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# **EXHIBIT A**



# Interface characterization of MgF<sub>2</sub>-coated LiCoO<sub>2</sub> thin films

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## Abstract

The electrochemical properties and interface reactions of pristine and coated LiCoO<sub>2</sub> films were characterized. MgF<sub>2</sub> was used as a new coating material to improve the electrochemical properties of the LiCoO<sub>2</sub> film electrode. To directly observe the interface reaction between the surface of the cathode and the electrolyte, a film electrode with a wide, flat surface was introduced in this study. The rate capability, cyclic performance, and stability at high temperature of the LiCoO<sub>2</sub> thin film were improved by MgF<sub>2</sub> coating. The concentration–depth profile and surface image of the LiCoO<sub>2</sub> film were investigated by SEM and XPS analyses before and after cycling. Pristine film showed significant Co dissolution and surface damage on cycling at high temperature (45 °C). However, both were efficiently depressed by the introduction of the MgF<sub>2</sub> coating. These results confirm that the MgF<sub>2</sub> coating layer successfully protected the surface of the cathode from the reactive electrolyte, leading to enhanced electrochemical properties for MgF<sub>2</sub>-coated LiCoO<sub>2</sub> films.

## Highlights

- The electrochemical properties and interface reactions of pristine and MgF<sub>2</sub>-coated LiCoO<sub>2</sub> films were characterized.
- MgF<sub>2</sub> coating layer successfully protected the surface of the cathode from the reactive electrolyte.
- This leads enhanced electrochemical properties for MgF<sub>2</sub>-coated LiCoO<sub>2</sub> films.



## Keywords

Surface coating; Electrochemical properties; Cathode; Lithium battery; Interface

## 1. Introduction

Lithium ion battery technology has developed rapidly as a result of the advances in and demand for electronic devices, electric vehicles, and energy storage devices [1], [2], [3], [4], [5]. The cathode is one of the key components in a lithium ion battery, affecting the discharge capacity, cyclic performance, rate capability, and thermal stability of the cell. One approach for improving the electrochemical properties of a cathode is surface modification by coating with stable materials, such as oxides [6], [7], [8], [9], [10], phosphates [11], [12], [13], [14], [15], or fluorides [16], [17], [18], [19]. The interface between the cathode and electrolyte actively reacts during charge and discharge processes, which affects the electrochemical stability as well as the lithium ion exchange kinetics. The coating layer has been reported to stabilize the interface reaction and improve the electrochemical properties of the cathode. However, it has been difficult to characterize this interface reaction directly because of the small particle size of the pristine powder, the thinness of the coating layer, and the rough surface of the positive electrode. In this work, a LiCoO<sub>2</sub> thin film electrode was introduced as a pristine cathode, to investigate in detail the interface reaction between the electrolyte and the coating layer of the pristine cathode. The surface of a thin film cathode is much wider and smoother, which may offer opportunity for careful observation of the interface reaction between the cathode and electrolyte. As a new fluoride coating material, MgF<sub>2</sub> was introduced in this work. An inexpensive element, Mg has been used as a doping material to enhance the electrochemical properties of cathodes [20], [21]. Moreover, MgO has already been used as a coating material on LiCoO<sub>2</sub> to improve cyclic stability [22], [23]. In particular, our approach was inspired by the fact that other fluorides, such as AlF<sub>3</sub>, were very effective in modifying cathode surfaces [16], [17], [18], [19]. In this study, we investigated the interface reaction between a MgF<sub>2</sub>-coated thin-film cathode and electrolyte, and characterized the reason for enhanced properties as a result of surface coating.

