Metal-phosphate coating on LiCoO$_2$ cathodes with high cutoff voltages

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Abstract

Metal-phosphate coating on LiCoO$_2$ cathodes improved the cycle-life performance with high charge-cutoff voltages. The optimum annealing temperature and coating thickness for the excellent electrochemical properties of the metal-phosphate-coated LiCoO$_2$ cathodes were determined. Among the metal-phosphate-coating materials, the Al–P–O coating enhanced the electrochemical properties most efficiently. The EPMA results (after cycles) with a 4.8 V cutoff confirmed that most of the nanoscale coating layers, particularly the P component, had dissolved during cycling.

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1. Introduction

LiCoO$_2$ cathode materials have been used in most commercial Li-ion cells because of their high energy density and good electrochemical properties. LiCoO$_2$ cathode materials are typically charged up to $\sim$4.2 V versus Li (Li$_{0.5}$CoO$_2$), yielding a specific capacity below $\sim$140 mAh/g. LiCoO$_2$ cathode materials show serious capacity loss during cycling above 4.3 V at the expense of obtaining more specific capacity [1,2]. However, metal-oxide-coated LiCoO$_2$ powders showed excellent capacity retention at high cutoff voltages [3–8]. Recently, the AlPO$_4$ coating was reported to enhance the thermal stability as well as the capacity retention at high cutoff voltages [9–11]. The AlPO$_4$ coating was also applied to the cathode as LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ [12,13] and the anode as SnO$_2$ [14].

This paper reports various metal-phosphate materials as a nanoscale coating layer on the LiCoO$_2$ cathode to determine a coating material with better electrochemical properties than AlPO$_4$. Recently, Cho and co-workers reported a comparison among different metal-phosphate-coated LiCoO$_2$ [15]. However, since the cathodes were coated with the same weight percent of metal nitrate, each coating layer may not be in the optimum condition. To compare the coating effects of metal phosphates meaningfully, the electrochemical comparison should not be performed under the same coating condition, but under the optimum condition for each metal-phosphate coating. Therefore, under various coating conditions, the cycle-life performance at cutoff voltages of 4.6 V and 4.8 V is examined to identify the optimum coating conditions among the various metal phosphates.
2. Experimental

The metal-phosphate-nanoparticle solution was prepared by slowly dissolving metal nitrate (Al(NO$_3$)$_3$·9H$_2$O, Fe(NO$_3$)$_3$·9H$_2$O, Sr(NO$_3$)$_2$, or Ce(NO$_3$)$_3$·6H$_2$O) and ammonium phosphate ((NH$_4$)$_2$HPO$_4$) in distilled water with constant stirring. Subsequently, LiCoO$_2$ (with an average particle size of ~10 μm) was added to the coating solution, and mixed thoroughly. The slurry was dried in an oven at 120 °C for 6 h and annealed in a furnace at various temperatures (from 400 °C to 900 °C) for 5 h. Based on the assumption of a uniform coating (with the same structure of isolated particles in Fig. 1) on the spherical LiCoO$_2$ powders, the estimated thickness of the metal phosphate (M = Al, Fe, Sr, or Ce) in the optimum coating condition (in the following Fig. 10) was ~40 nm, ~14 nm, ~13 nm, or ~13 nm, respectively. The microstructures of the metal-phosphate-coating materials and the coated LiCoO$_2$ were characterized by X-ray diffraction (XRD) (M18XHF-SRC, MAC Science) using Cu Kα. Electron-probe microanalysis (EPMA) (JXA-8900R, JEOL) was performed to observe the coating morphology.

The electrolyte used was 1 M LiPF$_6$ with ethylene carbonate/diethyl carbonate/ethyl-methyl carbonate (EC/DEC/EMC) (30:30:40 vol.%, Cheil Industries Inc.). The cycling tests of the coin-type half-cells (with a Li-metal anode) were performed using different charge-cutoff voltages of 4.6 V and 4.8 V. The cycling tests were proceeded by charging and discharging at 0.1 C rate for the first cycle, followed by two cycles at 0.2 C rate, the fourth cycle at 0.5 C rate, and finally at 1 C (=140 mA/g) rate for the remaining cycles.

