Electrochemical stability in cerium-phosphate-coated LiCoO₂ thin films

Donggi Ahn, Chunjoong Kim, Joon-Gon Lee, Byoungsoo Kim, Yejun Park, and Byungwoo Park^{a)}

Department of Materials Science and Engineering and Research Center for Energy Conversion and Storage, Seoul National University, Seoul 151-744, Korea

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The electrochemical stability of LiCoO₂ thin films was improved by cerium-phosphate coating deposited at room temperature. The cerium-phosphate coating layer also effectively suppressed the increase of charge-transfer resistance during cycling. However, the cycling stability and the initial capacity of the coated LiCoO₂ thin films deteriorated as the annealing temperature increased, different from other metal-phosphate coating. These phenomena were attributed to the interdiffusion between the cerium-phosphate coating layer and LiCoO₂ thin film, instead of the nanocrystal formation in the amorphous coating layer.

I. INTRODUCTION

LiCoO₂ is presently the most widely used cathode material in rechargeable lithium ion batteries because of its ease of synthesis and excellent electrochemical properties. Layered Li_xCoO₂ cathode is typically charged up to 4.2 V ($0.5 < x < 1$), yielding a specific capacity below ~140 mAh/g.¹⁻⁴ When charged to 4.4 V or above (to access more than 50% of its theoretical capacity), this material shows a relatively severe capacity fading after extended cycling. This is attributed to structural changes in the unit-cell volume,¹⁻³ an increase in cobalt dissolution into the organic electrolyte,⁴ a loss of oxygen,⁵ and a formation of electrochemically resistive surface films.⁶

To improve the electrochemical performance of LiCoO₂ at high potential, metal-ion doped cathodes are intensively studied. Substitutions of various cations for Co have been reported to enhance the structural stability during charge and discharge.⁷⁻⁹ The other method for improving the cycling stability is coating the surface of cathode materials with various metal oxides or metal phosphates.¹⁰⁻¹⁷ The nanoscale AlPO₄ coating on LiCoO₂ powders improved the thermal stabilities and the electrochemical performances at high cutoff voltages and current rates compared with the bare and the Al₂O₃-coated LiCoO₂.¹⁵⁻¹⁸ Recently, research on the coating of LiCoO₂ powders with MPO₄ (M = Al, Ce, Sr, Fe, etc.) were reported.¹⁹ However, it was shown that the CePO₄ coating on LiCoO₂ powders was not so effective compared with the other metal phosphate coating, even

with the high Ce-O bonding energy of 8.24 eV.²⁰ Therefore, cerium phosphate was chosen in a thin-film geometry to identify the mechanisms involved with the metal-phosphate coating.

The powder-composite electrodes, which are composed of active materials, polymer binders, and carbon blacks, are not suitable for studying the intrinsic properties of LiCoO₂ because of the unexpected potential distribution and interfaces among the electrode components. The LiCoO₂ cathode in thin-film geometry, however, only has a cathode/electrolyte interface. Therefore, the thin-film LiCoO₂ can exhibit the intrinsic properties of the cathode materials without worrying about the electrical insulation among the powders.^{11,21-23} In this article, the effect of cerium-phosphate coating is investigated for the enhanced electrochemical properties in thin-film LiCoO₂.

II. EXPERIMENTAL

The LiCoO₂ thin films were deposited on thermally oxidized SiO₂/Si (100) substrates by radio frequency (rf) magnetron sputtering. The stoichiometric LiCoO₂ target was fabricated by cold-pressing commercial LiCoO₂ powders, followed by sintering at 1000 °C for 10 h in air. A Pt current collector was deposited before the LiCoO₂ film deposition, and a TiO₂ underlayer was deposited to improve the Pt adhesion to the substrate. The deposition rate was ~2 nm/min with an rf power of 100 W, and LiCoO₂ films with different thicknesses (~400 and ~600 nm) were deposited. The as-deposited amorphous LiCoO₂ films were annealed to crystallize at 700 °C in an oxygen atmosphere of 20 mTorr for 2 h. The cerium-phosphate coating layers were deposited at room temperature (RT) on top of the crystallized LiCoO₂ films by

^{a)}Address all correspondence to this author.
e-mail: byungwoo@snu.ac.kr
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rf magnetron sputtering using a CePO₄ target. After the cerium-phosphate deposition, the coated samples were annealed at various temperatures ranging from RT to 700 °C in an oxygen atmosphere of 20 mTorr for 2 h. Bare LiCoO₂ thin films were also annealed at 700 °C at the equivalent condition.