## 2. Experimental

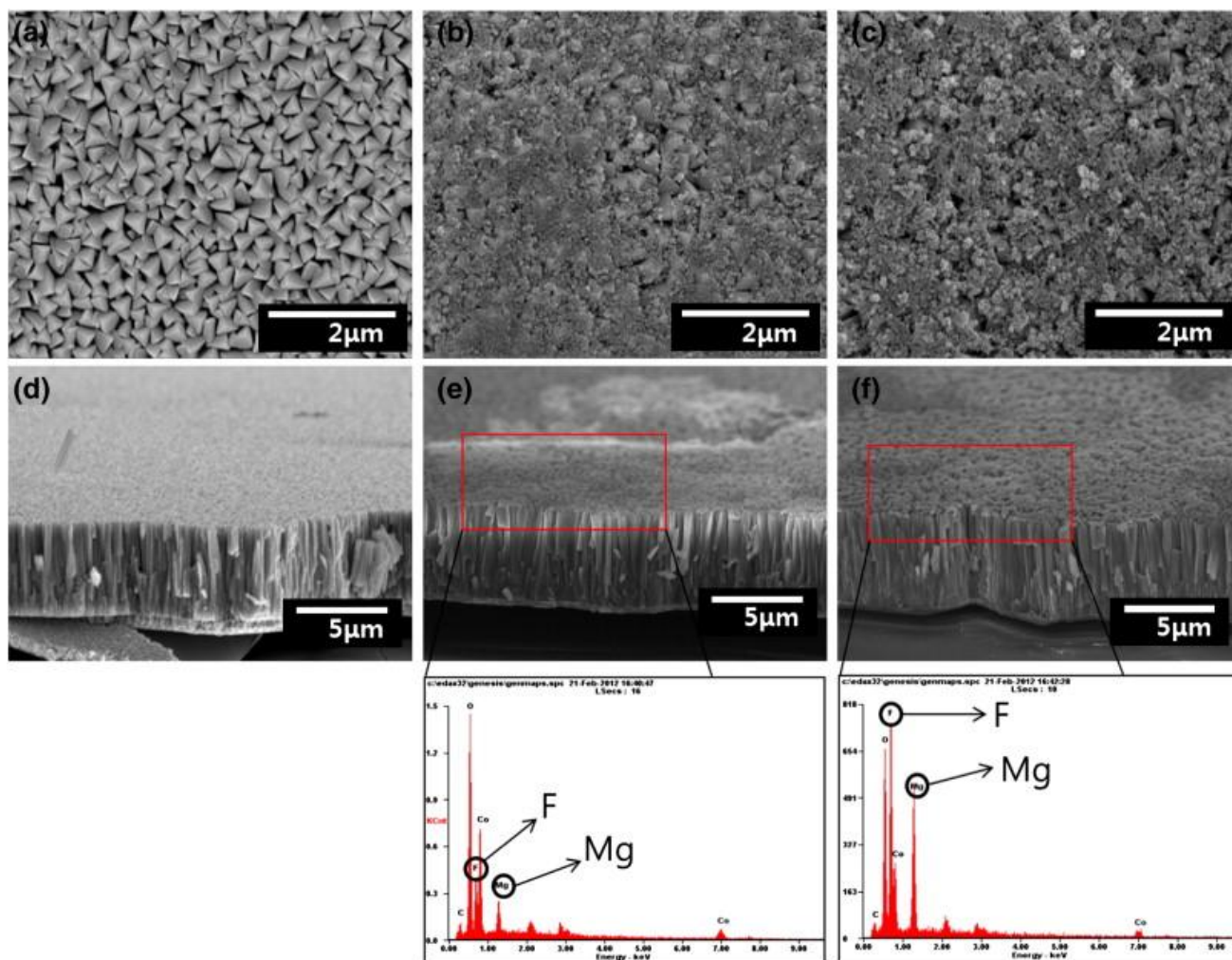
The pristine LiCoO<sub>2</sub> thin film, with a thickness of ~4 μm, was a commercial product from GS NanoTech Co. For the synthesis of the MgF<sub>2</sub> coating solution, magnesium nitrate hexahydrate [Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O], ammonium phosphate [(NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub>] (Aldrich, 99%), and ammonium fluoride [NH<sub>4</sub>F, Aldrich] were dissolved in 10 mL of a mixed solvent consisting of distilled water, 1-butanol, and acetic acid (wt. ratio of 1:2:2) with continuous stirring for 2 h at 25 °C. The effect of coating on the cathode electrochemical properties is significantly affected by the thickness of the coating material [24]. In this study, the concentration of the coating solution was adapted as a tool for controlling the thickness of the coating material: two MgF<sub>2</sub> coating solutions at 0.05 and 0.1 M were prepared. A solution was coated onto a LiCoO<sub>2</sub> thin film substrate using a spin-coater (K-359 model S-1, Kyowa Riken Co., Ltd.). The coated LiCoO<sub>2</sub> thin films were heat-treated in a rapid thermal annealing (RTA) system at 400 °C for 30 min. The pristine LiCoO<sub>2</sub> thin film was also heat-treated at 400 °C for 30 min before testing, to compare properties under the same fabrication conditions. The microstructures of the films were observed using field emission scanning electron microscopy (FE-SEM, Nova Nano 200).

