

Surface Characterization of ZrO₂ Coated LiCoO₂ Thin Film During Storage

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Received May 13, 2011, Accepted June 14, 2011

Key Words : Cathode, Surface coating, Lithium battery, Thin film, SIMS

Surface modification by coating is one of the most effective methods for improving the electrochemical property of the cathodes of lithium-ion batteries. In previous studies, the surface of the cathode powder has been coated with stable oxides,¹⁻⁶ phosphates,⁷⁻¹⁰ and fluorides¹¹⁻¹³ to obtain enhanced cyclic performance, rate capability, and thermal stability. However the coating effect is highly dependent upon the control of interface reaction.¹⁴⁻¹⁶ Thus, careful characterization of the interface reaction among the cathode, coating layer, and electrolyte is essential to obtain an optimum surface coating. However, it has been difficult to characterize the interface reaction directly, because of the small particle size of the pristine powder, very low thickness of coating layer, and rough surface of positive electrode. To solve this problem, the thin film electrode was successfully introduced as a pristine cathode to investigate the interface reaction among the electrolyte, coating layer, and pristine cathode in detail.¹⁷ The surface of a thin film cathode is much wider and smoother than that of a bulk-type electrode, which may offer a good chance for a careful observation of the interface reaction of coating layer. In this work, the surface damage of a pristine and ZrO₂-coated LiCoO₂ thin film during storage was focused to confirm the coating effect. Specially, the damaged surface was directly observed by SEM and depth profile of elements was measured by SIMS before and after storage.

The ZrO₂ coating layer was confirmed in the previous work.¹⁷ The coating thickness was controlled through the concentration of the coating solution. The ZrO₂-coated LiCoO₂ films were prepared using 0.1 and 0.2 mol % coating solutions. The two coated samples obtained in this manner are hereafter called sample 1 (the sample fabricated using 0.1 mol % coating solution) and sample 2 (the sample fabricated using 0.2 mol % coating solution). Considering the concentration of the coating solution, sample 2 will have a thicker coating layer than sample 1. The pristine and coated samples showed similar discharge capacities and cyclic performances at 30 °C with a current density of 0.2 mA·cm⁻².¹⁷ To characterize the electrochemical properties of the samples under more chemically unstable conditions, the current density and measuring temperature were increased to 0.4 mA·cm⁻² and 45 °C, respectively. Under these measurement conditions, the effect of coating on the electrochemical property of the samples was clearly observed. As shown in Figure 1, the initial discharge capacities of the pristine and

sample 2 (with a relatively thick coating layer) were similar. However, the discharge capacity of sample 1 was significantly higher (~250 mAh·cm⁻²) than that of the pristine sample (<200 mAh·cm⁻²). Moreover, the cyclic performance of cathodes was noticeably enhanced after surface coating. The discharge capacity of the pristine film rapidly dropped during cycling at 45 °C. However, the coated sample still maintained a stable cyclic performance under the same measurement conditions. Enhancement in the discharge capacity and cyclic performance owing to surface coating has been previously reported.³⁻⁷ The electrolyte produces acid on reacting with the moisture from the air, and attacks the surface of the cathode, which leads to deterioration of electrochemical properties of the cathode. However, when the surface of the cathode is coated with a stable material, the coating layer may protect the surface from the attack of acidic electrolyte. So, it can reduce the 'damage' of cathode and improve discharge capacity and cyclic performance.

To observe the effect of coating on the suppression of surface damage of the cathode, the samples (cycled under the condition described in Fig. 1) were charged to 4.25 V and stored at a constant temperature of 90 °C for 1 week. During the storage period, in the charged state at high temperature, chemical reactions between the electrolyte and the surfaces will become more activated; therefore, the surface of the cathode film will be seriously damaged. Figure 2 shows the SEM images of the pristine and coated

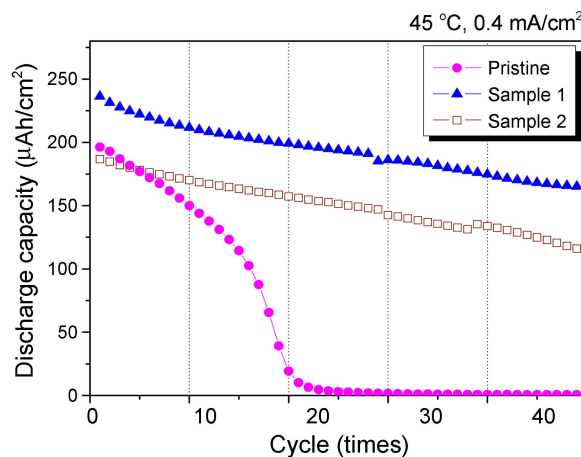


Figure 1. Discharge capacities and cyclic performances of pristine and ZrO₂ coated LiCoO₂ films at a current density of 0.4 mA·cm⁻² (45 °C).

