

Novel LiCoO₂ Cathode Material with Al₂O₃ Coating for a Li Ion Cell

Jaephil Cho,[†] Yong Jeong Kim,[‡] and Byungwoo Park^{*,‡}

Samsung SDI Co., Ltd., Chonan, Chungchongnam-Do, Korea, and School of Materials Science and Engineering, Seoul National University, Seoul, Korea

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A high-performance LiCoO₂ cathode was successively fabricated by a sol–gel coating of Al₂O₃ to the LiCoO₂ particle surfaces and subsequent heat treatment at 600 °C for 3 h. Unlike bare LiCoO₂, the Al₂O₃-coated LiCoO₂ cathode exhibits no decrease in its original specific capacity of 174 mA h/g (vs lithium metal) and excellent capacity retention (97% of its initial capacity) between 4.4 and 2.75 V after 50 cycles. A similar excellent capacity retention of the coated LiCoO₂ is also observed in a Li ion cell (C/LiCoO₂). This is because the high concentration of Al atoms at the particle surface region leads to the enhancement of structural stability of LiCoO₂ during cycling, which originates from the disappearance of the phase transition from a hexagonal to monoclinic phase.

Introduction

Hexagonal α -NaFeO₂-type LiCoO₂ is structurally the most stable cathode material among its structural analogue, such as LiNiO₂ and LiMnO₂.^{1–3} However, it shows relatively large capacity fading after extended cycling.^{4–7} This was reported to be due to anisotropic expansion and contraction during cycling that leads to the formation of microcracks in the particles, causing structural degradation of the material.⁸ The structural stability of Li_{1–x}CoO₂ is maintained only for a limited compositional range of 0 < x < 0.5, while its stability rapidly deteriorates for x > 0.5, i.e., excessive removal of Li ions from LiCoO₂.^{5,7} This phenomenon is attributed to the structural transition from a hexagonal to monoclinic phase at x ~ 0.5 (4.1 to 4.2 V vs lithium metal), accompanying a 1.2% expansion along the c direction with negligible variation in the a direction.^{9,10} This expansion is far above the tolerance (~0.1%) for the elastic strain of oxides including cathode materials.¹¹ To overcome this problem, doping with Al and Mg in

LiCo_{1–y}M_yO₂ has been studied. However, the structural stability of the materials during cycling was not improved.^{12,13} Even worse, these materials showed a deterioration in their initial capacities relative to bare LiCoO₂. Partial substitution of metal ions for Co did not improve the structural instability of LiCoO₂ during cycling either. In this paper, a new method of improving structural stability through the sol–gel coating of Al₂O₃ on the surface of LiCoO₂ particles without sacrificing its initial capacity is reported. The cycling behavior of an Al₂O₃-coated LiCoO₂ material was evaluated in coin-type half and Li ion cells with various C rates (0.1–1C rate) between 4.4 and 2.75 V.

Experimental Section

LiCoO₂ powder was prepared by employing Co₃O₄ (average particle size of 5 μ m) and finely ground LiOH·H₂O powders as starting materials. Co₃O₄ and LiOH·H₂O were mixed in the mole ratio of 1:1.05 and fired in an oxygen stream for 24 h at 900 °C. Excess LiOH·H₂O was used to compensate for the loss of Li during firing. LiCoO₂ powders with an average particle size of 10 μ m, sampled from the batches by sieving through a 500-mesh screen (26 μ m), were used for Al₂O₃ coating. To obtain a sol–gel coating of LiCoO₂ powders, aluminum ethylhexanoate diisopropoxide (Al(OOC₈H₁₅)(OC₃H₇)₂) was dissolved in 2-propanol, followed by continuous stirring at 21 °C for 20 h. The surfaces of LiCoO₂ were then immersed in the coating solution such that the total amount of coating solution corresponded to 5 wt % of LiCoO₂ powders. During firing, the aluminum alkoxide gel on the LiCoO₂ particles was first decomposed into amorphous Al₂O₃ and then crystallized. After LiCoO₂ coated with aluminum alkoxide gel was dried at 150 °C for 1 h, the batch was then fired at 600 °C for 3 h.

The coin-type test cells (2016 size) contained a test cathode, a carbon or Li metal anode, and a 20- μ m-thick microporous polyethylene separator in an electrolyte solution of 1 M LiPF₆ in ethylene carbonate/dimethyl carbonate (EC/DMC) (1:1 vol %). The test cathode consisted of 92 wt % cathode material, 4

* Corresponding author. E-mail: byungwoo@snu.ac.kr.

[†] Samsung SDI Co., Ltd.