The electrochemical characterizations of the coated LiCoO<sub>2</sub> films were performed in non-aqueous 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. X-ray photoelectron spectroscopy (XPS, PHI 5000 VersaProbe (Ulvac-PHI))

analysis was used to obtain depth-concentration profiles of the elements (Co, O, Mg, and F) for the samples, which may offer good information about the interface reaction between the cathode and electrolyte.

### 3. Results and discussion

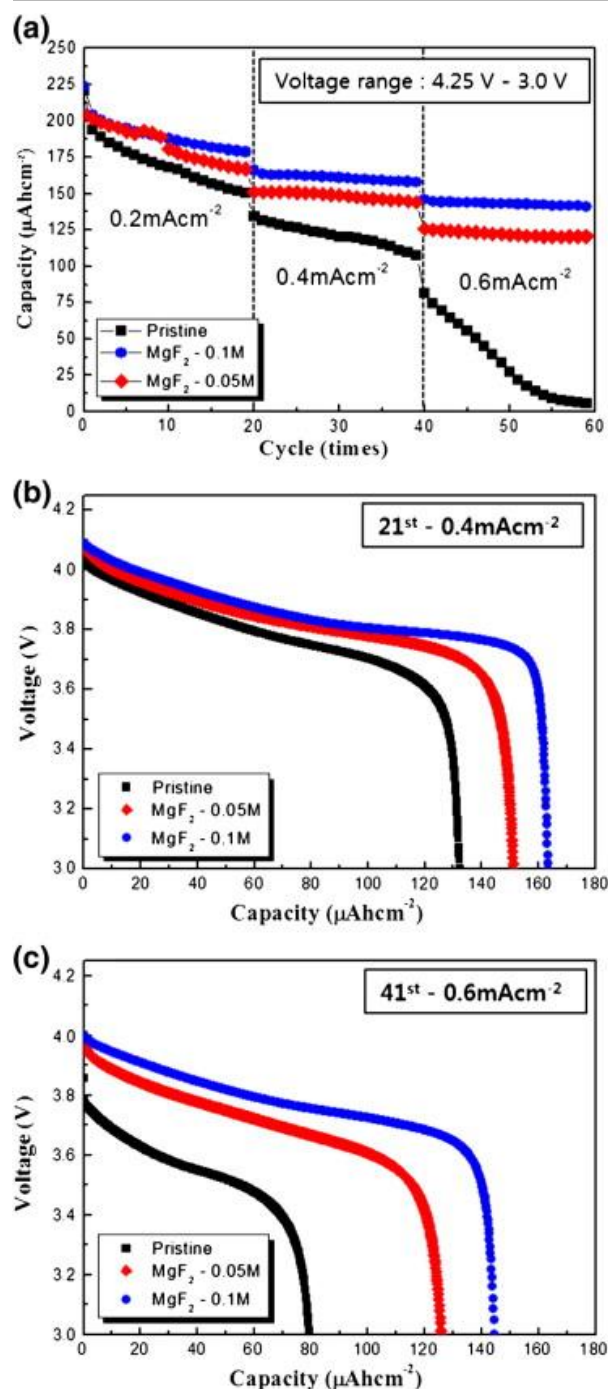
The surface morphologies of pristine and coated films were observed using SEM images. To obtain coating layers with different thicknesses, the concentration of the coating solution was controlled to 0.05 or 0.1 M. As shown in Fig. 1a, the pristine LiCoO<sub>2</sub> film exhibited a smooth and clean surface without any hetero-particles. In contrast, numerous nanosized particles appeared on the surface of the MgF<sub>2</sub>-coated film. In the cross-sectional image, the LiCoO<sub>2</sub> film seemed to have a columnar structure. The coating layer was also observed clearly in the cross-sectional images of the coated film. As shown below Fig. 1e and f, Mg and F elements were distinctly detected via energy-dispersive X-ray spectroscopy (EDS), which confirmed the formation of a MgF<sub>2</sub> coating layer on the surface of the LiCoO<sub>2</sub> pristine film. Notably, the coated film prepared from the 0.1 M coating solution exhibited larger EDS peaks indicative of Mg and F elements than the coated film prepared from the 0.05 M coating solution. This implies that the coated film prepared from the 0.1 M coating solution was thicker than that prepared from the 0.05 M solution, although it was difficult to exactly measure the thickness of the coating layer. Generally, the coating materials are likely to react with elements of the pristine cathode, such as Li and Co, because their small particle sizes lead to high surface free energy [15], [19]. Therefore, it was anticipated that the MgF<sub>2</sub> coating layer would react with the LiCoO<sub>2</sub> surface and form a coating layer with a new composition, consisting of Mg, F, Co, and Li.



