

# Suppression of interface reaction of LiCoO<sub>2</sub> thin films by Al<sub>2</sub>O<sub>3</sub>-coating

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**Abstract** Al<sub>2</sub>O<sub>3</sub>-coated LiCoO<sub>2</sub> thin films were prepared to characterize the effects of coating in detail. The LiCoO<sub>2</sub> film electrodes served as effective pristine cathodes to investigate the interface reaction between a cathode and electrolyte because they have wide and smooth surface and do not contain conducting agents (such as carbon) or binders. The electrochemical properties, surface morphology, and concentration profile (vs. depth) were characterized to identify the effects of coating. The Al<sub>2</sub>O<sub>3</sub>-coated film showed a much improved rate capability and cyclic performance compared with those of the pristine film. Specifically, based on the results of SIMS analyses and SEM images, dissolution of transition-metal ions and surface damage during storage at high temperature were suppressed by Al<sub>2</sub>O<sub>3</sub> coating. This result directly shows the successful protective effect of surface coating, which is associated with enhanced electrochemical properties of the coated film.

**Keywords** Cathode · Surface coating · Lithium battery · Thin film

## 1 Introduction

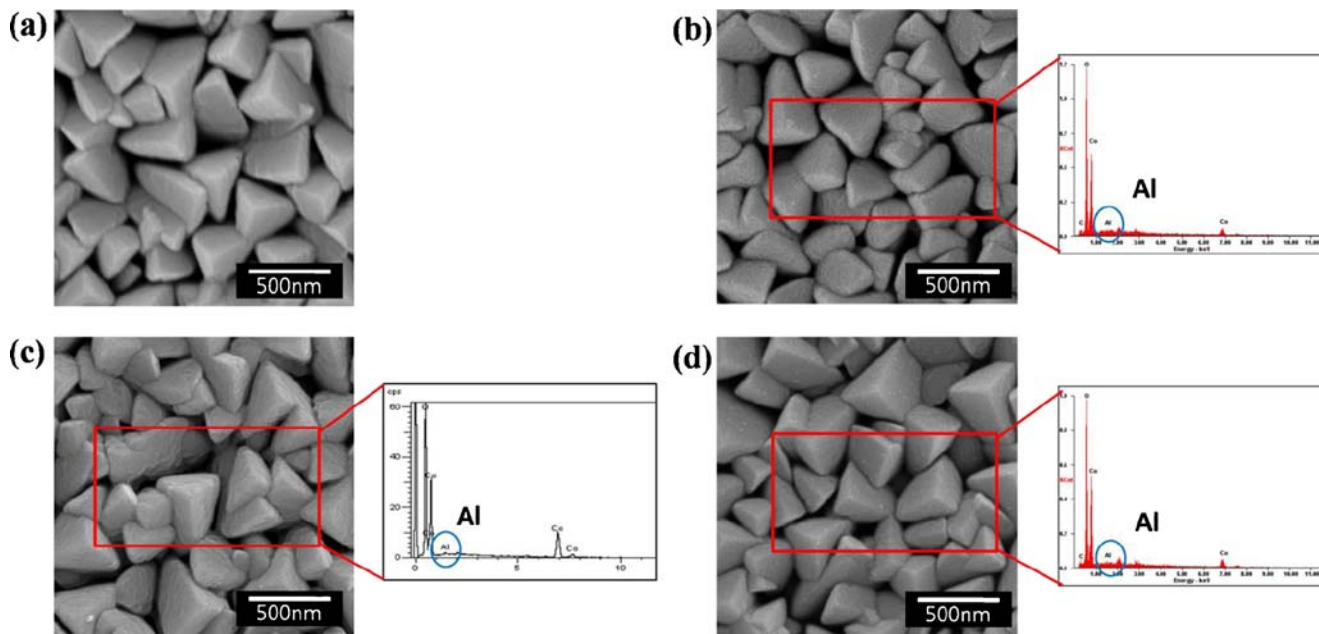
Since Sony commercialized rechargeable lithium batteries, they have played a significant role in our lives. Nowadays, lithium ion batteries have become the dominant power source for applications ranging from portable electronics to hybrid electric vehicles [1–8]. Among the several

components of lithium ion batteries, the cathode has a key role in determining the capacity, cycle life, and rate capability of the cell. Therefore, various research studies have attempted to improve the electrochemical properties of a cathode [9–13].

