Nanostructural Effect of AlPO4-Nanoparticle Coating on the Cycle-Life Performance in LiCoO2 Thin Films

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To control the nanostructure of an AlPO4-coating layer, nanoparticles with three AlPO4 phases were synthesized: amorphous, tridymite, and cristobalite phases. These colloids were layered on LiCoO2 thin films by spin coating, and subsequently annealed at 400°C. The interdiffusion variations at the interface were eliminated by the spin-coating method, while the cycle-life performance of the coated cathode depended on the nanostructure of the AlPO4-nanoparticle-coating layer. The LiCoO2-thin-film cathode coated with amorphous nanoparticles and annealed at 400°C showed the best cycle-life performance, and effectively suppressed the degradation of Li+-diffusion kinetics during cycling.

Hexagonal LiCoO2 (R3m) is widely used as a cathode material in commercial Li-ion batteries owing to its superior electrochemical performance. However, LiCoO2 is used only at half of its theoretical capacity (=274 mAh/g) because it exhibits very serious capacity loss from the Li removal.

To study the nanostructural effect of AlPO4-coating layer, the AlPO4 nanoparticles with amorphous, tridymite, and cristobalite phases were obtained after drying at 90°C. In addition, cristobalite nanoparticles were formed, when 0.1 M Al(NO3)3·9H2O and phosphoric acid (0.1 M H3PO4) were dissolved in distilled water. Then, the solution was titrated to pH 4 by ammonia water (0.1 M NH4OH) until cristobalite nanoparticles were obtained. Ammonium nitrate (NH4NO3), a by-product of all the syntheses, was eliminated by a centrifugal method before the structure and morphology of AlPO4 nanoparticles were analyzed. Spin coating for AlPO4 nanoparticles on LiCoO2 was used with the as-synthesized solutions, and the by-product in the coating layer was decomposed after annealing at 400°C. (NH4NO3 gets completely decomposed at 200°C).

The LiCoO2 thin films were deposited on thermally oxidized SiO2/Si(100) substrates using magnetron sputtering. The targets (2-in. diameter) for the LiCoO2 deposition were fabricated by cold-pressing commercial powders, followed by sintering at 1000°C for 10 h in air. The deposition to achieve approximately 600 nm thick LiCoO2 was carried out at a pressure of 20 mTorr with an Ar/O2 ratio of 3/1 after presputtering for 1 h. To obtain good-quality LiCoO2, all the films were annealed at 700°C in an oxygen atmosphere at 100 mTorr for 2 h. Pt was used as a current collector, and a TiO2 underlayer was deposited by reactive sputtering of Ti to improve Pt adhesion to the substrate. The AlPO4-nanoparticle layer was coated on LiCoO2 thin films by spin coating using the AlPO4-nanoparticle solutions with amorphous, tridymite, or cristobalite phase. The structural and compositional characterizations of AlPO4 nanoparticles and AlPO4-coated LiCoO2 films were investigated by X-ray diffraction (XRD), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS).

The electrochemical characteristics of LiCoO2 films were investigated using beaker-type half-cells, which consisted of a Li-metal sheet as the counter and reference electrode, a LiCoO2 film with an active area of approximately 1 cm2 as the working electrode, and 1 M LiPF6 in EC/DEC (1/1 vol %) (Cheil Industries, Inc.) as the electrolyte. Each cell was electrochemically cycled up to 100 cycles between 4.4 and 2.75 V at the rate of 0.4 mA/cm2 (corresponding to 12 C, with 1 C = 140 mAh/g). At all the charge-discharge cutoff steps, the cell voltages were potentiostated until the current decreased to 0.04 mA/cm2. To determine the apparent Li+ diffusivities as a function of the cell potential, a galvanostatic intermittent titration technique (GITT) with current steps of 0.4 mA/cm2 at 10 s intervals was used for both the bare and AlPO4-coated LiCoO2 films. The cells were allowed 10 mins to equilibrate between steps.

Results and Discussion

To study the nanostructural effect of AlPO4-coating layer, the AlPO4 nanoparticles with amorphous, tridymite, and cristobalite
phases were synthesized in distilled water. Figure 1 shows the XRD patterns of these three phases after drying at 90°C and annealing at 400°C. The crystalline nanoparticles after drying at 90°C match well with the references of tridymite (JCPDS no. 48-0652) and cristobalite AlPO₄ (JCPDS no. 10-0500) are marked.

As shown in Fig. 1c, the colloidal cristobalite nanoparticles were transformed to tridymite after 400°C annealing.

As shown in Fig. 2, both the amorphous and cristobalite nanoparticles are spherical with a size of 20–50 nm, while the tridymite nanoparticles are plate shaped and large (~200 nm diameter). These nanoparticles were coated on LiCoO₂ films by spin coating, and all the coated samples were annealed at the same temperature (400°C) to eliminate any variations of interdiffusion between AlPO₄ and LiCoO₂.