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Fig. 1. SEM images of the pristine and coated LiCoO<sub>2</sub> thin film electrodes. (a) Surface of the pristine film; (b) surface of the MgF<sub>2</sub>-coated film using 0.05M coating solution; (c) surface of the MgF<sub>2</sub>-coated film using 0.1 M coating solution; (d) cross-sectional image of the pristine film; (e) cross-sectional image of the MgF<sub>2</sub>-coated film using 0.05M coating solution; and (f) cross-sectional image of the MgF<sub>2</sub>-coated film using 0.1 M coating solution (EDS spectra of coating layers are shown below Fig. 1e and f).

The electrochemical properties of the pristine and coated LiCoO<sub>2</sub> thin films were characterized to investigate the effectiveness of the MgF<sub>2</sub> surface modification. Fig. 2a presents the discharge capacities of the pristine and MgF<sub>2</sub>-coated LiCoO<sub>2</sub> thin films as a function of current density between 3.0 and 4.25V. The current density was increased stepwise, from 0.2 to 0.4 to 0.6 mA·cm<sup>-2</sup>. The cell was cycled 20 times at a given current density, and then increased to a higher current density. As observed in Fig. 2a, the pristine and coated films showed similar discharge capacities during the initial cycle. However, as the increase of current densities, the discharge capacity of the pristine film was significantly decreased. As the film electrodes do not contain a conducting agent such as carbon, their electrochemical properties may be vulnerable under fast charge-discharge conditions. Considering that the average capacity of the LiCoO<sub>2</sub> thin film was ~50 μAh·cm<sup>-2</sup>·μm<sup>-1</sup>, the current densities of 0.2, 0.4, and 0.6 mA·cm<sup>-2</sup> could be converted into 1, 2, and 3 C rates, respectively, which seemed to be fast cycling conditions for the film electrode. In contrast, the MgF<sub>2</sub>-coated LiCoO<sub>2</sub> thin film delivered a higher discharge capacity than did the pristine film at current densities of 0.4 and 0.6 mA·cm<sup>-2</sup>, which showed that surface modification with MgF<sub>2</sub> coating enhanced the rate capability of the LiCoO<sub>2</sub> film electrode. Theoretically, the MgF<sub>2</sub> layer is a non-conducting material for Li ions and electrons. Thus, it might be supposed that the coating layer would block the intercalation of Li ions and the movement of electrons, which would decrease the discharge capacity and rate capability. However, the actual capacity being measured is limited by various hindrances, such as the unwanted interface layer formed by the reaction between the cathode and electrolyte. It is well known that acid (such as HCl and HF) can be generated from the reaction between water and salts (such as LiClO<sub>4</sub> and LiPF<sub>6</sub>) in the electrolyte. An extremely small amount of water (less than few tens of ppm) is enough to initiate this reaction. The acid-containing 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 deteriorates the electrochemical properties of the “pristine” cathode. However, when the surface of the cathode is covered with a coating layer, the coating material serves as a protective layer, preventing direct contact with the reactive electrolyte. This may suppress the dissolution of the transition metal and the formation of an unwanted interface layer. Therefore, a coating layer does not just hinder lithium intercalation and electron movement, but rather, it functions as protection from the reactive electrolyte, which drives the enhancement of the electrochemical properties such as discharge capacity and rate capability.