Surface modification by coating with stable materials is one effective approach to enhance the electrochemical properties of a cathode. The interface reaction between the cathode and electrolyte plays a very important role in determining the electrochemical properties of lithium ion batteries. The reactive electrolyte leads to surface damage of the cathode during the charge–discharge process, which may deteriorate the structural stability of the cathode and decrease the capacity and cyclic performance of the cell. Coating with oxides [14–18], phosphates [19–23], or fluorides [24–27] has successfully suppressed these interface reactions and enhanced the electrochemical properties of the cathode. 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 the coating layer, and rough surface of the positive electrode.

Herein, a LiCoO<sub>2</sub> thin film was applied as a pristine cathode to investigate the interface reaction between the cathode and electrolyte in detail. The surface of a thin film cathode is much wider and smoother than that of a bulk-type electrode, which offers a good chance for careful observation of the interface reaction of the coating layer. Moreover, thin film cathodes do not contain carbon or binders; therefore, the pure interface layer between the coating material and pristine cathode can be easily characterized using surface-concentration analysis tools. Al<sub>2</sub>O<sub>3</sub>, a typical stable oxide, was adopted as a coating material for the surface modification of the LiCoO<sub>2</sub> film. This study focused on the interface reaction between the Al<sub>2</sub>O<sub>3</sub>-coated LiCoO<sub>2</sub> thin film and electrolyte. Specifically, the surface

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**Fig. 1** SEM images of LiCoO<sub>2</sub> thin films. (a) Pristine, (b) Al<sub>2</sub>O<sub>3</sub>-coated (using 0.05 M solution), (c) Al<sub>2</sub>O<sub>3</sub>-coated (using 0.1 M solution), (d) Al<sub>2</sub>O<sub>3</sub>-coated (using 0.2 M solution). (The right sides of b–d present EDS analyses of the surface of the given sample)

morphology and depth profile of the elements before and after cycling (and storage) were characterized in detail.

## 2 Experimental

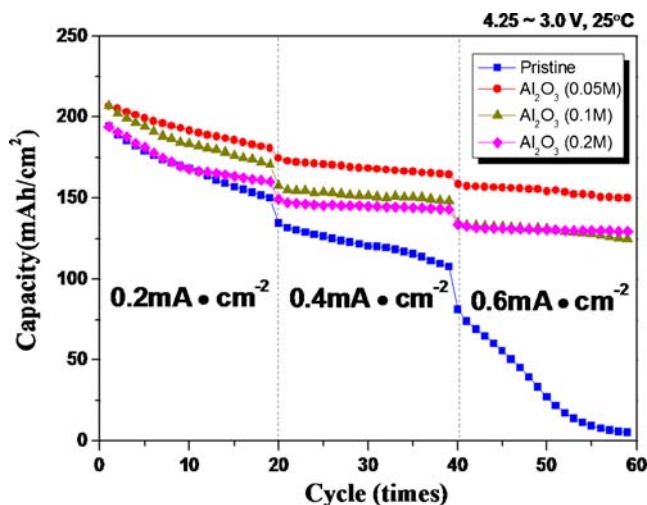
The pristine LiCoO<sub>2</sub> thin film was supplied by GS Nano-Tech Co. The thickness of the LiCoO<sub>2</sub> film was ~4 μm. To prepare the coating solution, aluminum nitrate nonahydrate [Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, Aldrich] was dissolved in 10 mL of a mixed solvent consisting of distilled water, 1-butanol, and acetic acid. The solution was stirred continuously for 1 h at 25°C, after which it was coated onto a LiCoO<sub>2</sub> thin film substrate using a spin coater (K-359 model S-1, supplied by Kyowariken). The coated LiCoO<sub>2</sub> thin films were heat-treated in a rapid thermal annealing (RTA) system at 400°C for 30 min. A pristine LiCoO<sub>2</sub> thin film was also heat-treated at 400°C for 30 min to compare its properties under the same fabrication conditions. The microstructures of the films were observed by field emission scanning electron microscopy (FE-SEM; JEOL-JSM 6500F).

