**The Enhancement of Cycle-Life Performance in LiCoO₂ Thin Film by Partial Al₂O₃ Coating**

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The electrochemical properties of Al₂O₃-coated LiCoO₂ thin films with a partial coating coverage were investigated. The Al₂O₃-coated LiCoO₂ films showed better cycle-life performances with 100% coating coverage. In addition, the Al₂O₃-coating layer with a partial coverage of 50% clearly enhanced the electrochemical properties of LiCoO₂ cathodes even at 60°C. The Al₂O₃-coating layer suppresses Co dissolution from LiCoO₂, consequently enhancing the cycle-life performance.

**Keywords:** Li-ion battery, Al₂O₃, LiCoO₂, nanoscale, coating

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**1. INTRODUCTION**

Commercial rechargeable lithium-ion batteries use LiCoO₂ cathodes extensively due to their high energy density and good cycle-life performance. However, when charged to 4.4 V or above, this material shows relatively severe capacity fading after extended cycling. This is attributed to structural changes in LiCoO₂, cobalt dissolution into the electrolyte, oxygen loss, and the formation of electrochemically resistive surface films.

Surface modification through coating with various metal oxides and metal phosphates is an effective method to resolve the problem of severe capacity fading at high cutoff voltages. It has been found that even partial or non-uniform metal-oxide coating also enhances the cycle-life performance of cathode materials. In this article, the effects of Al₂O₃-coating coverage on the electrochemical properties of thin-film LiCoO₂ are reported.

**2. EXPERIMENTS**

The LiCoO₂ thin films were prepared by using magnetron sputtering on thermally-oxidized Si (100) substrates. All the films were then annealed at 700°C in an oxygen atmosphere for 30 min, and the Al₂O₃ thin films were deposited on the LiCoO₂ films by the reactive sputtering of an Al target with a coating coverage of 0%, 50%, or 100%. After the Al₂O₃ deposition, the coated and uncoated samples were annealed at 400°C for 2 h.

**3. RESULTS AND DISCUSSION**

To evaluate the electrochemical properties of both the bare and the Al₂O₃-coated LiCoO₂ thin films, beaker-type half cells were used. A Li-metal sheet was used as a counter/reference electrode, ~1 cm² of active area LiCoO₂ cathode as a working electrode, and 1 M LiPF₆ in ethylene carbonate/diethyl carbonate as the electrolyte. The cells were cycled over the voltage range of 4.4 and 2.75 V at 25°C and 60°C.

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those of the Al₂O₃-coated LiCoO₂ films during 200 cycles show better performances. For 100% Al₂O₃-coated LiCoO₂ films, a slight increase of polarization is observed in the initial cycle. However, as the cycles continue, the polarization in the charge and discharge processes is not noticeable. Lithium-ion migration through the coating layer gets easier as the cycling goes on, and the coating layer is expected to act as a solid electrolyte. The characteristic profiles of the coated cathodes worsen as the coating coverage decreases from 100% to 50%.

The cycle-life performances at 60°C of the bare and Al₂O₃-coated LiCoO₂ thin films with different coverage ratios are represented in Fig. 3. The initial capacity and the capacity retention of the bare LiCoO₂ films appear to deteriorate at higher temperature. Dramatic degradation of bare LiCoO₂ films is observed, because more significant Co dissolution from the cathode occurs at 60°C than at 25°C. It has been reported that LiCoO₂ powders exhibit more intense Co dissolution at elevated temperatures, and this causes significant capacity loss in LiCoO₂ cathodes. The Al₂O₃-coated LiCoO₂ films with 50% coverage exhibit rapid capacity fading after ~130 cycles at 60°C. However, the initial capacity and the capacity retention of the Al₂O₃-coated LiCoO₂ at 60°C are better with 100% Al₂O₃-coating coverage. Similarly, the 100% coated-Al₂O₃ LiCoO₂ film shows excellent cycle-life performances even at higher temperature, compared with the uncoated-LiCoO₂ films.

Wang’s group reported that alumina nanoparticles soaked
in an electrolyte improved the cycle-life performances of LiCoO$_2$.$^{[16]}$ Whether a dispersion of alumina nanoparticles in electrolytes or a uniform Al$_2$O$_3$ coating on LiCoO$_2$ is more effective for enhancing cycle-life performance remains an open question. With surface modifications, the Al$_2$O$_3$-coating layer reduces the amount of direct HF attack, while preventing Li$^+$ transport and electron conduction. However, alumina nanoparticles in an electrolyte cannot initially prevent the direct HF attack until the nanoparticles scavenge HF from the electrolyte. Myung et al. reported that the Al$_2$O$_3$-coated Li$_{1.05}$Ni$_{0.4}$Co$_{0.15}$Mn$_{0.4}$O$_2$ cathode material exhibited high electrochemical properties due to the HF scavenging of Al$_2$O$_3$ layer.$^{[17]}

4. CONCLUSIONS

The electrochemical properties of Al$_2$O$_3$-coated LiCoO$_2$ thin films with a different surface coverage of 0%, 50%, and 100% were studied. As discussed above, the LiCoO$_2$ films with even 50% coating coverage showed notably enhanced performances. However, details on the mechanisms of the scavenging effects need to be further identified.

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REFERENCES