3. Results and discussion

Fig. 1 shows a comparison of the XRD patterns of the synthesized nanoparticles. The XRD patterns of the Al–P–O, Fe–P–O, and Ce–P–O particles after 700 °C annealing confirmed the AlPO$_4$ (tridymite, JCPDS No. 48-0652), FePO$_4$ (quartz, JCPDS No. 29-0715), and CePO$_4$ (monazite, JCPDS No. 32-0199), respectively. The phase of Sr–P–O is Sr$_5$(PO$_4$)$_3$OH (strontium hydroxyapatite, JCPDS No. 33-1348). The nanoscale coating layers on LiCoO$_2$ are rarely
detected by XRD, with the exception of Ce–P–O (Fig. 2). The XRD pattern of Ce–P–O-coated LiCoO₂ does not present the CePO₄ phase, but the CeO₂-phase (JCPDS No. 34-0394) precipitates. The nanoparticle or amorphous coating layer with an approximately 10–40 nm thickness is barely detected by XRD. Because of the heat treatment at 700 °C with LiCoO₂, the actual phase of the coated materials may be also different from the isolated particles. Metal phosphates may react with Li and even Co from LiCoO₂ during annealing at 700 °C, and transform into a new nanostructure with an intrinsic stress in the coating layer. Therefore, it is difficult to identify the actual phase of the nanoscale layer. Accordingly, each metal-phosphate-coated LiCoO₂ is mentioned as Al–P–O-, Fe–P–O-, Sr–P–O-, and Ce–P–O-coated LiCoO₂, respectively.

EPMA was performed to check the degree of encapsulation for the coated cathodes. Though the spatial resolution of EPMA is a few micrometer, the overall features of coating morphologies can be verified. The Co, P, and M mappings across the cross-sectioned LiCoO₂ powders are shown in Fig. 3. In the cases of the Al–P–O- and Fe–P–O-coated LiCoO₂, metal and P components are almost completely encapsulated on the cathode surface. On the other hand, Sr and Ce components are aggregated on the LiCoO₂ surface. Therefore, each estimated thickness on the assumption of uniform coating is different from the actual thickness. In the case of Ce–P–O-coated LiCoO₂, by considering the X-ray diffraction (Fig. 2) and the EPMA images (Fig. 3), the nanoscale coating layer may be a mixture of CeO₂ and Ce–P–O phases, probably with some interdiffusion with the LiCoO₂ matrix.

The cycle-life performance of the bare and Al–P–O-coated LiCoO₂ as a function of the annealing temperatures (Fig. 4) [16] and coating concentrations (Fig. 5) [17]. Even though the coatings were prepared under different conditions, the coated cathodes with various charge-cutoff voltages show a superior cycle-life performance to the bare ones up to 50 cycles. The Al–P–O-coated cathodes annealed at 600 °C or 700 °C show a better cycle-life performance than that annealed at 400 °C, because the coating layer annealed at 600 °C or 700 °C may have a better crystallinity and adhesion on the LiCoO₂ powder than that annealed at 400 °C [16]. The capacity retention improves as the coating concentration (thickness) increases. However, beyond a ~40 nm coating thickness, the electrochemical performance deteriorates, possibly due to the limited electronic conduction among the powders. Transmission electron microscopy

![Fig. 2. XRD patterns of the metal-phosphate-coated LiCoO₂ cathodes, after annealing at 700 °C.](image-url)
confirmed that the actual thickness of the coating with an estimated thickness of \( \sim 40 \) nm (for 1.0 wt.% of AlPO_4 in LiCoO_2) was 10–15 nm [9,17]. The 1.0 wt.% coating thickness suppressed cobalt dissolution without any severe loss of electronic conductivity [17].

Among the Fe–P–O-coated cathodes with \( \sim 40 \)-nm thick coating thickness, the 700 °C-annealed cathode has the best capacity retention and initial rate property (Fig. 6). The coated cathode annealed at 900 °C may induce Fe–P–O to diffuse in the LiCoO_2 powder, and have a less active surface. The \( \sim 14 \)-nm thick coating layer annealed at 700 °C is the most effective in the Fe–P–O-coated LiCoO_2 with a charge cutoff of 4.6 V and 4.8 V (Fig. 7). Like the Al–P–O-coated LiCoO_2 powders [17], the Fe–P–O-coating layer may suppress cobalt dissolution at a high charge cutoff, but resist the Li\(^+\) conduction with some electronic insulation during the electrochemical cycles [7,15].