Electrochemical characterization of the coated LiCoO<sub>2</sub> films was performed in nonaqueous half-cells. The active area of each film used for the electrochemical test was about 1 cm×1 cm. Li foil was used as the counter electrode. The electrolyte was 1 M LiClO<sub>4</sub> in propylene carbonate (PC). The cells were subjected to galvanostatic cycling using a WonATech system. Secondary ion mass spectrometry (SIMS) analysis was used to characterize both coated and pristine films to 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<sup>+</sup> primary ion beam with an energy of 5.0 kV was used. The beam current was 30 nA and the raster size was 200 μm×200 μm.

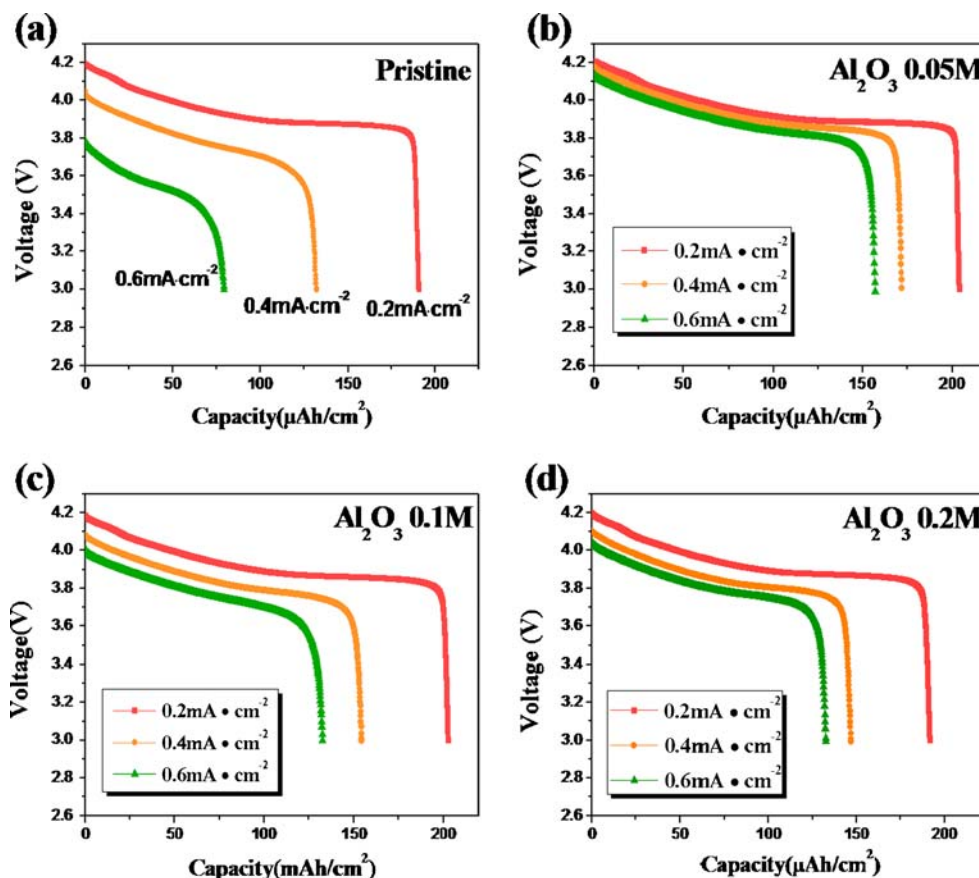
## 3 Results and discussion

The vulnerable surface of the cathode may be protected by surface coating using stable materials such as oxides.



