Substrate Effect on the Microstructure and Electrochemical Properties in the Deposition of a Thin Film LiCoO₂ Electrode

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An LiCoO₂ thin-film cathode was deposited onto sintered alumina and Si/SiO₂ substrates. After annealing at 800°C in O₂ for 30 min, the film deposited on alumina consisted of large particles with several cracks, whereas the film deposited on the Si substrate was composed of very small and uniform particles. The films deposited on Si showed improved electrochemical properties, such as a larger discharge and rate capability, over those for the alumina substrate electrode, which can be attributed to differences of the particle size, surface morphology, and the low electrical resistance of the current collector.

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Table I. Film thickness measured by a profilometer.

<table>
<thead>
<tr>
<th>Deposition time (h)</th>
<th>Thickness as-deposited (Å)</th>
<th>Thickness after heat-treatment (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>~2900</td>
<td>~1500</td>
</tr>
<tr>
<td>6</td>
<td>~3700</td>
<td>~2700</td>
</tr>
<tr>
<td>8</td>
<td>~4700</td>
<td>~4000</td>
</tr>
</tbody>
</table>

High-voltage positive electrode materials such as LiMO₂ (M = Co, Ni, Mn, etc.) are being developed for use in rechargeable lithium batteries.1-4 Of these, LiCoO₂ has been studied more extensively due to its favorable electrochemical properties and ease of manufacture. Fabrication of these materials as thin-film cathodes for application in all-solid-state microbatteries has been another interesting field of research owing to the miniaturization and the reduced power consumption of many kinds of electronic devices. Thin films have also received much attention from the standpoint of investigating the intrinsic electrochemical properties of lithiated transition metal oxides because mixed or composite electrodes, consisting of polymer binder and electronically conducting carbonaceous powders, do not show the characteristic electrochemical properties of these oxides.5

Various methods have been used to fabricate thin-film electrodes. In previous work, we fabricated LiCoO₂ thin-film cathodes on stainless steel by electron-beam evaporation,6 Shokoohi et al.7 deposited LiMn₂O₄ on quartz and nickel substrates using an electron-beam evaporator, Antaya et al.8 prepared and characterized LiCoO₂ films by laser ablation, and Wang et al.9 used radio-frequency (rf) sputtering to deposit lithium phosphorous oxy nitride (LiPON) glass electrolyte and LiCoO₂ thin films on an alumina substrate.

In thin-film deposition, the substrate plays an important role in determining the microstructure and surface morphology of films deposited on it. Because these two parameters, i.e., the microstructure and morphology, affect the electrochemical properties of lithium intercalation electrodes, choosing an appropriate substrate for the deposition of electrode materials is critical for developing a thin-film electrode for lithium microbatteries.

In this study, we fabricated thin-film LiCoO₂ on two different substrates, i.e., alumina with a rough surface and an Si wafer with a smooth surface, and investigated substrate effects on the microstructural and electrochemical properties of thin-film cathodes.

Experimental

The LiCoO₂ thin films (1 cm² area) were fabricated on sintered Al₂O₃ and thermally oxidized SiO₂/Si (100) substrates by rf magnetron sputtering with a stoichiometric LiCoO₂ target (2 in. in diam). The target was fabricated by cold pressing commercial LiCoO₂ powder (Merck) at 24 t for 30 min and sintering at 800°C for 2 h in air. A 3000 Å Pt current collector was deposited prior to LiCoO₂ film deposition. In the case of the SiO₂/Si substrate, a 300 Å Ti layer was incorporated between the substrate and Pt current collector in order to enhance the adhesion of Pt to the SiO₂ surface. The substrate holder was water cooled to minimize the preferential re-evaporation of the lower melting lithium and thereby avoid alteration of the stoichiometry of the ternary compound formed during the deposition process. The distance between the target and substrate was 5 cm. Film deposition was carried out in the presence of 5 mTorr Ar/O₂, and the total gas flow rate was 12 standard cubic centimeters per minute (sccm) with the ratio Ar/O₂ = 9:3 sccm after presputtering for 1 h. The film thickness was controlled by the deposition time (4, 6, and 8 h, which is listed in Table I) under constant rf power (50 W) and working-pressure conditions. The average deposition rate was typically 9-12 Å/min.

