

## The Enhancement of Cycle-Life Performance in LiCoO<sub>2</sub> Thin Film by Partial Al<sub>2</sub>O<sub>3</sub> Coating

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The electrochemical properties of Al<sub>2</sub>O<sub>3</sub>-coated LiCoO<sub>2</sub> thin films with a partial coating coverage were investigated. The Al<sub>2</sub>O<sub>3</sub>-coated LiCoO<sub>2</sub> films showed better cycle-life performances with 100% coating coverage. In addition, the Al<sub>2</sub>O<sub>3</sub>-coating layer with a partial coverage of 50% clearly enhanced the electrochemical properties of LiCoO<sub>2</sub> cathodes even at 60°C. The Al<sub>2</sub>O<sub>3</sub>-coating layer suppresses Co dissolution from LiCoO<sub>2</sub>, consequently enhancing the cycle-life performance.

**Keywords:** Li-ion battery, Al<sub>2</sub>O<sub>3</sub>, LiCoO<sub>2</sub>, nanoscale, coating

### 1. INTRODUCTION

Commercial rechargeable lithium-ion batteries use LiCoO<sub>2</sub> cathodes extensively due to their high energy density and good cycle-life performance.<sup>[1]</sup> 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 LiCoO<sub>2</sub>,<sup>[2]</sup> cobalt dissolution into the electrolyte,<sup>[3]</sup> oxygen loss,<sup>[4]</sup> and the formation of electrochemically resistive surface films.<sup>[5]</sup>

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.<sup>[6-13]</sup> It has been found that even partial or non-uniform metal-oxide coating also enhances the cycle-life performance of cathode materials.<sup>[14,15]</sup> In this article, the effects of Al<sub>2</sub>O<sub>3</sub>-coating coverage on the electrochemical properties of thin-film LiCoO<sub>2</sub> are reported.

### 2. EXPERIMENTS

The LiCoO<sub>2</sub> 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 Al<sub>2</sub>O<sub>3</sub> thin films were deposited on the LiCoO<sub>2</sub> films by the reactive sputtering of an Al target with a coating coverage of 0%, 50%, or 100%. After the Al<sub>2</sub>O<sub>3</sub> deposition, the coated and uncoated samples were annealed at 400°C for 2 h.

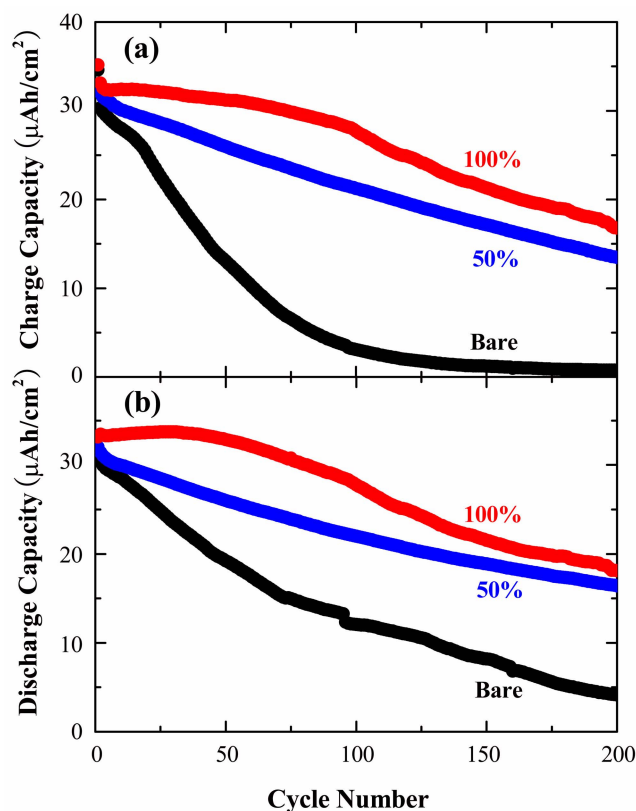
To evaluate the electrochemical properties of both the bare and the Al<sub>2</sub>O<sub>3</sub>-coated LiCoO<sub>2</sub> thin films, beaker-type half cells were used. A Li-metal sheet was used as a counter/reference electrode, ~1 cm<sup>2</sup> of active area LiCoO<sub>2</sub> cathode as a working electrode, and 1 M LiPF<sub>6</sub> 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.