**Fig. 2** Discharge capacities and cyclic performances of pristine and Al<sub>2</sub>O<sub>3</sub>-coated LiCoO<sub>2</sub> thin films in the voltage range of 3.0–4.25 V at current densities of 0.2, 0.4, and 0.6 mA·cm<sup>-2</sup>

**Fig. 3** The first voltage profiles of the LiCoO<sub>2</sub> films at current densities of 0.2, 0.4, and 0.6 mA·cm<sup>-2</sup> as a function of the capacity (the first cycle shown in Fig. 2 at each current density). (a) Pristine, (b) Al<sub>2</sub>O<sub>3</sub>-coated using 0.05 M solution, (c) Al<sub>2</sub>O<sub>3</sub>-coated using 0.1 M solution, (d) Al<sub>2</sub>O<sub>3</sub>-coated using 0.2 M solution



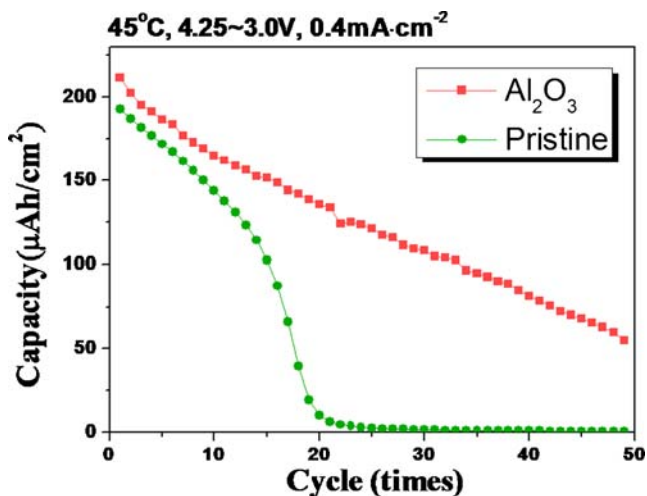
However, the coating materials themselves are basically non-conductive, so a thick surface coating could limit the diffusion of lithium ions and electrons. Thus, the thickness of the coating layer is an important factor in determining its effects. In this work, the concentration of the coating solution was adapted as a tool for controlling coating thickness. In this manner, three coated LiCoO<sub>2</sub> films were prepared using 0.05, 0.1, and 0.2 M coating solutions. Figure 1 presents scanning electron microscope (SEM) images of the pristine and Al<sub>2</sub>O<sub>3</sub>-coated LiCoO<sub>2</sub> thin films. The surface of each film consisted of small polyhedral grains that were about 200–500 nm in size. The crystal faces and edges of the grains were smooth and did not contain any heterophase particles. As shown in Fig. 1(b–d), the coating layers of the coated films were not clearly observable in the SEM images, which may be due to the thinness of the coating.

However, the existence of Al on the surface of the coated film was confirmed using energy-dispersive X-ray spectroscopy (EDS) analysis, which implied that the Al<sub>2</sub>O<sub>3</sub> coating layer was successfully formed on the surface of the LiCoO<sub>2</sub> film.

The electrochemical properties of the pristine and coated LiCoO<sub>2</sub> thin films were characterized to identify the effects of coating on the rate capacity and cyclic performance. Figure 2 shows the discharge capacities of the pristine and Al<sub>2</sub>O<sub>3</sub>-coated LiCoO<sub>2</sub> thin films in the voltage range of 3.0–4.25 V. The current density increased from 0.2 to 0.4 and 0.6 mA·cm<sup>-2</sup>, which are converted ~1 C, 2 C, and 3 C rates, respectively, considering the average capacity of a LiCoO<sub>2</sub> thin film is ~50 μAh·cm<sup>-2</sup>·μm<sup>-1</sup>. The cell was cycled 20 times at a given current density and then increased to a higher current density. As shown in Fig. 2, the films coated

