Sr-P-O-, and Ce-P-O-coated $LiCoO_2$ appear to slightly increase and then begin to decrease, compared with those of the bare and Al-P-O-coated $LiCoO_2$. This may result from the slow kinetics of the coated cathodes at the initial discharge state.[19, 22]

To investigate the nanostructural effect of the $AlPO_4$-coating layer, the $AlPO_4$ nanoparticles with amorphous, tridymite, or cristobalite phases were synthesized in distilled water. As shown in Fig. 3, while both the amorphous and cristobalite nanoparticles are spherical with sizes of 20 - 50 nm the tridymite nanoparticles are plate-shaped with ~200 nm in diameter. These nanoparticles were coated on $LiCoO_2$ by spin coating, and all the samples were annealed at 400°C.

The cycling tests were carried out between 4.4 and 2.75 V at 0.4 mA/cm^2 (= 12 C) to examine the cycle-life performance of the $AlPO_4$-nanoparticle-coated-$LiCoO_2$ thin films. The cycle-life performances of the bare and $AlPO_4$-coated $LiCoO_2$ thin films with various nanoparticles are shown in Fig. 4. Among the three nanostructures of the $AlPO_4$-coating layer, the $LiCoO_2$ coated with amorphous nanoparticles exhibits the best cycle-life performance, while the $LiCoO_2$ coated with cristobalite nanoparticles shows a similar behavior to the bare $LiCoO_2$ thin film. It appears that the cycle-life performance of the $AlPO_4$-coated $LiCoO_2$ is affected by the nanostructures of the coating nanoparticles.

The apparent Li^+ diffusivities of the bare and the $AlPO_4$-coated $LiCoO_2$ thin films during Li^+ intercalation (discharging) were measured by GITT (galvanostatic intermittent titration technique) at every 20 cycles, as shown in Fig. 5.[19-21] As cycles continue, the Li^+ diffusivities of the bare get rapidly decreased, and the cells die after 60 cycles. However, the degradation of Li^+-diffusion kinetics is suppressed in the $AlPO_4$-nanoparticle-coated cathodes. The apparent Li^+ diffusivities of the amorphous-nanoparticle-coated sample are quite similar to those of the initial cycle even after 60 cycles. The diffusivities of the $LiCoO_2$ thin films coated with both tridymite and cristobalite nanoparticle decrease by approximately one order of magnitude after 60 cycles. These results confirm that the cycle-life performance of $AlPO_4$-nanoparticle-coated $LiCoO_2$ strongly depends on the nanostructures of the $AlPO_4$-coating layer.

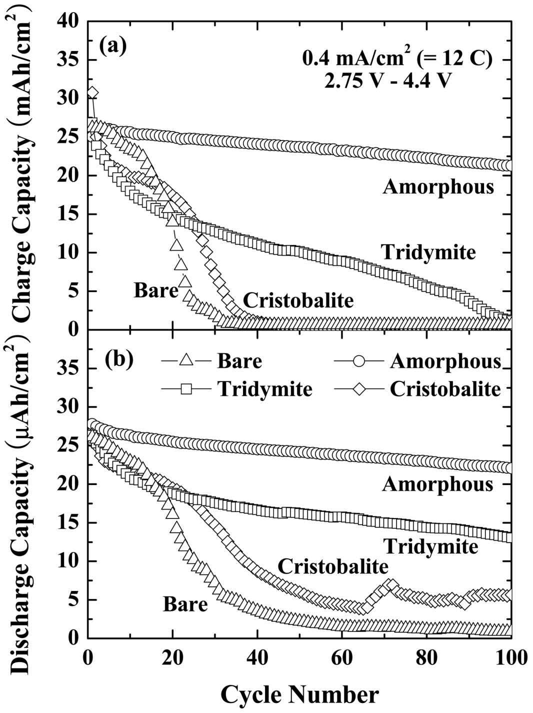

Fig. 4. (a) The charge- and (b) discharge-capacity retention of the bare and $AlPO_4$-nanoparticle-coated $LiCoO_2$ thin films. (Reproduced with permission from B. Park.[17] Copyright 2006, The Electrochemical Society.)

4. CONCLUSIONS

Nanoscale interface control of surface modification on $LiCoO_2$ powders with various metal-phosphate materials (Al-P-O, Fe-P-O, Ce-P-O, or Sr-P-O) has been carried out for the electrochemical enhancement of $LiCoO_2$ cathode material. The metal-phosphate coating on the $LiCoO_2$ powders enhanced cycle-life performance with high charge-cut-off voltages, and the Al-P-O coating was the most effective for improving the cycle-life performance. Three different phases of Al-P-O (amorphous, tridymite, or cristobalite) were coated on the $LiCoO_2$ thin film by spin coating to investigate the nanostructural effect of Al-P-O-coating layer. It was confirmed that the amorphous-nanoparticle-coated-$LiCoO_2$ thin film provided the best cycle-life performance and effectively suppressed the degradation of Li^+ diffusivi-

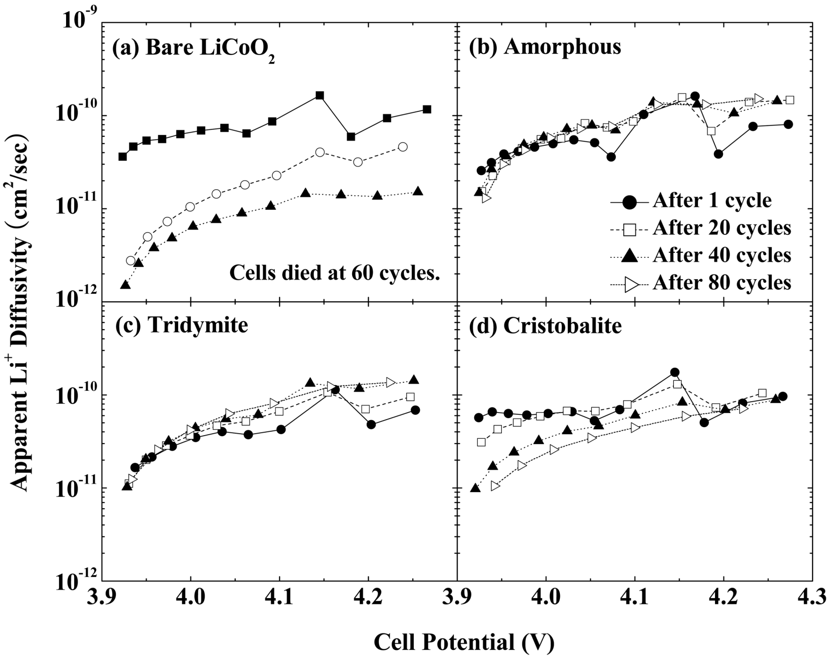

Fig. 5. Apparent Li^+ diffusivities during discharge for the (a) bare, and the $LiCoO_2$ thin films coated with (b) amorphous, (c) tridymite, and (d) cristobalite $AlPO_4$ nanoparticles. (Reproduced with permission from B. Park.[17] Copyright 2006, The Electrochemical Society.)

ties. The control of nanostructure is therefore found to be crucial in the enhancement of $LiCoO_2$ cathode materials.

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