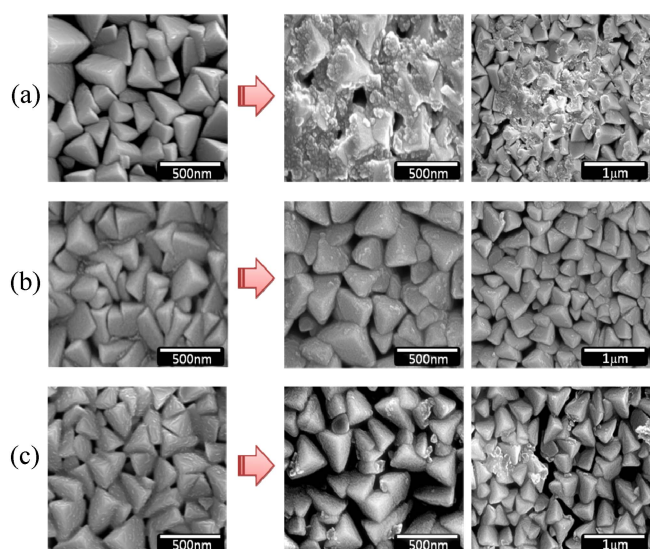


Figure 2. SEM images of pristine and ZrO_2 -coated LiCoO_2 thin films before and after storage (90°C , 1 week): (a) pristine, (b) sample 1, and (c) sample 2.

films before and after storage. As expected, the surface of the pristine film was significantly damaged during storage. The pristine film surface showed clear crystal faces and edges before storage. However, after storage, some grains partly collapsed and small particles appeared on the surface of the film (Fig. 2(a)). As shown on left side of Figure 2(b)

and 2(c), the surface images of the coated samples were similar to those of the pristine sample before storage. However, the relatively rough surface grains reveal the existence of ZrO_2 coating layer. It is noticeable that the surface grains of the coated samples were intact during storage, in contrast to the pristine sample, which indicates that the coating layer successfully protected the LiCoO_2 film from the attack of the acidic electrolyte during storage. Since the coating method was introduced, a lot of reports have been published about it. However, it has been very difficult to directly investigate the interface layer between the cathode and electrolyte by SEM, because the size of the cathode powder (having a circular shape) is of the order of several micrometers and the thickness of the coating layer on the surface of the powder is 10–100 nm. Some researchers have characterized the coating interface layer using transmission electron microscopy (TEM)⁶; however, it could offer only limited information because TEM experiments involve preparation of the sample, which can destroy or modify the interface. In this study, we could directly confirm the coating's effect of suppression of the surface damage by SEM by introducing thin film electrode. This work serves as a valuable support to the role of the coating layer.

To obtain more information about the interface reaction between the electrode and electrolyte, the concentration profile vs. depth of the electrode was investigated by secondary ion mass spectrometry (SIMS). Figure 3 shows the depth