**Table 1** Discharge capacities and capacity retention values of pristine and coated LiCoO<sub>2</sub> thin films at various current densities (values of initial cycle at respective current densities). Percentages refer to capacity retention compared with the discharge capacity at a 0.2 mA·cm<sup>-2</sup>

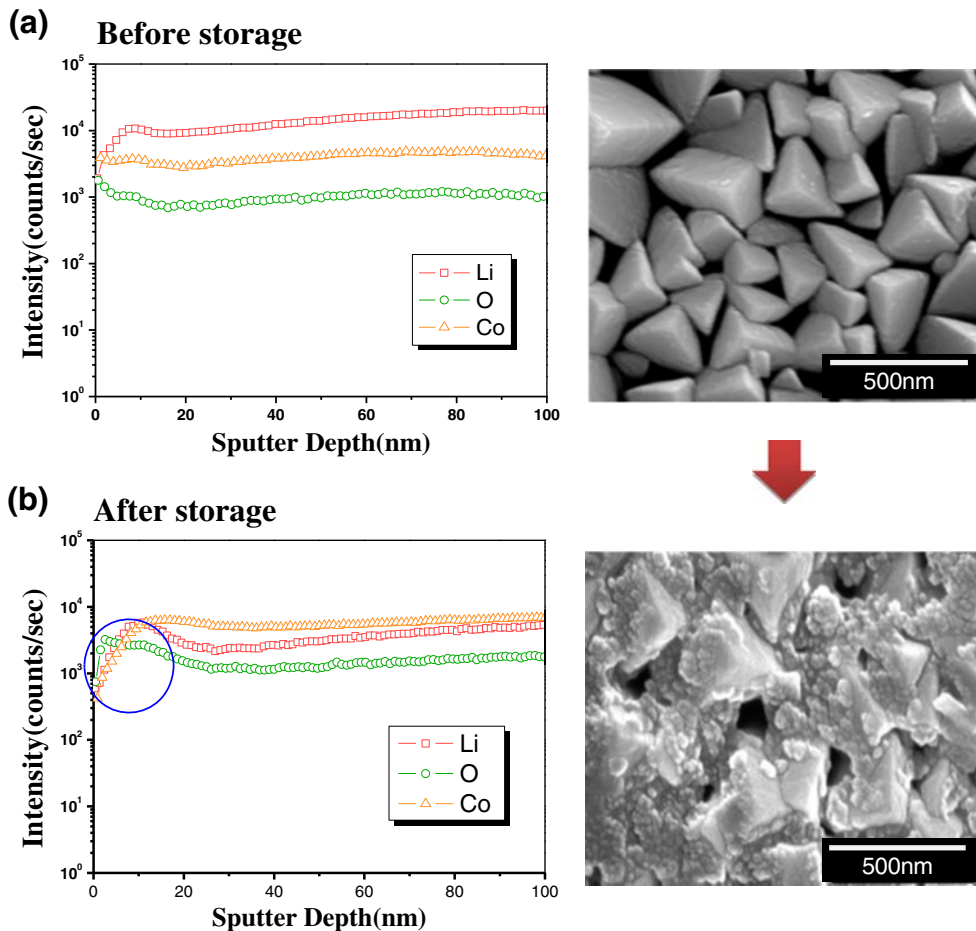
	(a) Pristine (μAh·cm <sup>-2</sup> )	(%)	(b) 0.05M Al <sub>2</sub> O <sub>3</sub> -coated (μAh·cm <sup>-2</sup> )	(%)	(c) 0.1M Al <sub>2</sub> O <sub>3</sub> -coated (μAh·cm <sup>-2</sup> )	(%)	(d) 0.2M Al <sub>2</sub> O <sub>3</sub> -coated (μAh·cm <sup>-2</sup> )	(%)
0.2mA·cm <sup>-2</sup>	190.71	100	204.1	100	202.83	100	191.79	100
0.4mA·cm <sup>-2</sup>	132.31	69.38	171.8	84.17	154.35	76.1	146.88	76.58
0.6mA·cm <sup>-2</sup>	79.463	41.67	156.89	76.87	132.84	65.49	132.5	69.13