In order to obtain the desired layer structure, films were heat-treated at 800°C in an oxygen atmosphere for 30 min with ±10°C/min heating and cooling rates. Structural identification of the films was achieved with an X-ray diffractometer (D/MAX-250H, Rigaku) using Cu Kα radiation and a graphite monochromator. The morphologies of the films were studied by scanning electron microscopy (SEM, Kevek 5-4200, Hitachi). The film composition was investigated by Rutherford backscattering spectroscopy (RBS) and elastic recoil detection (ERD) to measure the ratios of Co/O and Li/Co, respectively.

Glass-beaker-type cells were used to evaluate the electrochemical properties of the LiCoO₂ film cathodes. The electrochemical cell consisted of lithium metal sheets as counter and reference electrodes and a LiCoO₂ film as a working electrode, and 1 M LiClO₄ in propylene carbonate electrolyte. The half-cell tests were carried out in an Ar-filled glove box at 30°C.

Results and Discussion

The compositional analysis revealed that the stoichiometry of the annealed film was exactly LiCoO₂, which was obtained by numerous adjustments of deposition parameters such as the distance between the substrate and the target, Ar/O₂ gas ratio, working pressure, rf power, and so on. Figure 1 shows the X-ray diffraction (XRD) pattern of LiCoO₂ heat-treated at 800°C, 30 min in an O₂ atmosphere. After annealing, the (003) peak of a LiCoO₂ film was detected at 2θ = 18.6° and the other peaks of the LiCoO₂ film appeared at the same positions as those of powder LiCoO₂.
However, it was found that the most intense peak was (101) at \( \theta = 37.7^\circ \). This fact means that the film has a preferred orientation and that the Li\(^+\) diffusion path is perpendicular to the substrate.\(^{11}\) The peaks marked with solid squares were attributed to the Pt current collector and the alumina substrate.

Figure 2 shows a cyclic voltammogram of annealed film on the Si substrate obtained at a scan rate of 0.1 mV/s. The potential was varied between 3.5 and 4.1 V. As shown in Fig. 2, the anodic and cathodic peak currents are symmetrical about the potential axis indicating that the thin-film LiCoO\(_2\) electrochemical reaction is highly reversible, i.e., the deintercalated lithium ions can be reintercalated reversibly. The same results were obtained for the annealed film on the alumina substrate.

The basic difference in the substrate between the alumina and the Si substrate is their surface morphology. The roughness (average height of protruding surface from the bottom) of the bare alumina substrate was about 0.19 \( \mu \)m and smoothed to about 0.17 \( \mu \)m after deposition on the Pt current collector, whereas the Si substrate was completely flat. Therefore, the surface morphologies of the crystallized film on each substrate were very different from each other.
Figure 3 shows the surface morphologies of the as-deposited thin-film LiCoO$_2$ on the alumina and Si substrate and annealed at 800°C for 30 min in O$_2$ atmosphere, respectively. As shown in Fig. 3a, the as-deposited film on the alumina substrate had a rough surface that was related to the morphology of the alumina substrate. On the other hand, the as-deposited film on the Si substrate showed a flat and uniform surface morphology. In the case of the annealed film on the alumina substrate, large particles with several cracks were observed, whereas on the Si substrate, very fine and uniform particles without cracks were formed. After annealing, the characteristic morphologies of films deposited on the alumina and Si substrates originated from the bare substrate surface. These cracks are believed to be caused by thermal stress during high-temperature heat-treatment. The linear thermal expansion coefficient, $\alpha$, of alumina at 800°C (for sintered alumina, about $7.50 \times 10^{-6}/\degree$C)$^{12}$ is about two times larger than that of Si ($4.31 \times 10^{-6}/\degree$C)$^{13}$ at the same temperature. Although the value of $\alpha$ for LiCoO$_2$ film is not known at present, because the thermal expansion of alumina is larger than that of Si, we can assume that cracking due to the thermal stress should be present only in the alumina substrate.