### 3. RESULTS AND DISCUSSION

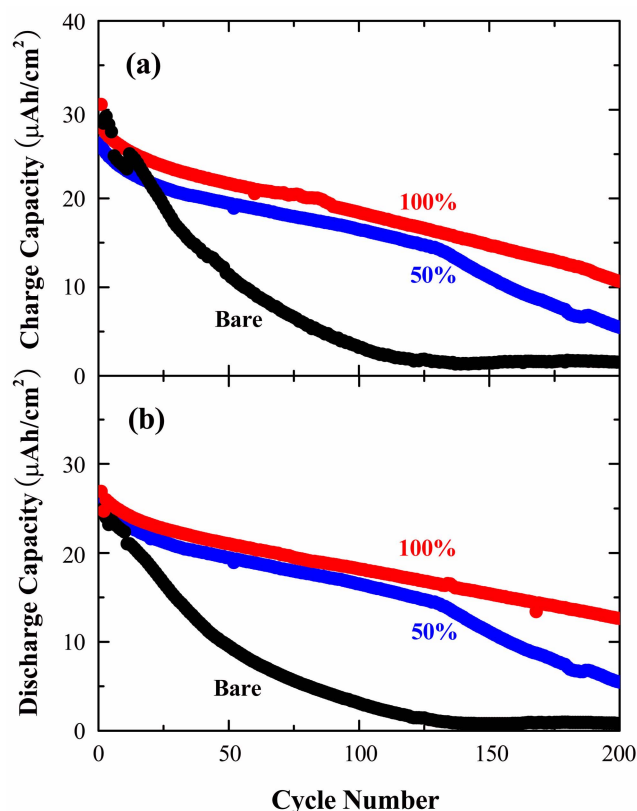
The Al<sub>2</sub>O<sub>3</sub>-coated LiCoO<sub>2</sub> thin film electrodes with 0%, 50%, or 100% coverage were cycled between 4.4 and 2.75 V with an applied current density of 0.4 mA/cm<sup>2</sup> (= 12 C) at 25°C. The cycle-life performances of the bare and Al<sub>2</sub>O<sub>3</sub>-coated films (with 50% and 100% coating coverage) are shown in Fig. 1, excluding the capacities of the constant-voltage mode. The Al<sub>2</sub>O<sub>3</sub>-coated LiCoO<sub>2</sub> films exhibit enhanced capacity retention with increased coating coverage. Even the Al<sub>2</sub>O<sub>3</sub>-coated LiCoO<sub>2</sub> with only 50% coverage retains up to ~33% of its initial charge capacity after 200 cycles, whereas the bare LiCoO<sub>2</sub> exhibits almost zero capacity. It was previously reported that an Al<sub>2</sub>O<sub>3</sub> coating with a partial coverage of ~40% improved the capacity retention of LiCo<sub>0.94</sub>Fe<sub>0.06</sub>O<sub>2</sub>.<sup>[14]</sup> Oh *et al.* also reported that Al<sub>2</sub>O<sub>3</sub>-coated LiCoO<sub>2</sub> powders even with ~14% coverage enhanced cycle-life performances.<sup>[15]</sup> The improvement of capacity retention is observed more in the charging process than in the discharging.

Figure 2 illustrates the voltage profiles of the bare and Al<sub>2</sub>O<sub>3</sub>-coated LiCoO<sub>2</sub> thin films with a coating coverage of 0%, 50%, or 100% at 25°C. Over 200 cycles, the profiles of bare LiCoO<sub>2</sub> films severely deteriorate. On the contrary,