**Fig. 4** Cyclic performances of pristine and  $\text{Al}_2\text{O}_3$ -coated  $\text{LiCoO}_2$  thin films in the voltage range of 3.0–4.25 V at a current density of  $0.4 \text{ mA}\cdot\text{cm}^{-2}$  ( $45^\circ\text{C}$ ). The coated film was prepared using the 0.1 M coating solution

using 0.05 and 0.1 M coating solutions presented slightly higher discharge capacities at the initial cyclings. Theoretically, the  $\text{Al}_2\text{O}_3$  layer does not participate in the lithium intercalation–deintercalation process; therefore, a coating on the surface may decrease the theoretical capacity of the cath-

**Fig. 5** Depth profile of constituent elements measured by SIMS and SEM surface image of the pristine  $\text{LiCoO}_2$  film. (a) Before storage; (b) after storage



ode. However, it should be considered that measurement of the capacity was limited by various hindrances, such as an unwanted interface layer formed by reaction between the cathode and electrolyte. Although the  $\text{Al}_2\text{O}_3$  coating layer cannot intercalate lithium ions, it may protect the surface of the cathode from the reactive electrolyte and suppress the formation of an unwanted interface layer. This may facilitate lithium diffusion and increase the measured discharge capacity. In contrast, the film coated using 0.2 M coating solution showed a similar discharge capacity to the pristine film. As the coating layer thickness increases, it may act as an obstacle to electron conduction and intercalation and deintercalation of lithium. An overly thick coating layer may also deteriorate the discharge capacity of the cathode.

As the current density increased, the discharge capacity of the pristine film significantly decreased. Specifically, the cyclic performance decreased rapidly under high current density conditions. The film electrodes do not contain conducting agents, such as carbon, so their electrochemical properties could significantly deteriorate at fast charge–discharge conditions. However, surprisingly, the  $\text{Al}_2\text{O}_3$  surface coating increased the discharge capacity and stabilized the cyclic performance of the  $\text{LiCoO}_2$  thin film at high current densities, as shown in Fig. 2. Figure 3 presents the initial voltage profile