The charge-discharge profiles and the normalized discharge capacity vs. cycle number of films deposited on the Si and alumina substrates are shown in Fig. 4. When the cutoff voltage ranged from 3.5 to 4.05 V at 50 $\mu$A/cm$^2$, the discharge capacity of the film on the Si substrate was about 27 $\mu$Ah/cm$^2$ $\mu$m$^{-1}$ after 150 cycles. On the other hand, the film on the alumina substrate also showed very stable cycling characteristics with an average capacity decrease rate of 0.05% per cycle. Therefore, the substrate surface roughness did not significantly affect the electrode cyclability within the measured cycles.

Electrochemical properties such as rate capability, peak potential, and peak current at various scan rates and cyclabilities are very sensitive to the microstructure and surface condition of the electrode material. Therefore, a comparison of electrochemical properties for these electrodes with different microstructure and surface morphology is interesting and useful to provide better understanding of the electrode characteristics of a rechargeable lithium microbattery.

Figure 5 shows the anodic (deintercalation) and cathodic (intercalation) peak potential variation of each electrode as a function of scan rate and film thickness, respectively. The peak potentials of the films deposited on the alumina substrate are always higher upon anodic scan and lower upon cathodic scan than those of the film deposited on the Si substrate for the same thickness at all investigated scan rates. This result implies that films deposited on the alumina substrate have a larger resistance to ionic transport than films on the Si substrate. In this study, although an exact and detailed investigation in the microstructural differences between these two electrodes was not completed, similar charge-discharge potential curves at low currents (up to 50 $\mu$A/cm$^2$) for these two types of films were observed. Therefore, we believe that the wide divergence of peak potential for the electrodes deposited on the alumina substrate can be attributed to the large particle size.

Figure 6 shows the rate capability of these two films for various discharge current densities. The rate capability for films on the Si substrate was better than that of films on the alumina substrate. At a low discharge rate up to 50 $\mu$A/cm$^2$, all films sustained about 90% of the discharge capacity at 10 $\mu$A/cm$^2$. However, the films on the alumina substrate showed a very steep capacity decrease above 100 $\mu$A/cm$^2$, whereas films on the Si substrate retained 90% at such a high discharge rate. These phenomena are likely due to the difference in the surface area related to the particle size of these two films and the electronic resistance of the current collectors deposited on these two substrates. The small particle size increases the specific surface area resulted in an improved intercalation kinetics and lowered actual current densities. The electronic resistances of Pt current collectors on these two substrates were measured by an accurate ohmmeter and are listed in Table II. The high resistance of the current collector deposited on the alumina substrate could be caused by the microscopic variability of thickness as observed by SEM (not shown here). Consequently, the rate capability of films deposited on the smooth Si substrate is better than that of films deposited on the
rough alumina substrate, especially at high current density.

From these results, it should be recognized that the selection of an appropriate substrate is important for fabricating the thin film electrodes with high rate capability, especially considering the application of microbatteries to devices requiring a high pulse current such as a microsensor or a hazard card.

Table II. Electrical resistance of the Pt current collector measured by an ohmmeter.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Length x width (cm)</th>
<th>Resistance (Ω)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt on the alumina substrate</td>
<td>2.5 x 1</td>
<td>4.3</td>
</tr>
<tr>
<td>Pt on the Si substrate</td>
<td>2.5 x 1</td>
<td>2.4</td>
</tr>
</tbody>
</table>

* The length between two probes was 2.5 cm.

Conclusions

We investigated the substrate effect on the microstructure and electrochemical properties of thin-film LiCoO₂ electrodes. The surface morphology of a film deposited on an alumina substrate was rough and showed several cracks induced by the large linear thermal expansion coefficient of the alumina substrate. Annealed films on the Si substrate consisted of very small particles and exhibited no cracks. These microstructural differences gave films on the Si substrate improved electrochemical properties such as a rate capability compared to the alumina substrate case. Moreover, the electrical resistance of current collector deposited on the alumina substrate was about two times larger than that of current collector deposited on the Si substrate. Therefore, it was concluded that the choice of an appropriate substrate is very important for fabricating a thin-film electrode with high rate capability.

Acknowledgments

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References