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Fig.2. (a) Discharge capacities and cyclic performance of the pristine and MgF<sub>2</sub>-coated LiCoO<sub>2</sub> thin films; (b) discharge profiles of the pristine and MgF<sub>2</sub>-coated films at a current density of  $0.4\text{mA}\cdot\text{cm}^{-2}$  (21st cycle of Fig. 2a); (c) discharge profiles of the pristine and MgF<sub>2</sub>-coated films at a current density of  $0.6\text{mA}\cdot\text{cm}^{-2}$  (41st cycle of Fig. 2a).

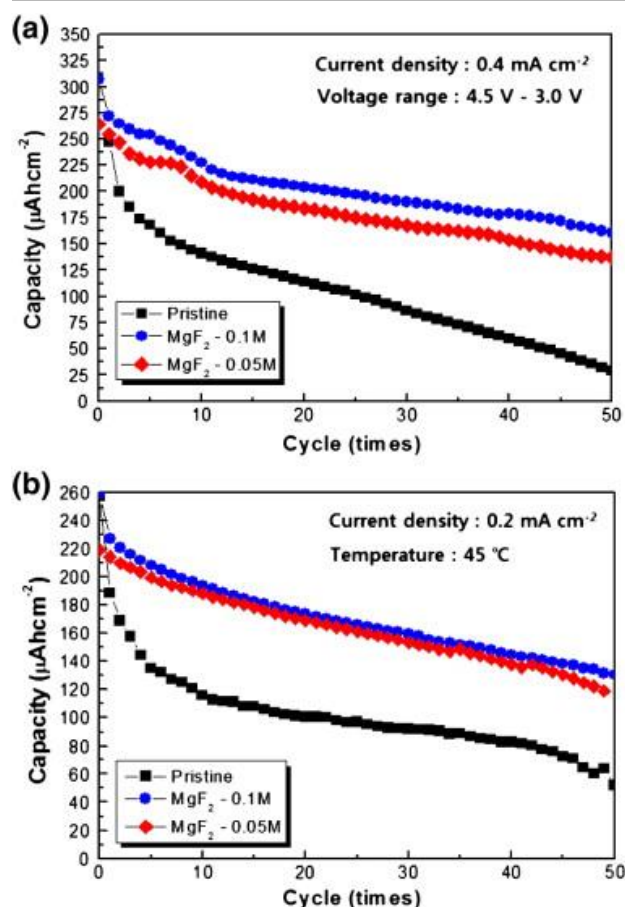
Fig.2b and c shows the voltage profiles of the pristine and MgF<sub>2</sub>-coated film at current densities of 0.4 and  $0.6\text{mA}\cdot\text{cm}^{-2}$  (21st and 41st cycles of Fig.2a). The rate capability of the LiCoO<sub>2</sub> film was significantly enhanced by MgF<sub>2</sub> surface coating. In particular, the coated film prepared from the 0.1M coating solution exhibited better rate capability than that prepared from the 0.05M coating solution, which implied that too thin of a coating layer was insufficient to obtain a suitable coating effect. Table 1 summarizes the discharge capacity and capacity retention values at the various current densities (the values of the initial cycles at the respective current densities). Pristine