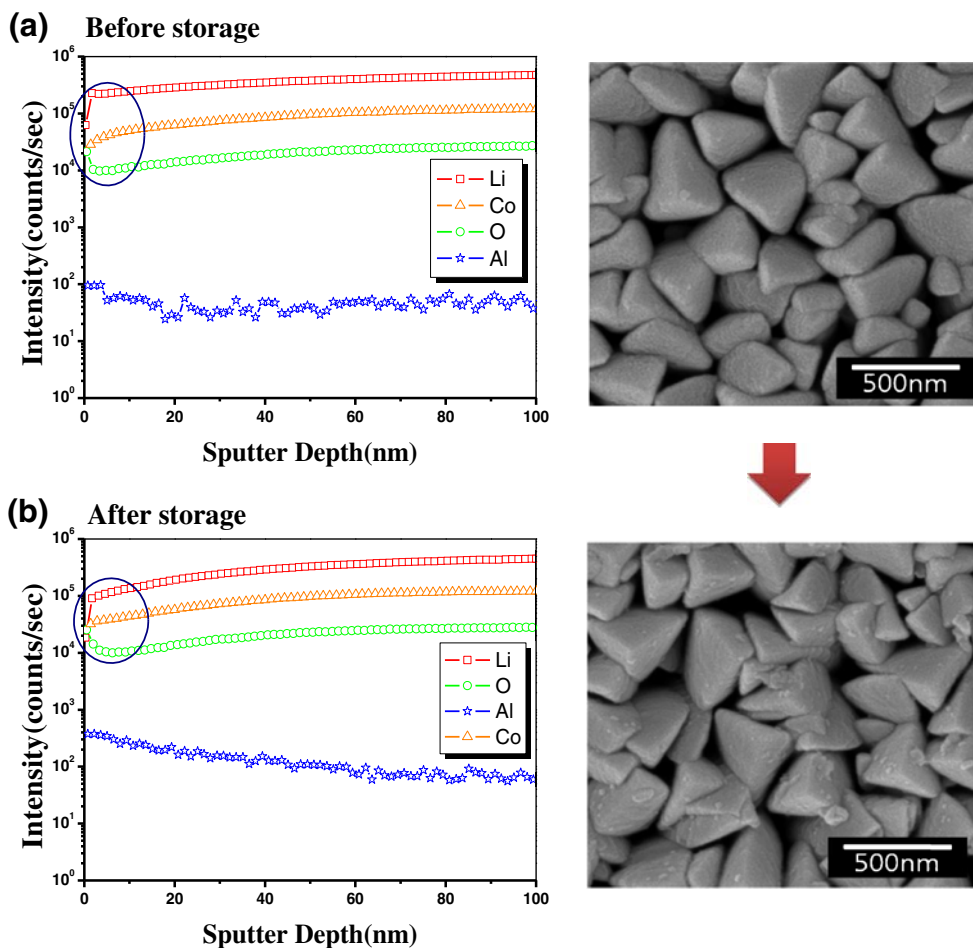
of the pristine and Al<sub>2</sub>O<sub>3</sub>-coated films at current densities of 0.2, 0.4, and 0.6 mA·cm<sup>-2</sup> as a function of the capacity (the first cycle seen in Fig. 2 at each current density). The pristine film showed a capacity retention of ~42 % at a current density of 0.6 mA·cm<sup>-2</sup> (relative to its capacity at a current density of 0.2 mA·cm<sup>-2</sup>). In contrast, the capacity retentions of the coated samples were ~77 % (0.05 M coating solution), ~65 % (0.1 M coating solution), and ~69 % (0.2 M coating solution). This clearly demonstrates that the rate capability of the film was improved by Al<sub>2</sub>O<sub>3</sub> coating. Table 1 summarizes the discharge capacity and capacity retention values at various current densities (the values of the initial cycles at the respective current densities).

To investigate the effect of coating under severe conditions, the pristine and coated films were cycled at high temperature (45°C). The high temperature promotes chemical reactions between the electrolyte and the electrode surfaces; thus, it is expected that the electrode will undergo significant damage. As anticipated, the discharge capacity of the pristine film rapidly dropped to almost zero during 20 cycles, as shown in Fig. 4. The cyclic performance of the Al<sub>2</sub>O<sub>3</sub>-coated film (using 0.1 M coating solution) also deteriorated at high temperature; however, the coated films showed considerably enhanced cyclic performance compared to that of the pristine film.

The improvement by Al<sub>2</sub>O<sub>3</sub> surface coating of properties such as rate capability and cyclic stability at high temperature may be attributed to the protective effect of the coating layer against the reactive electrolyte. Generally, the electrolyte contains a small amount of water, so acid is produced by the interaction of salts (such as LiClO<sub>4</sub> and LiPF<sub>6</sub>) and water. The acidic electrolyte attacks the surface of the cathode during cycling. This leads to dissolution of transition metals such as Co and forms an unwanted interface layer, which deteriorate the structural stability and electrochemical properties of the cathode. However, the coating material could serve as a protective layer that prevents direct contact with the reactive electrolyte. This may suppress dissolution of the transition metal and formation of the unwanted interface layer, which leads to the enhancement of the electrochemical properties.