Figure 3 shows the cross-sectional TEM image of the AlPO₄-coated LiCoO₂ film with amorphous nanoparticles after annealing at 400°C. The AlPO₄-coated LiCoO₂ film is found to be 50 nm thick, uniform, and continuous. To confirm the existence of the AlPO₄-coating layer and the extent of interdiffusion at the interface, the three AlPO₄-coated LiCoO₂ thin films were measured by XPS (Fig. 4). For AlPO₄, the binding energies of Al 2p, P 2p, and O 1s are 74.5, 133.5, and 531 eV, respectively. These three binding energies correspond with the references of AlPO₄ in all the films. In the case of the cristobalite-coated thin film, new peaks (corresponding to P₂O₅) in the spectra of P 2p and O 1s emerge at 135 and 533 eV, respectively, and the binding energy of Al 2p moves higher. However, the amorphous and tridymite nanoparticles do not exhibit any new apparent peaks. The existence of new peaks in the cristobalite-coated thin film indicates that some cristobalite AlPO₄ in the coating layer was transformed to P₂O₅ during annealing at 400°C, a finding that was probably related to the XRD result of Fig. 1c. As shown in Fig. 4c and d, no spectra from LiCoO₂ for O 1s and Co 2p are found. In the case of LiCoO₂, the binding energy of O 1s is 529.1 eV, and the peaks corresponding to Co 2p₁/₂ and 2p₃/₂ are present at 794.8 and 779.6 eV, respectively. These XPS spectra confirm that the interdiffusion at the interface is not significant, in comparison to the previous study on the AlPO₄-coating layer deposited by sputtering. Therefore, it is expected that these thin films show only the nanostructural effect of AlPO₄-coating layer on the cycle-life performance of LiCoO₂, assuming that the effect of coating-layer phase (amorphous, tridymite, or cristobalite) on the interdiffusion length is negligible.

To examine the cycle-life performance of AlPO₄-nanoparticle-coated LiCoO₂ thin films, the cycling tests were carried out between 4.4 and 2.75 V at 0.4 mA/cm² (≈12 C). Figure 5 shows the cycle-life performances of bare and AlPO₄-coated LiCoO₂ films with various nanoparticles, excluding the capacity at

![Figure 1. XRD of AlPO₄ nanoparticles, after drying at 90°C and annealing at 400°C, with (a) amorphous, (b) tridymite, and (c) cristobalite phases. The peak positions and intensities of tridymite (JCPDS no. 48-0652) and cristobalite AlPO₄ (JCPDS no. 10-0500) are marked.](image1)

![Figure 2. TEM images of AlPO₄ nanoparticles, after drying at 90°C, with (a) amorphous, (b) tridymite, and (c) cristobalite phases.](image2)

![Figure 3. TEM image of AlPO₄-coated LiCoO₂ thin film. The AlPO₄ nanoparticles with the amorphous phase were coated on the LiCoO₂ thin film by spin coating, and annealed at 400°C.](image3)
the constant voltage mode. Among the three nanostructures of the AlPO4-coating layer, LiCoO2 coated with amorphous nanoparticles and annealed at 400°C exhibits the best cycle-life performance, whereas that coated with cristobalite nanoparticles shows a similar behavior to bare LiCoO2. The cycle-life performance of AlPO4-coated LiCoO2 depends on the nanostructure of the coating layer. The coating layer also plays an important role in the Li+-diffusion kinetics at the electrode/electrolyte interface. On the voltage profiles of LiCoO2 cathodes, all the coated samples during the first discharge show a larger IR drop than the bare sample. However, the plateau voltages of the coated samples increase during the second discharge, indicating that the AlPO4-coating layer at initial cycling acts as a barrier for the Li+ migration. As the cycling increases, channels for Li+ migration start to form in the coating layer, and the coating layer may act well as a solid electrolyte, as reported in the previous publication.10 In particular, the sample coated with amorphous nanoparticles shows a similar plateau voltage to bare LiCoO2 at the second cycle (Fig. 6). The coating layer with amorphous nanoparticles may have been activated during cycling, and effectively improved the cycle-life performance of LiCoO2.

To evaluate the Li+ migration in the coating layer during cycling, the apparent Li+ diffusivities of LiCoO2 were measured at every 20 cycles using GITT (Fig. 7). Details of the GITT methods are described elsewhere.10,18,19 The previous study on Al2O3-coated LiCoO2 thin films reported that the Al2O3 coating effectively inhibited the degradation of Li+-diffusion kinetics in LiCoO2 during cycling.10 Figure 7 shows the Li+ diffusivities as a function of the cell potential for bare and AlPO4-nanoparticle-coated cathodes during Li+ intercalation (discharging). With the increasing cycle number, the Li+ diffusivities for the bare sample rapidly deteriorated, with all cells dying after 60 cycles, whereas all the coated cathodes exhibit effective suppression of the degradation of Li+-diffusion kinetics. Even after 60 cycles, the sample coated with amorphous nanoparticles maintains similar Li+ diffusivity to that at the initial cycle. For the samples coated with the tridymite and cristobalite nanoparticles, the diffusivities decreased by approximately one order of magnitude after 60 cycles. These results confirm that the nanostructure of the AlPO4-coating layer strongly affects the cycle-life performance of LiCoO2.

Figure 4. XPS spectra corresponding to (a) Al 2p, (b) P 2p, (c) O 1s, and (d) Co 2p for the AlPO4-coated LiCoO2 thin films with amorphous, tridymite, and cristobalite nanostructures. The marked peak positions are from AlPO4 (—) and P2O5 (—) standard samples (Refs. 14 and 15).

Figure 5. (a) The charge- and (b) discharge-capacity retention of the bare and AlPO4-nanoparticle-coated LiCoO2 thin films between 4.4 and 2.75 V at 0.4 mA/cm2 (=12 C). At each charge-discharge cutoff step, the cell voltage was potentiostated until the current decreased to 0.04 mA/cm2. The charge and discharge capacities exclude the extra capacities from the constant-voltage mode.
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Figure 6. Voltage profiles of the bare and various AlPO₄-nanoparticle-coated LiCoO₂ thin films between 4.4 and 2.75 V at 0.4 mA/cm² during the (a) first and (b) second cycles.

Figure 7. Apparent Li⁺ diffusivities as a function of cell potential for the (a) bare and AlPO₄-coated LiCoO₂ thin films coated with (b) amorphous, (c) tridymite, and (d) cristobalite nanoparticles, as determined by GITT during Li intercalation (discharging).