Beaker-type half cells were used to evaluate the electrochemical properties of the bare and the cerium-phosphate-coated LiCoO₂ thin films. The cells were made up of Li-metal sheets as a counter and reference electrode, a LiCoO₂ cathode of ~1 cm² of active area as a working electrode, and 1 M LiPF₆ in ethylene carbonate/diethyl carbonate (1/1 vol%; Cheil Industries, Inc., Seoul, South Korea) as the electrolyte.^{11,22,23} The cells were electrochemically cycled over the voltage range of 2.75 and 4.4 V at the rate of 0.4 mA/cm² (= 12 C). At all the charge/discharge cutoff steps, the cell voltages were potentiostated until the current decreased to 10% of the charge/discharge rates. The electrochemical impedance spectroscopy (EIS) of the bare and coated LiCoO₂ films was used to measure the charge-transfer resistance of the cathodes from 10 mHz to 1 MHz with an ac signal amplitude of 5 mV. The EIS was measured at a 4.2 V charged state with a current less than 1 μA/cm² during the first cycle and after the 10th, 30th, and 60th cycles. The structural characterization of LiCoO₂ films was performed by x-ray diffraction (XRD; M18XHF-SRC, Mac Science Co., Japan) using Cu K_α, scanning electron microscopy (SEM; JSM-6330F, JOEL, Japan), and transmission electron microscopy (TEM; JEM-3000F, JEOL, Japan). The chemical stoichiometry of the cerium-phosphate layer on Si substrate was determined by electron-probe microanalysis (JXA-8900R, JEOL, Japan).

III. RESULTS AND DISCUSSION

The cycle-life performances of the bare and 50-nm-thick Ce-P-O-coated LiCoO₂ (600 nm) thin films were studied as a function of annealing temperature ranging from RT to 700 °C, as shown in Fig. 1. The extra capacity from the constant-voltage mode is excluded. A 50-nm-thick Ce-P-O coating at RT significantly improves the capacity retention of a LiCoO₂ thin-film cathode in contrast to the CePO₄-coated powder samples.¹⁹ However, the Ce-P-O-coated LiCoO₂ thin films show that the capacity retention becomes more deteriorated as the annealing temperature increases. The charge capacities (Li⁺ deintercalation) of the bare and coated LiCoO₂ films (especially for 700 °C) exhibit severe deterioration compared with the discharge capacities (Li⁺ intercalation). Recently, Kim et al.¹¹ have reported that the Li⁺ deintercalation in bare LiCoO₂ has slower kinetics than Li⁺ intercalation, as confirmed by a galvanostatic intermittent titration technique. Also, the Al₂O₃ coating on LiCoO₂ thin films improved the electrochemical proper-

FIG. 1. (a) Charge capacities and (b) discharge capacities versus cycle number of bare and 50-nm-thick Ce-P-O-coated LiCoO₂ (600 nm) thin films as a function of annealing temperature ranging from RT to 700 °C. The cells were cycled with a constant-voltage mode between 4.4 and 2.75 V at 0.4 mA/cm² (= 12 C), and the cycle-life performance excludes the extra capacity from the constant-voltage mode.

ties of Li⁺ deintercalation more efficiently than those of the Li⁺ intercalation, exhibiting similar charge and discharge capacities.^{11,22}

The voltage profiles of the bare and 50-nm-thick Ce-P-O-coated LiCoO₂ (600 nm) thin films at RT are shown in Fig. 2. The profiles of bare LiCoO₂ films become steeper with increasing cycle number up to 80 cycles at 0.4 mA/cm². In contrast, the change in the voltage profiles of the Ce-P-O-coated LiCoO₂ during 80 cycles is more gradual. The polarization of bare LiCoO₂ shows significant deterioration after cycling compared with that of the Ce-P-O-coated cathode. The large polarization is thought to be caused by the slow Li⁺ diffusion in LiCoO₂ and the increased electric resistance of the active materials.