In order to characterize the interface reaction between the LiCoO<sub>2</sub> thin film and electrolyte, secondary ion mass spectrometry (SIMS) analysis was performed. The pristine and coated samples (using 0.1 M solution) were charged to 4.25 V and stored at 90°C for 1 week to accelerate the surface reaction between the cathode and electrolyte. The concentration profiles (vs. depth) of the pristine and coated films were then measured by SIMS. The amounts of Co-

**Fig. 6** Depth profile of constituent elements and SEM surface image of the Al<sub>2</sub>O<sub>3</sub>-coated LiCoO<sub>2</sub> film (using 0.1 M solution). (a) Before storage; (b) after storage. The coated film was prepared using the 0.1 M coating solution



containing ion ( $^{133}\text{Cs}^{59}\text{Co}^+$ ), O-containing ion ( $^{133}\text{Cs}^{16}\text{O}^+$ ), Li-containing ion ( $^{133}\text{Cs}^7\text{Li}^+$ ), and Al-containing ion ( $^{133}\text{Cs}^{27}\text{Al}^+$ ) were recorded for the pristine and coated samples. Figure 5 shows the concentration profile of the pristine film. Except for a slight deviation at the surface, the concentrations of Li, Co, and O were almost homogeneous within the measured depth before the storage test. However, after the storage test, the Co concentration near the surface significantly decreased, as shown in Fig. 5(b). This indicates that the transition metal (Co) of  $\text{LiCoO}_2$  was considerably dissolved by the electrolyte, so an unwanted interface layer was formed at the surface of the cathode during the storage process. The SEM images on the right side of Fig. 5 also clearly show that the surface was seriously damaged during high temperature storage. The clean and clear polyhedral grains of the pristine film were dramatically changed after storage, and the surface of the  $\text{LiCoO}_2$  film was almost completely covered with a rough layer, which may have been formed by reaction with the acidic electrolyte. This reflects the damage of the surface during storage.

In contrast, the concentration profile and SEM images of the  $\text{Al}_2\text{O}_3$ -coated film (using 0.1 M solution) after storage distinctly demonstrated the protective effect of the coating layer, as shown in Fig. 6. The  $\text{Al}_2\text{O}_3$  coating layer was not clearly presented in the profile due to a high background intensity of Al-containing ions. However, it is notable that the Co concentration of the coated film was stably maintained during the storage process. In addition, as shown on the right side of Fig. 6(b), the surface morphology of the coated film remained relatively clear after storage, without a heterogeneous layer or damaged grains. The SIMS data and surface images before and after storage directly confirm that the  $\text{Al}_2\text{O}_3$  coating layer successfully served as protection from the reactive electrolyte. Consequently, the dissolution of Co ion by the electrolyte, the formation of the unwanted layer at the interface, and the serious damage to the cathode surface were effectively prevented by the coating layer, which may enhance the electrochemical properties of the  $\text{LiCoO}_2$  film electrode.

#### 4 Conclusions

As a new approach, a  $\text{LiCoO}_2$  thin film was introduced as a pristine cathode to characterize the effects of surface coating more efficiently.  $\text{Al}_2\text{O}_3$ , a typical stable oxide, was coated onto the  $\text{LiCoO}_2$  thin film. The cyclic performance, rate capability, and stability during storage of the  $\text{LiCoO}_2$  thin film were significantly improved by  $\text{Al}_2\text{O}_3$  surface coating. The protective effect of the coating material was directly identified from the concentration profile (vs. depth) measured by SIMS. The transition metal (Co) component of the pristine  $\text{LiCoO}_2$  film was considerably dissolved during

storage at high temperature ( $90^\circ\text{C}$ ). However, the coated film maintained a stable Co concentration after storage, which clearly reflects that the Co dissolution was successfully suppressed by the  $\text{Al}_2\text{O}_3$  coating layer. SEM images of the surface also confirm that the surface damage to the film electrode was significantly decreased by  $\text{Al}_2\text{O}_3$  coating. This result shows that the enhanced electrochemical properties of the coated electrode can be attributed to effective protection by the coating layer.

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