[‡] Seoul National University.

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wt % polyvinylidene fluoride, and 4 wt % carbon black. To balance the coin-type Li ion cells C/LiCoO₂, the weight ratio of the meso-phase pitch-based carbon fiber (MCF) to uncoated and coated LiCoO₂ was 1.1 to 1. Each test electrode contained 32 ± 2 mg of the active material. Each cell was aged for 24 h at room temperature before commencing the electrochemical tests, and the internal resistance of as-prepared Li ion cells was 90 ± 5 m Ω . The cycling tests of the coin-type Li ion cells were performed using a charge cutoff voltage with 4.4 V at various charge and discharge rates of constant current using a multichannel cycler (Toyo) having a better than 0.5% current accuracy. The cycling tests of Li/LiCoO₂ cells were carried out initially by charging and discharging the cell at 0.1C rate for 1 cycle, followed by 49 cycles at 0.3C rate.

An empirical relationship between equilibrium potential and the degree of Li⁺ extraction from Li_{1-x}CoO₂, which was similar to one previously used,⁹ was used to determine the value of *x*. The composition (*x*) in Li_{1-x}CoO₂ was calculated from the charge capacity, assuming 100% Columbic efficiency for the reaction: LiCoO₂ → Li_{1-x}CoO₂ + *x*Li⁺ + *x*e⁻. The coin-type half cells in Li/LiCoO₂ were charged at 0.1C rate to the predetermined voltages and then potentiostated for 30 h until the current was equivalent to 0.02C rate. The coin cells were disassembled to remove the Li_{1-x}CoO₂ cathodes, followed by rinsing them with DMC to remove the LiPF₆ salt from the cathodes.

Result and Discussion

X-ray diffraction (XRD) patterns of the coated LiCoO₂ specimens heat-treated at 400 °C were shown to be a single phase in the *R*3*m* space group.¹⁴ However, there was no indication of any Al₂O₃ phase. This suggests that coated Al₂O₃ exists as either an Al₂O₃ thin film or a solid solution (LiCo_{1-y}Al_yO₂) by a reaction with LiCoO₂. A slight contraction of the lattice constants *a* and *c* to *a* = 2.806 Å and *c* = 14.065 Å was observed in the coated LiCoO₂, from *a* = 2.81 Å and *c* = 14.08 Å for bare LiCoO₂. This indicates that the phases formed near the surface could be the solid solution LiCo_{1-y}Al_yO₂. To identify the spatial distribution of Al within the coated LiCoO₂ particles, an Al concentration profile was obtained by Auger electron spectroscopy (AES), as shown in Figure 1. The micrograph of the coated particles used for AES analysis is shown in Figure 1a. The concentration profile in Figure 1b clearly shows that the Al atoms are distributed only at the particle surface region. An abrupt decrease in the Al content from about 18 at. % without counting the Li concentration to a negligible concentration toward the particle center, which occurs simultaneously with an increase in the Co content, indicates that the solid solution LiCo_{1-y}Al_yO₂ with 0 < *y* < 0.5 is formed at the surface region. Since a sputter rate of 260 Å/min is obtained for SiO₂ with the same accelerating voltage of 10 keV, which is assuming that the sputter rate of the present sample is similar to that of SiO₂, the thickness of the Al-doped region was estimated to be the order of 0.1 μm. Considering the relatively low firing temperature of 600 °C, this coating effect is surely due to the limited inward diffusion of Al in the LiCoO₂ particles. Consequently, we suggest that the contraction along the *c*-axis of the coated sample is attributed to the formation of a solid solution LiCo_{1-y}Al_yO₂ localized at the surface region.

The initial capacity of the coated LiCoO₂ is identical to that of the uncoated one, showing 174 mA h/g