For the Sr–P–O-coated LiCoO_2 cathodes, \( \sim 13 \)-nm thick coating layer effectively enhances the capacity retention, exhibiting \( \sim 87 \) mAh/g and \( \sim 18 \) mAh/g (after 50 cycles) with charge-cutoff voltages of 4.6 V and 4.8 V, respectively (Fig. 8). The \( \sim 38 \)-nm thick and \( \sim 100 \)-nm thick Sr–P–O-coated LiCoO_2 has similar or worse electrochemical results than the bare LiCoO_2. In the case of Ce–P–O-coated cathodes, the increase in the coating thickness reduces the electrochemical properties (Fig. 9). The thickness effect in Sr–P–O- or Ce–P–O-coated LiCoO_2 on the electrochemical properties is more severe than in the Al–P–O- or Fe–P–O-coated cathode. The agglomerated Sr–P–O or Ce–P–O particles (as shown in Fig. 3) may impede the electric contact among the LiCoO_2 powders with high coating concentrations. In some cases of Fe–P–O-, Sr–P–O-, and Ce–P–O-coated cathodes, the capacities at the early cycles are lower than those of bare ones. However, as the cycling proceeds, the capacities become higher than those of the bare ones. As the charge/discharge reactions get repeated, the structural degradation by the accumulated Co and O
Fig. 4. Cycle-life performance of the ~40-nm thick Al–P–O-coated LiCoO$_2$ cathodes as a function of the annealing temperature [16].

Fig. 5. Cycle-life performance of the Al–P–O-coated LiCoO$_2$ cathodes annealed at 700 °C as a function of the coating concentration [17].
Fig. 6. Cycle-life performance of the ~40-nm thick Fe–P–O-coated LiCoO$_2$ cathodes as a function of the annealing temperature.

Fig. 7. Cycle-life performance of the Fe–P–O-coated LiCoO$_2$ cathodes annealed at 700 °C as a function of the coating concentration.
Fig. 8. Cycle-life performance of the Sr–P–O-coated LiCoO$_2$ cathodes annealed at 700 °C as a function of the coating concentration.

Fig. 9. Cycle-life performance of the Ce–P–O-coated LiCoO$_2$ cathodes annealed at 700 °C as a function of the coating concentration.
dissolution may contribute more severely to the capacity loss in the bare ones, compared to the electric-contact problems among the LiCoO₂ powders and Li⁺ diffusion through coating layers in the coated cathodes.

The cycle-life performances and the voltage profiles (with 4.8 V charge cutoff) of the metal-phosphate-coated LiCoO₂ at the optimized coating conditions are summarized in Figs. 10 and 11. The coated LiCoO₂ has a generally better cycle-life performance than the bare LiCoO₂. The Al–P–O-coated LiCoO₂ has the best initial rate properties and capacity retention among the coated LiCoO₂. The initial rate property of the Fe–P–O-coated LiCoO₂ (particularly with the charge cutoff of 4.6 V) is slightly poor compared to the Al–P–O-coated cathode, but the capacity retention is quite good. Even though the Sr–P–O- and Ce–P–O-coated LiCoO₂ also has a poor initial rate property, the capacity retention is better than that of the bare one. The apparent initial rate properties of the coated cathode may be different from the actual initial rate properties, due to the insufficient formation of solid electrolyte during the initial few cycles [7]. The Al–P–O-coated cathode shows plateau regions clearly, as shown in Fig. 11. The voltages at the initial stage of discharge from the Fe–P–O-, Sr–P–O-, and Ce–P–O-coated LiCoO₂ increase slightly then decrease, which is unlike the bare and Al–P–O-coated LiCoO₂. It may be because the kinetics of the coated cathodes at the initial discharge state does not follow the current rate sufficiently [7,15].

