Electrochemical Stability of Thin-Film LiCoO₂ Cathodes by Aluminum-Oxide Coating

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High-performance thin-film LiCoO₂ cathodes were successfully fabricated by aluminum-oxide coating. Both the galvanostatic charge-discharge experiments and the cyclic voltammmograms (CVs) showed enhanced electrochemical properties in the Al₂O₃-coated LiCoO₂ films compared to those in the uncoated ones. The improved cycling behaviors in the coated samples are caused by the suppression of cobalt dissolution from the LiCoO₂ thin films, with the formation of an aluminum-oxide solid electrolyte residing between the LiCoO₂ cathode and liquid electrolyte. Galvanostatic intermittent titration technique (GITT) results clearly showed that the Al₂O₃-coated samples had higher Li diffusivities than the uncoated ones after 80 cycles. The effect of Al₂O₃ thickness on the electrochemical properties up to 300 nm was also studied.

Introduction

LiCoO₂ cathode materials have been studied extensively because of their excellent electrochemical properties and the ease of synthesizing a hexagonal α-NaFeO₂ structure, where alternating planes containing Li and Co ions are separated by close-packed oxygen layers.1–4 Fabricating these materials as thin-film cathodes for all-solid-state microbatteries has been a major focus of research. This is due to the need to miniaturize various electronic devices, such as the monolithic hybridization with CMOS—RAM, back-up power systems for computer chips, small sensors, and hazard cards.5–8 Thin-film cathodes have also received much attention due to the intrinsic electrochemical properties of lithiated transition-metal oxides, and because composite powders with polymer binders and carbon blacks may not represent the characteristic electrochemical properties of these oxides.9–17 LiCoO₂ cathode materials are typically charged up to ~4.2 V vs Li (Li₀.₅CoO₂), yielding a specific capacity below ~140 mAh/g. Additional Li ions can be extracted from Li₀.₅CoO₂ by raising the charge cutoff voltage. However, overcharging is often found to cause significant deterioration in the stability of LiCoO₂ due to a monoclinic to hexagonal (M–H) phase transition, which induces extended defects (microcracks) between and within the particles,1–3 and potential surface reactions such as cobalt dissolution above 4.4 V.4 Recently, Cho et al.18–22 reported that a thin-film metal-oxide coating (Al₂O₃, ZrO₂, etc.) on the surface of LiCoO₂ powders showed excellent capacity retention even at the cutoff voltage of 4.4 V. However, the mechanisms for the effect of metal-oxide coating have not yet been clearly identified.

**References**

In this paper, a novel coating technology for improving the cycle-life performance in thin-film LiCoO$_2$ cathodes is reported. The effect of Al$_2$O$_3$ coating on cobalt dissolution from the LiCoO$_2$ films is investigated, and the Li diffusivities are determined during a Li intercalation and deintercalation. The Al$_2$O$_3$ coating thicknesses are also varied from 10 to 300 nm to determine the effects on the electrochemical properties.

**Experimental Section**

The LiCoO$_2$ thin films (1 cm$^2$) were deposited on thermally oxidized SiO$_2$/Si (100) substrates by rf magnetron sputtering using a stoichiometric LiCoO$_2$ target (2-in. diam.). The target was fabricated by cold-pressing commercial LiCoO$_2$ powders followed by sintering at 1000 °C for 10 h in air. A Pt current collector was deposited prior to the LiCoO$_2$ film deposition. To improve the Pt adhesion to the substrate, a TiO$_2$ underlayer was deposited by the reactive sputtering of Ti. LiCoO$_2$ thin-film deposition was conducted at a pressure of 20 mTorr with an Ar/O$_2$ ratio of 3:1 after presputtering for 1 h. The deposition rate was ~2 nm/min with an rf power of 100 W, and a 600-nm-thick film was deposited. To obtain good-quality LiCoO$_2$ thin films, all rf-sputtered films were annealed at 700 °C in an oxygen atmosphere of 10 mTorr for 30 min. The Al$_2$O$_3$ thin films were deposited on top of the crystallized LiCoO$_2$ films by the reactive sputtering of an Al target. After Al$_2$O$_3$ deposition, the coated samples were heat-treated at 400 °C for 5 h in flowing oxygen.

The structural characterization of LiCoO$_2$ films was performed by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The film composition and depth profile near the Al$_2$O$_3$-coated film surface were obtained using inductively coupled plasma–atomic emission spectroscopy (ICP–AES) and Auger electron spectroscopy (AES), respectively. The interface between the aluminum-oxide layer and LiCoO$_2$ was also characterized by energy-dispersive X-ray spectroscopy (EDS) in TEM.