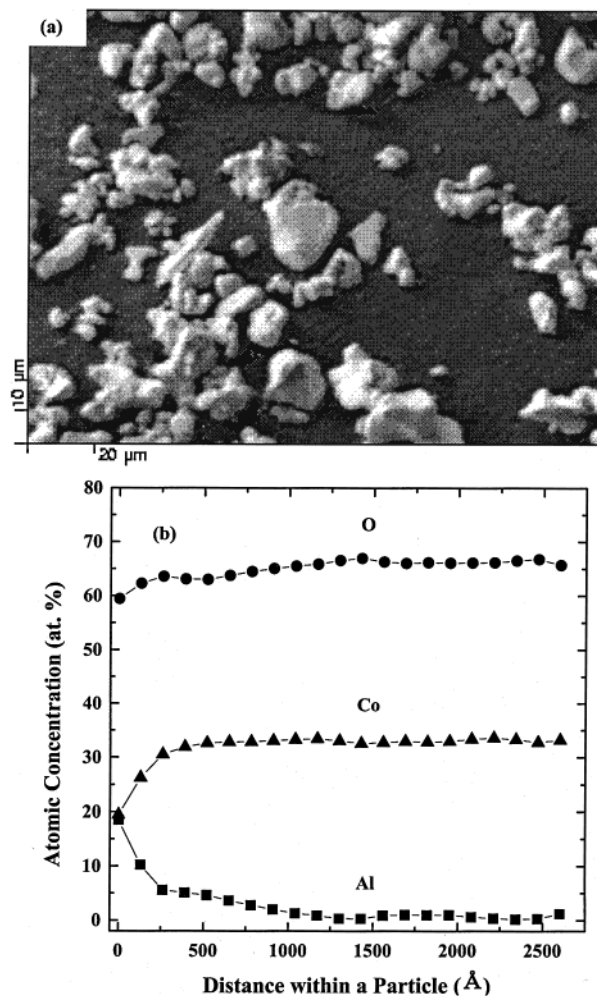


Figure 1. (a) The SEM micrograph of the Al₂O₃-coated LiCoO₂ particles and (b) concentration profiles of a coated LiCoO₂ particle by the AES analysis. The AES analysis was performed with the accelerating voltage of 10 keV.

between 4.4 and 2.75 V at the rate of 0.1C (=14 mA/g) in half-cells (Li/LiCoO₂) (Figure 2a). Cycling data indicate that the coated sample shows two-times higher capacity retention than the uncoated sample, which is 94% of the initial capacity at the 0.5C rate after 50 cycles (from 174 to 163 mA h/g) (Figure 2b). These values are also superior to those reported for LiCo_{0.75}Al_{0.25}O₂ having an initial capacity of 125 mA h/g between 4.4 and 2.5 V, and a capacity retention was 51% of the initial capacity after only 9 cycles.¹² Figure 2b clearly shows the coated LiCoO₂ has an excellent capacity retention up to the voltage cutoff on charge at 4.4 V, while the cycling stability of uncoated Li_{1-x}CoO₂ rapidly deteriorates for *x* > 0.5 (corresponding to ~4.1 V) due to the phase transition from hexagonal to monoclinic phase (details in the following Figure 3).

To examine such a difference in the cycle life, cyclic voltammograms of coated and bare LiCoO₂ were conducted up to the second cycle (Figure 3). In the figure, H and M represent the hexagonal and monoclinic phases, respectively. A striking difference in these cathodes is that the Al₂O₃-coated LiCoO₂ prepared at 600 °C has no monoclinic phase present (at ~4.15 V during charging and ~4.1 V during discharging) and shows only the hexagonal phase even up to 4.4 V. A phase transition from a hexagonal to monoclinic phase

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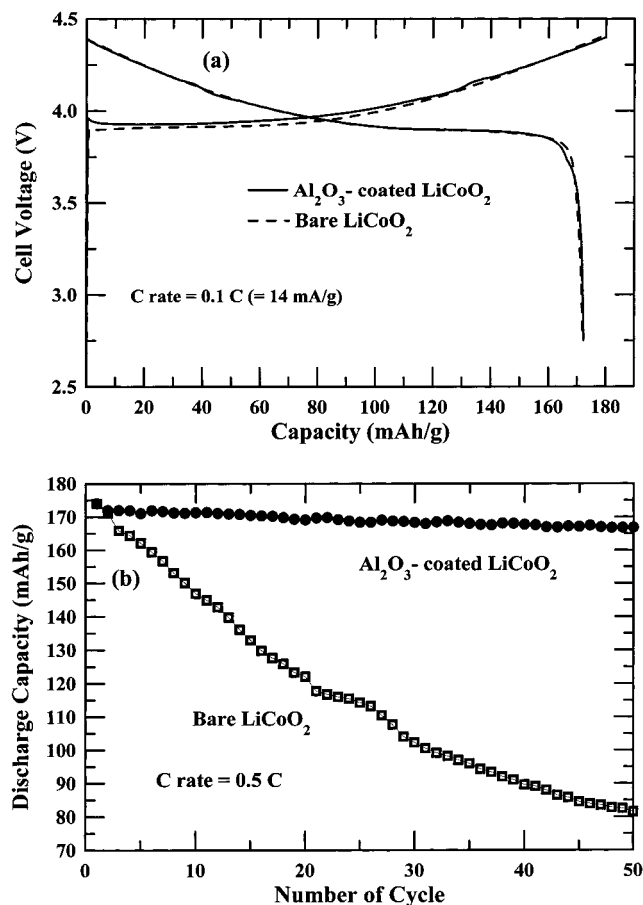


Figure 2. (a) Initial capacities and (b) cycle-life performances of bare and coated LiCoO_2 cathodes measured at the rate of $0.5C$ between 4.4 and 2.75 V in Li/LiCoO_2 .