The Ce-P-O coating thicknesses were varied from 50 to 200 nm to examine the possible questions of electronic insulation and Li⁺ diffusion through the Ce-P-O layer. Figure 3(a) shows that the variation in thickness (50–200 nm range) of the Ce-P-O coating layer, deposited at RT, on LiCoO₂ (400 nm) thin films does not affect the

FIG. 2. Voltage profiles of (a) bare and (b) LiCoO₂ (600 nm) thin films coated with 50-nm-thick Ce-P-O at RT. At each charge-discharge cutoff step, the cell voltage was potentiostated until the current decreased to 0.04 mA/cm².

capacity retention (~80%). However, the capacity retention of the bare LiCoO₂ thin film is only ~10% after 50 cycles. In addition, the initial capacities are almost independent of the coating thickness (0–200 nm range). This indicates that the Ce-P-O coating layer preserves the properties of the cathode surface exposed to the electrolyte solution as a solid electrolyte with a low electronic conductivity and a reasonably high Li⁺ conductivity.¹¹ If the coating layer is active for lithiation/delithiation, the cathode with thicker coating layer will have more capacity. However, as the thickness of the coating layer increased, the initial capacity and the capacity retention did not change much. To clarify the effect of annealing temperature on the cycling performance of Ce-P-O-coated LiCoO₂ thin films, the 200-nm-thick Ce-P-O-coated LiCoO₂ films were annealed at different temperatures (300–700 °C). In Fig. 3(b), as the annealing temperature increases, the initial capacity and the capacity retention of the Ce-P-O-coated LiCoO₂ clearly deteriorate. The plan-view and cross-sectional SEM images show bare and LiCoO₂ (400 nm) thin films coated with Ce-P-O (200 nm) at RT, as shown in Fig. 4. The coating layer is uniformly deposited with a reasonably

FIG. 3. (a) The effect of Ce-P-O coating thickness on the capacity retention in 400-nm-thick LiCoO₂ thin films deposited at RT. (b) Cycle-life performance of 200-nm-thick Ce-P-O-coated LiCoO₂ (400 nm) thin-film cathodes as a function of annealing temperature ranging from RT to 700 °C.

sharp interface on top of the polycrystalline LiCoO₂ thin film. The Ce/P ratio of the cerium-phosphate layers deposited onto the SiO₂/Si substrate determined by electron-probe microanalysis was approximately 1.09.

To correlate the cycling performance of thin-film LiCoO₂ with the electrode kinetics, EIS was performed for bare and LiCoO₂ (400 nm) thin films coated with Ce-P-O (200 nm) annealed at different temperatures ranging from RT to 700 °C. All the Nyquist plots exhibit the representative spectra of LiCoO₂ cathodes consisting of two overlapping semicircles in the high-frequency range (1 Hz–1 MHz) and the linearly inclined (45°) part in the low-frequency range (10 mHz–1 Hz). In the two semicircles, the semicircle in the low-frequency range is normally considered as the charge-transfer resistance (R_{ct}) at the electrode/electrolyte interface, and the higher frequency contribution is attributed to the formation of solid-electrolyte interphase.^{24,25} Figure 5 shows that the solid-electrolyte interphase films on the LiCoO₂ surface were formed during the first cycle, and did not change much during the following cycles.^{6,24} All of the LiCoO₂

FIG. 4. Plan-view and cross-sectional SEM images of (a) bare and (b) LiCoO₂ (400 nm) thin films coated with Ce-P-O (200 nm) at RT.

thin films during the first cycle show similar R_{ct} (proportional to the diameter of the semicircle), indicating that R_{ct} at the interface of Ce-P-O coating layer and LiCoO₂ thin film is comparable with that of the electro-

FIG. 5. EIS spectra at the 4.2 V charged state of (a) bare LiCoO₂ (400 nm) thin film, and with 200-nm-thick Ce-P-O coating, (b) deposited at RT, and (c, d, and e) annealed at 300 °C, 500 °C, and 700 °C, respectively.