The XRD patterns of the cathodes after 50 cycles are shown in Fig. 12. The full-width at half maximum (FWHM) of each peak increases compared to those from the cathode before cycling (Fig. 2). FWHM reflects the non-uniform distribution of local strain and the crystallite size [17–19]. The non-uniform distribution of local strain is caused by Co dissolution during cycling [7,15,16,19]. However, the discrepancy between the capacity retention and peak broadening among the M–P–O-coated LiCoO₂ powders needs to be clarified. One reason may be that the Li-concentration gradients inside the powder (especially at the 4.8 V cutoff voltage) may interfere in the FWHM analysis, due to the incident-angle- (or (h k l)) dependent penetration of X-rays (0.154 nm).

The EPMA images of the cathodes after cycling (Fig. 13) show that the coating layers are less uniform than those before cycling. Furthermore, the phosphorous component disappears more than the metal components in the coating layer. However, the Al component sustains its initial coating morphology relatively well, and the coating morphology

![Fig. 10. Cycle-life performance of the metal-phosphate-coated LiCoO₂ cathodes with charge-cutoff voltages of 4.6 V and 4.8 V at the optimized coating condition.](image-url)
Fig. 11. Plots of discharge profiles of metal-phosphate-coated LiCoO$_2$ in coin-type half cell between 4.8 V and 3 V. The cycling tests were proceeded by charging and discharging at 0.1 C rate for the first cycle, followed by two cycles at 0.2 C rate, the fourth cycle at 0.5 C rate, and finally at 1 C (=140 mA/g) rate for the remaining cycles.

Fig. 12. XRD patterns of the metal-phosphate-coated LiCoO$_2$ after 50 cycles with a 4.8 V cutoff voltage.
of Fe component also remains even with more dissolution than the Al component, showing good capacity retentions. The Sr and Ce components, however, remain scarcely on the LiCoO$_2$ powders, so the Sr–P–O and Ce–P–O coating layers may not effectively impede the Co dissolution, thus lead to poor capacity retentions (Fig. 10).

We initially speculated that the metal–oxygen bonding energy [20] in metal phosphates (with PO$_4$ polyanions) correlates with the electrochemical properties by coating. Although the bonding energy of Ce–O is the highest as 8.24 eV [20], the capacity retention was similar to that of the bare LiCoO$_2$. However, the bonding energy of Al–O in the aluminum-phosphate coating (which shows the best electrochemical properties) is approximately 5.40 eV [20]. The bonding energies of Fe–O and Sr–O are 4.24 eV and 4.71 eV, respectively [20]. For the optimum electrochemical properties by nanoscale coating, several factors are surely involved, such as bond energy, coating morphology, interdiffusion (between the coating layer and LiCoO$_2$), electronic conductivity, Li$^+$ diffusivity, etc. [7,9,11,16,17,20–22]. In addition, the survival of the coating layer during cycling with a steep voltage drop at the interface with the electrolyte should be considered. More detailed mechanisms of the metal-phosphate-coating effects need to be identified.

4. Conclusions

Metal-phosphate coating on the LiCoO$_2$ cathodes improves the cycle-life performance with high charge-cutoff voltages. Annealing at high temperatures may cause the formation of a solid-electrolyte layer intermixed between the nanoscale coating layer and the LiCoO$_2$ powder. The appropriate coating layer can suppress the structural degradation.
by reducing the rate of Co dissolution, with reasonable Li\(^+\) conduction and insignificant electronic insulation. Therefore, the proper annealing temperature and coating thickness are related to the optimum electrochemical properties of the metal-phosphate-coated LiCoO\(_2\) cathodes. In particular, \(\sim 100\) nm scale Sr–P–O and Ce–P–O nanoparticles were aggregated on the surface of LiCoO\(_2\), compared to the uniform Al–P–O and Fe–P–O coating layer. Thus, the M–P–O coating against the attacking electrolyte may not be effective, and the electrochemical properties were not enhanced greatly. The cycle-life performances at the optimized condition confirmed that the Al–P–O coating is the most efficient among the metal-phosphate-coating materials investigated in this study. The EPMA results (before and after cycles) showed that the coating materials, especially the P component, may be dissolved during cycling. Further studies are currently underway to optimize the coating chemistry, nanostructures, and morphology for the enhanced electrochemical properties.

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