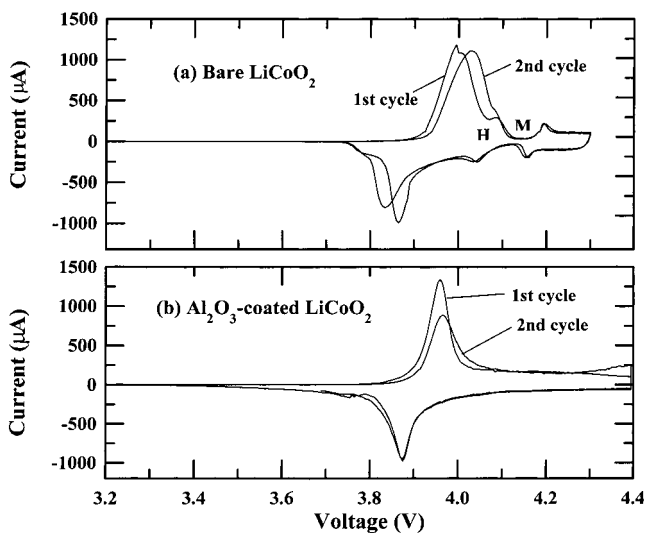


Figure 3. (a) Cyclic voltammograms of the uncoated LiCoO_2 cathode and (b) Al_2O_3 -coated LiCoO_2 cathode. The scan rate was 0.02 mV/s. H and M in (a) denote the hexagonal and monoclinic phase, respectively.

is the major cause of structural degradation in LiCoO_2 .^{4,7} This contrasts to the uncoated LiCoO_2 that clearly shows the phase transition (Figure 3a). Therefore, it is easily expected that the disappearance of the phase transition results in negligible strain and microcracks.

Lattice constants a and c , as a function of x in $\text{Li}_{1-x}\text{CoO}_2$, during the first charge were determined from

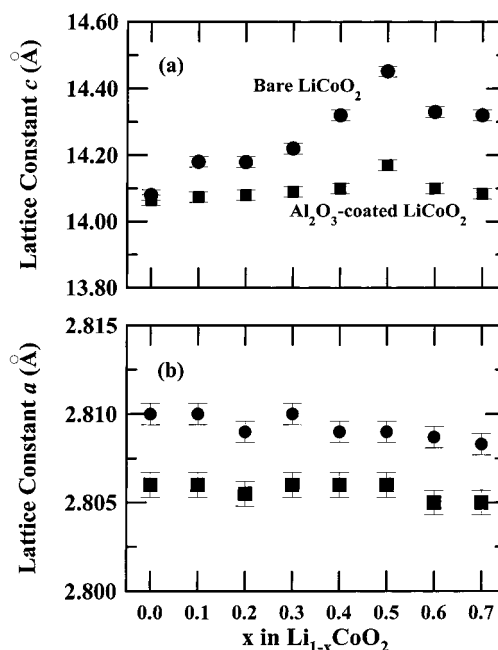


Figure 4. Variation of lattice constants a and c in the bare and coated $\text{Li}_{1-x}\text{CoO}_2$ as a function of x .