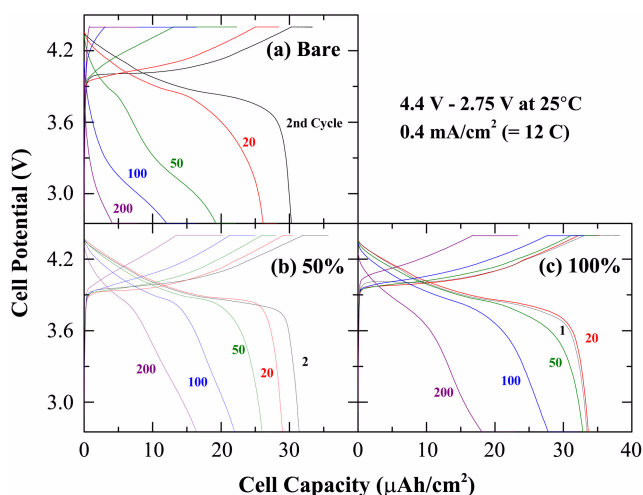
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**Fig. 1.** (Color) (a) The charge- and (b) discharge-capacity retention of bare and Al<sub>2</sub>O<sub>3</sub>-coated LiCoO<sub>2</sub> thin films. The cells were cycled between 4.4 and 2.75 V at 0.4 mA/cm<sup>2</sup> (= 12 C) and 25°C.



**Fig. 3.** (Color) (a) The charge- and (b) discharge-capacity retention of bare and Al<sub>2</sub>O<sub>3</sub>-coated LiCoO<sub>2</sub> films with a different coverage. The cells were cycled between 4.4 and 2.75 V at 0.4 mA/cm<sup>2</sup> and 60°C.



**Fig. 2.** (Color) Voltage profiles of the (a) bare, and Al<sub>2</sub>O<sub>3</sub>-coated LiCoO<sub>2</sub> films with (b) 50%, and (c) 100% surface coverage.

those of the Al<sub>2</sub>O<sub>3</sub>-coated LiCoO<sub>2</sub> films during 200 cycles show better performances. For 100% Al<sub>2</sub>O<sub>3</sub>-coated LiCoO<sub>2</sub> 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. Lith-

ium-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.<sup>[7,12,13]</sup> 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 Al<sub>2</sub>O<sub>3</sub>-coated LiCoO<sub>2</sub> thin films with different coverage ratios are represented in Fig. 3. The initial capacity and the capacity retention of the bare LiCoO<sub>2</sub> films appear to deteriorate at higher temperature. Dramatic degradation of bare LiCoO<sub>2</sub> films is observed, because more significant Co dissolution from the cathode occurs at 60°C than at 25°C. It has been reported that LiCoO<sub>2</sub> powders exhibit more intense Co dissolution at elevated temperatures, and this causes significant capacity loss in LiCoO<sub>2</sub> cathodes.<sup>[8]</sup> The Al<sub>2</sub>O<sub>3</sub>-coated LiCoO<sub>2</sub> films with 50% coverage exhibit rapid capacity fading after ~130 cycles at 60°C. However, the initial capacity and the capacity retention of the Al<sub>2</sub>O<sub>3</sub>-coated LiCoO<sub>2</sub> at 60°C are better with 100% Al<sub>2</sub>O<sub>3</sub>-coating coverage. Similarly, the 100% coated-Al<sub>2</sub>O<sub>3</sub> LiCoO<sub>2</sub> film shows excellent cycle-life performances even at higher temperature, compared with the uncoated-LiCoO<sub>2</sub> films.

Wang's group reported that alumina nanoparticles soaked

in an electrolyte improved the cycle-life performances of LiCoO<sub>2</sub>.<sup>[16]</sup> Whether a dispersion of alumina nanoparticles in electrolytes or a uniform Al<sub>2</sub>O<sub>3</sub> coating on LiCoO<sub>2</sub> is more effective for enhancing cycle-life performance remains an open question. With surface modifications, the Al<sub>2</sub>O<sub>3</sub>-coating layer reduces the amount of direct HF attack, while preventing Li<sup>+</sup> 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<sub>2</sub>O<sub>3</sub>-coated Li<sub>1.05</sub>Ni<sub>0.4</sub>Co<sub>0.15</sub>Mn<sub>0.4</sub>O<sub>2</sub> cathode material exhibited high electrochemical properties due to the HF scavenging of Al<sub>2</sub>O<sub>3</sub> layer.<sup>[17]</sup>

#### 4. CONCLUSIONS

The electrochemical properties of Al<sub>2</sub>O<sub>3</sub>-coated LiCoO<sub>2</sub> thin films with a different surface coverage of 0%, 50%, and 100% were studied. As discussed above, the LiCoO<sub>2</sub> 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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