The electrochemical characteristics of the LiCoO$_2$ thin films were investigated using both galvanostatic charge–discharge experiments and cyclic voltammograms (CVs). Beaker-type half-cells were used to characterize the electrochemical properties of both the uncoated and Al$_2$O$_3$-coated LiCoO$_2$ thin films. The electrochemical cells consisted of Li-metal sheets as a counter and reference electrode, a LiCoO$_2$ film of approximately 1 cm$^2$ of active area as the working electrode, and 1 M LiPF$_6$ in EC/DEC (1/1 vol. %) (Cheil Industries Inc.) as the electrolyte. The cells were electrochemically cycled over the voltage range of 2.75 and 4.4 V with current rates of 0.2 and 0.4 mA/cm$^2$. At all the charge/discharge cutoff steps, the cell voltages were potentiostated until the current decreased to 10% of the charge/discharge rates. To determine the Li diffusivities as a function of the cell potential, a galvanostatic intermittent titration technique (GITT) with current steps of 0.4 mA/cm$^2$ for 10 s was used for both the uncoated and Al$_2$O$_3$-coated Li$_{1-x}$CoO$_2$ films. Ten minutes of equilibration were allowed between steps. CVs of both bare and Al$_2$O$_3$-coated Li$_{1-x}$CoO$_2$ films were recorded at a sweep rate of 0.1 mV/sec, during the first cycle, and after the 40th and 80th cycles at 0.2 mA/cm$^2$ in the voltage range of 2.75 and 4.4 V. Inductively coupled plasma–mass spectroscopy (ICP–MS) was used to measure the extent of cobalt dissolution into the electrolyte (with 1 mL), after floating the charged cathodes for 12 days.

**Results and Discussion**

The composition of the thin-film LiCoO$_2$ cathodes deposited onto the Pt current collector was determined using ICP–AES to obtain the Li/Co ratio and AES to obtain the O/Co ratio. The Li/Co and O/Co ratios determined by ICP–AES and AES are 1.15 and 2.05, respectively. The deviation from the ideal LiCoO$_2$ stishiometry probably originates from the presence of small amounts of Li$_2$O present in the films, which cannot be detected by XRD.

In Figure 1, the XRD patterns of Al$_2$O$_3$-coated LiCoO$_2$ films are compared with the patterns of the LiCoO$_2$ powders and the bare LiCoO$_2$ thin film. The XRD patterns of the Al$_2$O$_3$-coated films do not show any peak corresponding to the Al$_2$O$_3$ phase, suggesting that the crystallinity of the Al$_2$O$_3$ layer may be poor. In addition, Figure 1 shows a crystallized LiCoO$_2$ thin film with a preferred (003) orientation of hexagonal LiCoO$_2$.

Figure 2 shows the cross-sectional TEM image of an Al$_2$O$_3$-coated LiCoO$_2$ with a continuous coating on top
of the polycrystalline LiCoO₂ thin film. The EDS shows the Al components in the coating layer, indicating a sharp interface between an aluminum-oxide layer and LiCoO₂.

To test the cycle-life performance of the bare and 30-nm-thick Al₂O₃-coated LiCoO₂ thin films, half cells were cycled in the voltage range of 2.75 and 4.4 V at 0.2 and 0.4 mA/cm², as shown in Figures 3 and 4, respectively. A 30-nm-thick Al₂O₃ coating significantly improves the retention capacity of the LiCoO₂ thin-film cathodes. The charge and discharge capacities of the bare LiCoO₂ get deteriorated to only ~3% and ~25% of the original capacity after 100 cycles (Figure 3(a)), whereas those of the Al₂O₃-coated LiCoO₂ retain ~64% and ~75% of the initial capacity at a current rate of 0.2 mA/cm² (Figure 3(b)). The charge capacities of the bare LiCoO₂ films for Li deintercalation (charging) exhibit faster deterioration than the discharge capacities for Li intercalation (discharging). Nonlinearity of charge and discharge capacities in the uncoated samples may be related to the damage of LiCoO₂ (such as the surface corrosion) during the electrochemical cycling. We have recently reported that the effect of an Al₂O₃ coating on the cycle-life performance was more pronounced at the higher current rate (0.8 mA/cm²). The insets in Figures 3 and 4 show the same cycle-life performance, including the extra capacity from the constant-voltage mode.

The Al₂O₃-coating thicknesses were varied from 10 to 300 nm to examine the possible questions of electronic insulation and Li migration through the Al₂O₃ layer. Figure 5(a) shows that the initial discharge capacities are almost independent of the coating thickness (0–300 nm range). In addition, the variation in the Al₂O₃ thickness ranging from 10 to 300 nm does not affect the capacity retention: ~70% and ~60% retention, respectively, at 0.2 and 0.4 mA/cm², whereas the capacity retention of the uncoated LiCoO₂ thin film is only ~25% after 100 cycles, as shown in Figure 5(b). This is possibly because the Al₂O₃ coating layer acts as a solid electrolyte with a low electronic conductivity and a reasonably high Li-ion conductivity. For example, the Li-ion conductivity of a Li₂O–Al₂O₃ (0.7:0.3) solid electrolyte is ~10⁻⁷ S/cm at room temperature.