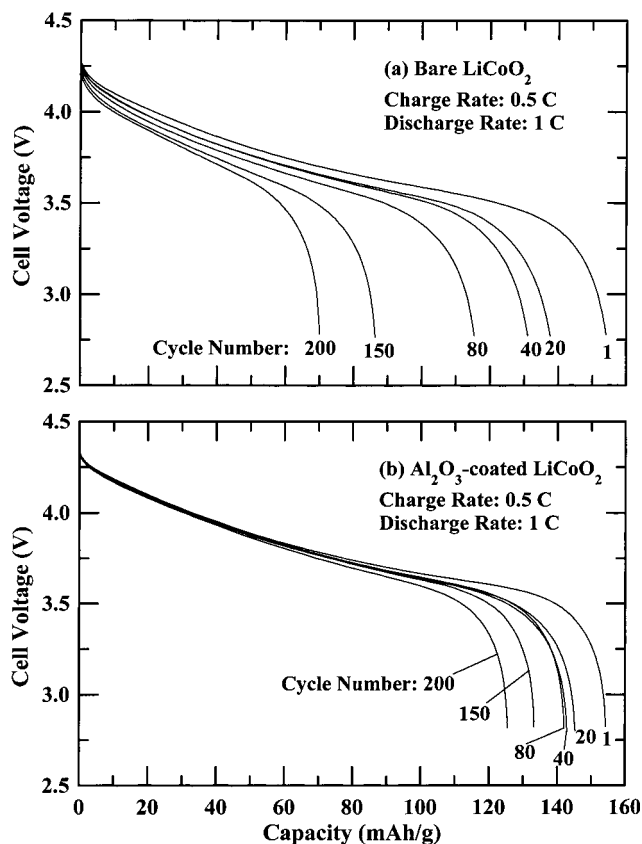


Figure 5. Plots of capacity retention of (a) bare LiCoO_2 and (b) coated LiCoO_2 heat-treated at 600 °C for 3 h as a function of cycle number. Charge and discharge rates are 0.5- and $1C$, respectively.

the XRD data of charged cathodes at different voltages (Figure 4). Even though the lattice constant a shows little variation during charge in both cases, the lattice constant c shows a clear shift when x is increased from 0 to 0.7: $1.7 \pm 0.1\%$ vs $0.14 \pm 0.02\%$ for the bare and coated one, respectively. This suggests that the struc-

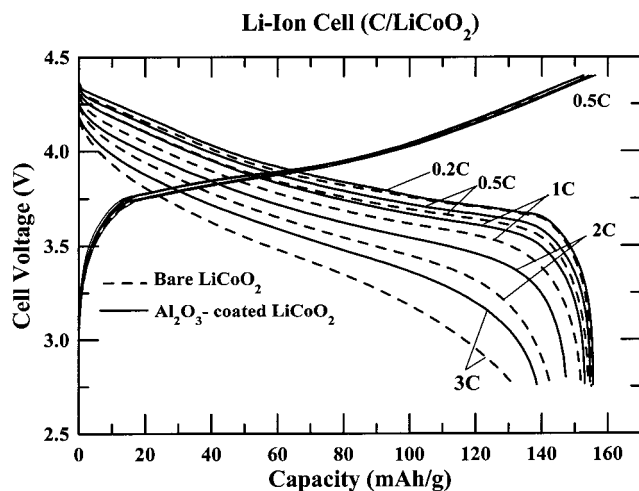


Figure 6. Rate capabilities of uncoated and coated LiCoO₂ at various discharge rates of 0.2-, 0.5-, 1-, 2-, and 3C. Charge rates were fixed at 0.5C.

tural stabilization originates from the Al₂O₃ coating. Hence, excellent stability of the coated LiCoO₂ during cycling is attributed to decreased strain along the *c* direction, as a result of the disappearance of a phase transition from a hexagonal to monoclinic phase.

Evaluation of the cycle-life performance of both bare and coated LiCoO₂ was also carried out in coin-type Li ion cells (C/LiCoO₂). The lower initial capacities of the cathodes (154 mA h/g) compared to those in the half-cells are due to the irreversible capacity loss of the MCF anode (Figure 5). After 200 cycles, the capacity loss of the coated LiCoO₂ appears to be four times superior to

that of bare LiCoO₂, only showing 19% capacity loss from its initial capacity (154 mA h/g). For the measurement of rate capability of both samples in the Li ion cells, the charge and discharge cutoff voltages were fixed to 4.4 and 2.75 V, respectively (Figure 6). The charge rate was fixed at 0.5C, and the discharge rate increased from 0.2- to 0.5-, 1-, 2-, and 3C rates. Results show that the coated LiCoO₂ not only has improved capacity retention but also an increased discharge voltage at higher C rates. However, such a high discharge-voltage profile compared to uncoated LiCoO₂ is minimal during cycling at the 0.2C rate. We believe that this effect is due to the relaxation of the LiCo_{1-y}Al_yO₂ solid solution formed near the surface, creating smooth pathways for the process of lithium insertion and extraction at higher C rates, thereby enhancing the lithium diffusion rate and lowering the cell resistance.

Conclusions

An innovative way to improve structural stability of LiCoO₂ by means of Al₂O₃ coatings has been demonstrated. The coated LiCoO₂ material shows a distinctly higher concentration of Al atoms at the surface than inside the particle, and the expansion of the *c*-axis is sharply decreased during cycling. In addition, Al₂O₃-coated LiCoO₂ cathodes lead to excellent capacity retention during cycling between 4.4 and 2.75 V. This effect has not been reported elsewhere, and more detailed studies are in progress to further investigate this unusual behavior.

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