lyte and bare LiCoO₂ film during the initial cycle. However, R_{ct} of the bare LiCoO₂ significantly increases, whereas that of the LiCoO₂ film with Ce-P-O coating deposited at RT is very small ($\sim 800 \Omega$) even after 60 cycles. The R_{ct} of the coated LiCoO₂ thin film increases as the annealing temperature increases. In particular, the Ce-P-O-coated LiCoO₂ annealed at 700 °C exhibits a steep increase of R_{ct} , similar to the bare LiCoO₂ sample. These are consistent with the cycling performance of the bare and Ce-P-O-coated LiCoO₂ [Fig. 3(b)] because the increase of R_{ct} is closely related to the deteriorated electrochemical properties of LiCoO₂, probably by Co dissolution, oxygen loss, structural degradation, nonuniform distribution of local strain, etc.^{11,12} It means that the Ce-P-O coating layer as a solid electrolyte can inhibit such a degradation during cycling.

The XRD patterns of 200-nm-thick Ce-P-O-coated LiCoO₂ (400 nm) thin films annealed at different temperatures exhibit preferred (003) orientation of hexagonal LiCoO₂, as shown in Fig. 6. The XRD patterns of the LiCoO₂ thin film coated with Ce-P-O at RT do not show any cerium-phosphate peaks, suggesting that the cerium-phosphate coating layer is amorphous (or

FIG. 6. XRD patterns (in a log scale) of 200-nm-thick Ce-P-O-coated LiCoO₂ (400 nm) thin films annealed at different temperatures, bare LiCoO₂ thin film, and LiCoO₂ powder, before cycling.

FIG. 7. Cross-sectional SEM images of Ce-P-O-coated LiCoO₂ thin films, (a) deposited at RT [from Fig. 4(b)], and annealed at (b) 300 °C, (c) 500 °C, and (d) 700 °C.

FIG. 8. TEM images of Ce-P-O-coated LiCoO₂, (a) deposited at RT and (b) annealed at 700 °C. (c, d) Magnified images of square region in (a) and (b), respectively. The arrows indicate the interface between the phosphate layer and LiCoO₂.

nanocrystalline). Because the Ce-P-O coating layer is deposited at RT, the formation of crystalline phosphate phase may not be easy. However, for the 500 and 700 °C annealed films, the (111) peak of CeO₂ becomes apparent.

The cross-sectional SEM images of Ce-P-O-coated LiCoO₂ thin films annealed at different temperatures are shown in Fig. 7. The images of the LiCoO₂ films with the coating layer deposited at RT and annealed at 300 °C confirm continuous coating on top of the LiCoO₂ thin films, whereas in the LiCoO₂ film annealed at 500 and 700 °C, the Ce-P-O coating layer looks diffuse. These are consistent with the cross-sectional TEM images of Ce-P-O-coated LiCoO₂ thin films, as shown in Fig. 8(a). The LiCoO₂ films with the Ce-P-O coating layer deposited at RT show a clear interface between the coating layer and LiCoO₂, which is separated by an amorphous Ce-P-O and a polycrystalline LiCoO₂ [Fig. 8(c)]. After 700 °C annealing, the interface of the coating layer and LiCoO₂ looks unclear [Fig. 8(b)], and nanocrystals of LiCoO₂, CeO₂, and CePO₄ are found in the coating layer [Fig. 8(d)]. Auger electron spectroscopy with sputtering also confirmed the intermixing of Ce and Co with the increased annealing temperature. From these results, the electrochemical properties of the Ce-P-O-coated LiCoO₂ thin films are more controlled by interdiffusion instead of the nanocrystal formation.

IV. CONCLUSIONS

The galvanostatic charge/discharge experiments exhibited that the Ce-P-O coating clearly enhanced the cycle-life performance of LiCoO₂ thin films, in contrast to the Ce-P-O-coated powder samples.¹⁹ In particular, the LiCoO₂ thin films coated with the Ce-P-O deposited at RT showed excellent electrochemical stability, with the suppression of the increase of the charge-transfer resistance in LiCoO₂ thin films. However, the cycling stability and the initial capacity deteriorated after annealing. These unusual results were attributed to the interdiffusion, instead of appropriate partial crystallization, for the optimum electrochemical properties observed in various nanoscale metal-phosphate coatings on LiCoO₂.

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