To clarify the reason the Al₂O₃-coated LiCoO₂ thin films showed better electrochemical performance than the bare ones, ICP–MS analysis was carried out after floating the films at 4.2, 4.4, 4.5, 4.6, and 4.7 V, respectively, for 12 days. As shown in Figure 6, the amount of cobalt dissolution from the uncoated LiCoO₂ films significantly increases with increasing charge-cutoff voltages, whereas an increase in cobalt dissolution from the Al₂O₃-coated ones is not significant. An increase in the fraction of Co⁴⁺ in Li₁₋ₓCoO₂ augments the reactivity with the electrolytes and acidic HF in the

electrolyte. Amatucci et al.\textsuperscript{4} reported that cobalt dissolution is closely related to a weakening of the crystal structure by the removal of the binding lithium. An Al\textsubscript{2}O\textsubscript{3} coating can effectively inhibit cobalt dissolution even at 4.7 V (\texttimes{} 100 ppm), which is much smaller than cobalt dissolution (\texttimes{} 1000 ppm) from the uncoated LiCoO\textsubscript{2} films.

Figure 7 shows the changes in the lattice constants c as a function of the cell potential during the first charge in the Li\textsubscript{1-x}CoO\textsubscript{2} thin films and powders.\textsuperscript{18–20} For thin films, each cell was charged at a 0.1 mA/cm\textsuperscript{2} rate to the predetermined voltages, then potentiostated until the current density decreased to 1 \textmu{}A/cm\textsuperscript{2}.

Further studies are necessary to identify the mechanisms that cause LiCoO\textsubscript{2} thin films to have a limited c-axis expansion.

The voltage profiles of the bare and 30-nm-thick Al\textsubscript{2}O\textsubscript{3}-coated LiCoO\textsubscript{2} thin films are shown in Figure 8. The profiles of the bare LiCoO\textsubscript{2} thin films become steeper with increasing the cycling number up to 80 cycles at 0.2 mA/cm\textsuperscript{2}. At each chargedischarge cutoff step, the cell voltage was potentiostated until the current decreased to 0.02 mA/cm\textsuperscript{2}.

The slight increase in cell potential is observed in the initial cycle of Al\textsubscript{2}O\textsubscript{3}-coated cathodes. This is attributed to the insulation of aluminum-oxide layer on the surface to the...
Li ions. From the second cycle on, the polarization in the charge and discharge processes of coated sample is not significant, which is because the Li–Al–O coating layer on the LiCoO$_2$ acts as a solid electrolyte as shown in Figure 5. Figure 9 shows the current profiles at a constant voltage of 4.4 V (Li deintercalation) and 2.75 V (Li intercalation) with the current rates reduced from 0.2 mA/cm$^2$ to 0.02 mA/cm$^2$ for decreasing the concentration gradient of Li in the cathode. The current profiles of the bare and Al$_2$O$_3$-coated LiCoO$_2$ films during the first cycling have similar decay constants. However, the currents of the Al$_2$O$_3$-coated LiCoO$_2$ films at the constant voltage of 4.4 and 2.75 V after the 80th cycle equilibrate more rapidly than those of the bare ones, due to the formation of a surface layer that can tolerate the electrochemical cycling with the high cutoff voltage.

Figure 10 shows the CVs of the bare and 30-nm-thick Al$_2$O$_3$-coated LiCoO$_2$ thin films at a scan rate of 0.1 mV/sec, which were carried out during the first cycle, and after the 40th and 80th charging/discharging cycles. The CVs of the Al$_2$O$_3$-coated LiCoO$_2$ films at the constant voltage of 4.4 and 2.75 V after the 80th cycle equilibrate more rapidly than those of the bare ones, due to the formation of a surface layer that can tolerate the electrochemical cycling with the high cutoff voltage. of the Al$_2$O$_3$-coated film during the first cycle is narrower than that of the bare one, although the anodic peaks (~3.96 V at a) are similar. In addition, in the bare LiCoO$_2$ thin films, the widths of both the cathodic and anodic peaks are remarkably broadened, and the peak positions become more separated as the number of cycles increases to 80, whereas the widths of the cathodic and anodic peaks of the Al$_2$O$_3$-coated samples are relatively sharp. This indicates that the Al$_2$O$_3$-coated LiCoO$_2$ thin films are more reversible than the bare ones, which is probably related to the suppression of cobalt dissolution from the cathode (Figure 6).