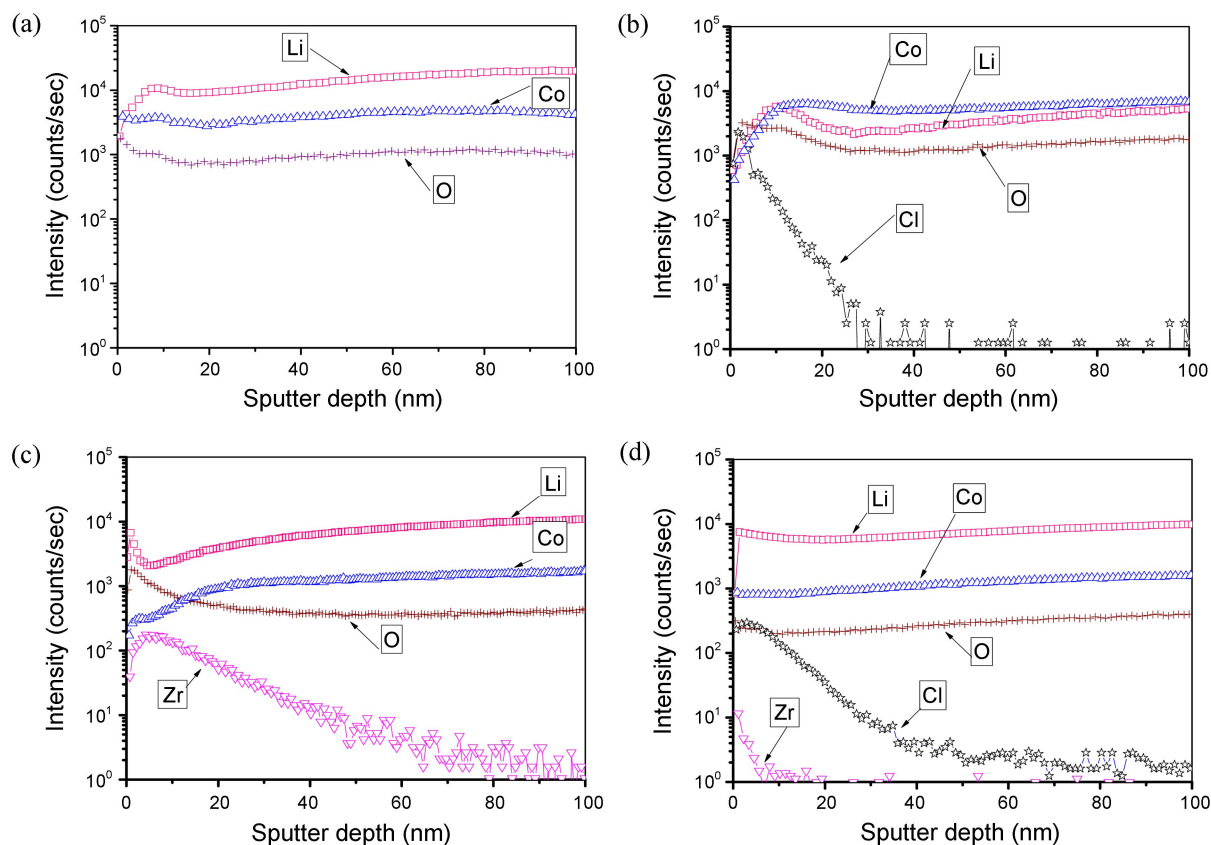


Figure 3. Depth profiles of pristine and ZrO_2 -coated LiCoO_2 thin film electrodes (sample 2) from constituent elements: (a) pristine sample before storage; (b) pristine sample after storage; (c) sample 2 before storage; and (d) sample 2 after storage.

profiles of the Co-containing ion ($^{133}\text{Cs}^{59}\text{Co}^+$), O-containing ion ($^{133}\text{Cs}^{16}\text{O}^+$), Li-containing ion ($^{133}\text{Cs}^7\text{Li}^+$), Zr-containing ion ($^{133}\text{Cs}^{90}\text{Zr}^+$), and Cl-containing ion ($^{133}\text{Cs}^{35}\text{Cl}^+$) recorded for the pristine and coated samples. Sample 2, with a relatively thick coating layer, was used as the coated sample for easier detection of Zr concentration. The intensity has been reported using a logarithmic scale in order to magnify the low-intensity signals. The pristine sample consisted of a homogeneous concentration of Li, Co, and O, except a little deviation in surface, before the electrochemical test (Fig. 3(a)). The coated sample clearly shows a 60~80-nm-thick ZrO_2 coating layer before the electrochemical test (Fig. 3(c)). Figures 3(b) and 3(d) present the depth profiles of the pristine and coated samples after the cycling and storage processes described above. In the profiles, it is confirmed that Co was dissolved on the surface of the pristine sample (Fig. 3(b)). However, in the coated film, the depth concentration of Co was very homogeneous (Fig. 3(d)). It is interesting to note that Zr almost vanished during cycling and storage. This indicates that the 60-70 nm thick ZrO_2 layer was destroyed by the acidic electrolyte during cycling and storage at high temperature. Instead, the active material (LiCoO_2) was successfully protected from any reaction with the electrolyte. This result explains the protective effect of the coating layer, which leads to the enhancement of the electrochemical property of the coated electrode.

In summary, we report the surface characterization of pristine and ZrO_2 coated LiCoO_2 thin film during storage. The coated sample maintained the smooth and clean surface even after storage at 90 °C for 1 week. However, the surface of pristine sample was significantly damaged after storage. The depth profiles measured by SIMS show that the ZrO_2 coating layer was sacrificed and almost destroyed by the reaction with the acidic electrolyte; however, the active material (LiCoO_2) was successfully protected from the attack of the acidic electrolyte. This result successfully explains the protective effect of the coating layer.

Experimental Section

The pristine LiCoO_2 thin film was supplied by GS Nano-Tech Co. To prepare the ZrO_2 coating solution, zirconium (IV) butoxide ($\text{Zr}[\text{O}(\text{CH}_2)_3\text{CH}_3]_4$) (Aldrich Co.) was dissolved in 20 mL of a mixed solvent consisting of distilled water, 1-butanol, and acetic acid. Then, the solution was stirred continuously for 1 h at 25 °C, after which it was coated onto the LiCoO_2 thin film substrate using a spin coater. The coated LiCoO_2 thin films were heat-treated in a rapid thermal annealing (RTA) system at 400 °C for 30 min. The microstructures of the films were observed by field emission

scanning electron microscopy (FE-SEM; JEOL-JSM 6500F). The electrochemical characterization of the coated LiCoO_2 films was performed in the non-aqueous half-cells. Li-foil electrode was used as a reference electrode. The electrolyte used was 1 M LiClO_4 in PC. The cells were subjected to galvanostatic cycling using a WonAtech system. Secondary ion mass spectrometry (SIMS) analysis was used to characterize the coated and the pristine films and obtain the constituent element information. These characterization measurements were performed using a CAMECA IMS-6f (Magnetic Sector SIMS) at the Korea Basic Science Institute (Busan center). A Cs^+ primary ion beam with beam energy of 5.0 kV was used. The beam current was 30 nA and the raster size was $200\ \mu\text{m} \times 200\ \mu\text{m}$.

Acknowledgments. This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (2009-0071073).

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