The effect of the Al$_2$O$_3$ coating on the Li intercalation/deintercalation kinetics during cycling was investigated by GITT, which is typically used for estimating the diffusivities of Li intercalation electrodes. In GITT, the sample is subjected to a constant-flux lithiation or delithiation, which is interrupted after an interval $\tau$, to allow the cell voltage to relax to its steady-state value. The temporary change in the cell potential caused by an outer current pulse allows the Li diffusivity to be determined. In this technique, the Li$_{1-x}$CoO$_2$ thin films were subjected to a constant-flux lithiation or delithiation (0.4 mA/cm$^2$) step. Sets of current pulses with an interval time $\tau = 10$ s were applied, and the

current was interrupted for 10 min after each current pulse of 10 s. Weppner and Huggins\(^\text{24}\) derived a simple expression for Li diffusivity in a thin film of intercalation electrode

\[
D_{Li} = \frac{4L^2}{\pi r^2} \left( \frac{\Delta E_s}{\Delta E_r} \right)^2 \quad \text{with} \quad r \ll r_c = L \frac{1}{D_{Li}^2} \quad (1)
\]

where \(L\) represents the film thickness of the LiCoO\(_2\) cathode, and \(\Delta E_r\) and \(\Delta E_s\) are the voltage changes during the current pulse and after the current pulse, respectively. The ideal density for the LiCoO\(_2\) thin film was used for utilizing this equation.

Figures 11 and 12 show the apparent Li diffusivities as a function of the cell potential during Li deintercalation (charging) and intercalation (discharging), respectively. The Li diffusivities of Al\(_2\)O\(_3\)-coated LiCoO\(_2\) are slightly lower than those of the bare one during the first Li deintercalation, as shown in Figure 11. The Li diffusivities in the bare LiCoO\(_2\) thin films during Li deintercalation (Figure 11) are in good agreement with the previous results obtained using either thin-film Li\(_{1-x}\)CoO\(_2\) cathodes\(^\text{7,10,12,29}\) or powder electrodes\(^\text{25,27,28,30}\). Note that the plots of the Li diffusivity vs the cell potential show a maximum at \(\approx 4.13\) V, corresponding to the monoclinic phase. In addition, two minima are observed at the cell potential corresponding to the phase transition between the hexagonal and monoclinic phase, which is similar to the previous reports by Jang et al.\(^\text{10}\).

As the cycling number increases, the Li diffusivity decreases owing to the degradation of the thin-film LiCoO\(_2\) cathodes. As shown in Figure 11, during Li deintercalation (charging), the Li diffusivities of the bare LiCoO\(_2\) thin films (in the range of approximately 4.15 and 4.3 V) decrease to \(\approx 5 \times 10^{-12}\) cm\(^2\)/sec after 80 cycles, compared to \(\approx 2 \times 10^{-11}\) cm\(^2\)/sec in the coated films. During Li intercalation (discharging), the Li diffusivities in bare samples are \(\approx 1 \times 10^{-11}\) cm\(^2\)/sec after 80 cycles, while the deterioration in the Li diffusivities in the coated ones remains at \(\approx 3 \times 10^{-11}\) cm\(^2\)/sec (Figure 12). These results suggest that an Al\(_2\)O\(_3\) coating on the LiCoO\(_2\) thin films can tolerate the electrochemical cycling with a high cutoff voltage of 4.4 V, which is attributed to the suppression of cobalt dissolution by Al\(_2\)O\(_3\) coating.

Further studies are currently underway to detail the microstructures of the Li–Al–O coating layer, and electric-potential distribution near the interface between the LiCoO\(_2\) cathode and the Li–Al–O coating layer. In addition, the effect of Al\(_2\)O\(_3\) coating on the oxidative decomposition of the electrolyte solution on the cathode surface needs to be identified.

**Conclusions**

The galvanostatic charge–discharge experiments showed that the cycle-life performance of the LiCoO\(_2\) thin films was significantly improved by an Al\(_2\)O\(_3\)-surface coating. These results correlate well with the suppression of cobalt dissolution during electrochemical cycling in the Al\(_2\)O\(_3\)-coated LiCoO\(_2\) thin films. Both the CVs and GITT results clearly showed that the Al\(_2\)O\(_3\)-

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coated samples had higher Li diffusivities after 80 cycles than the bare samples. In addition, the Al$_2$O$_3$ thickness up to 300 nm did not affect the capacity retention and initial capacities. Therefore, an aluminum-oxide solid electrolyte can modify the properties of the cathode surface, by residing between the LiCoO$_2$ cathode and the liquid electrolyte, which can enhance the electrochemical stability.

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