film showed a capacity retention of ~41.67% at a current density of 0.6mA·cm<sup>-2</sup>, compared with that at a current density of 0.2mA·cm<sup>-2</sup>. In contrast, the capacity retentions of the coated samples were ~61.35% (0.05M coating solution), and ~70.96% (0.1 M coating solution).

Table 1. Discharge capacities and capacity retention values of pristine and MgF<sub>2</sub>-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 0.2mA·cm<sup>-2</sup>.)

|                        | <b>Pristine (<math>\mu</math> Ah·cm<sup>-2</sup>)</b> | <b>%</b> | <b>0.05M MgF<sub>2</sub> coated<br/>LiCoO<sub>2</sub> film (<math>\mu</math> Ah·cm<sup>-2</sup>)</b> | <b>%</b> | <b>0.1M MgF<sub>2</sub> coated<br/>LiCoO<sub>2</sub> (<math>\mu</math> Ah·cm<sup>-2</sup>)</b> | <b>%</b> |
|------------------------|-------------------------------------------------------|----------|------------------------------------------------------------------------------------------------------|----------|------------------------------------------------------------------------------------------------|----------|
| 0.2mA·cm <sup>-2</sup> | 190.7                                                 | 100      | 204.8                                                                                                | 100      | 203.9                                                                                          | 100      |
| 0.4mA·cm <sup>-2</sup> | 132.3                                                 | 69.4     | 151.2                                                                                                | 73.8     | 163.5                                                                                          | 80.2     |
| 0.6mA·cm <sup>-2</sup> | 79.5                                                  | 41.7     | 125.7                                                                                                | 61.3     | 144.5                                                                                          | 71.0     |

The pristine and MgF<sub>2</sub>-coated LiCoO<sub>2</sub> films were cycled in the voltage range 4.5–3.0V (at a current density of 0.4mA·cm<sup>-2</sup>) to characterize the coating effect under more severe conditions. It has been reported that LiCoO<sub>2</sub> experiences structural instability in the high voltage range (i.e., above 4.25V), which leads to rapid capacity fading on cycling [25]. As shown in Fig. 3a, the discharge capacity of the pristine film rapidly dropped to ~10% of the initial value during 50cycles due to structural degradation. In contrast, the MgF<sub>2</sub>-coated film showed much enhanced cyclic performance under the same conditions, which encouraged us to believe that the MgF<sub>2</sub> coating layer was effective in inhibiting structural degradation on cycling at a high cut-off voltage. The enhancement of the structural stability of LiCoO<sub>2</sub> by surface modification has been reported previously [26]. Cho et al. proposed that coating materials can suppress structural degradation on cycling at high cut-off voltage because coatings can protect the cathode against the reactive electrolyte to prevent Co dissolution [26]. The protective effect of the MgF<sub>2</sub> coating layer was also confirmed by a cycling test at high temperature. Fig. 3b shows the cyclic performance of pristine and MgF<sub>2</sub>-coated LiCoO<sub>2</sub> films at 45 °C (voltage range was 4.25–3.0V). High temperature promotes chemical reactions between the electrolyte and the electrode surfaces; thus, it was expected that the electrode would undergo significant surface damage. As anticipated, the cyclic performance of the pristine film seemed to deteriorate at high temperature (Fig. 3b). However, it was clear that the MgF<sub>2</sub> coating layer improved the cyclic performance of the film electrode at 45 °C. This result also confirmed that MgF<sub>2</sub> was an effective coating layer for protecting the cathode surface from the reactive electrolyte on cycling.



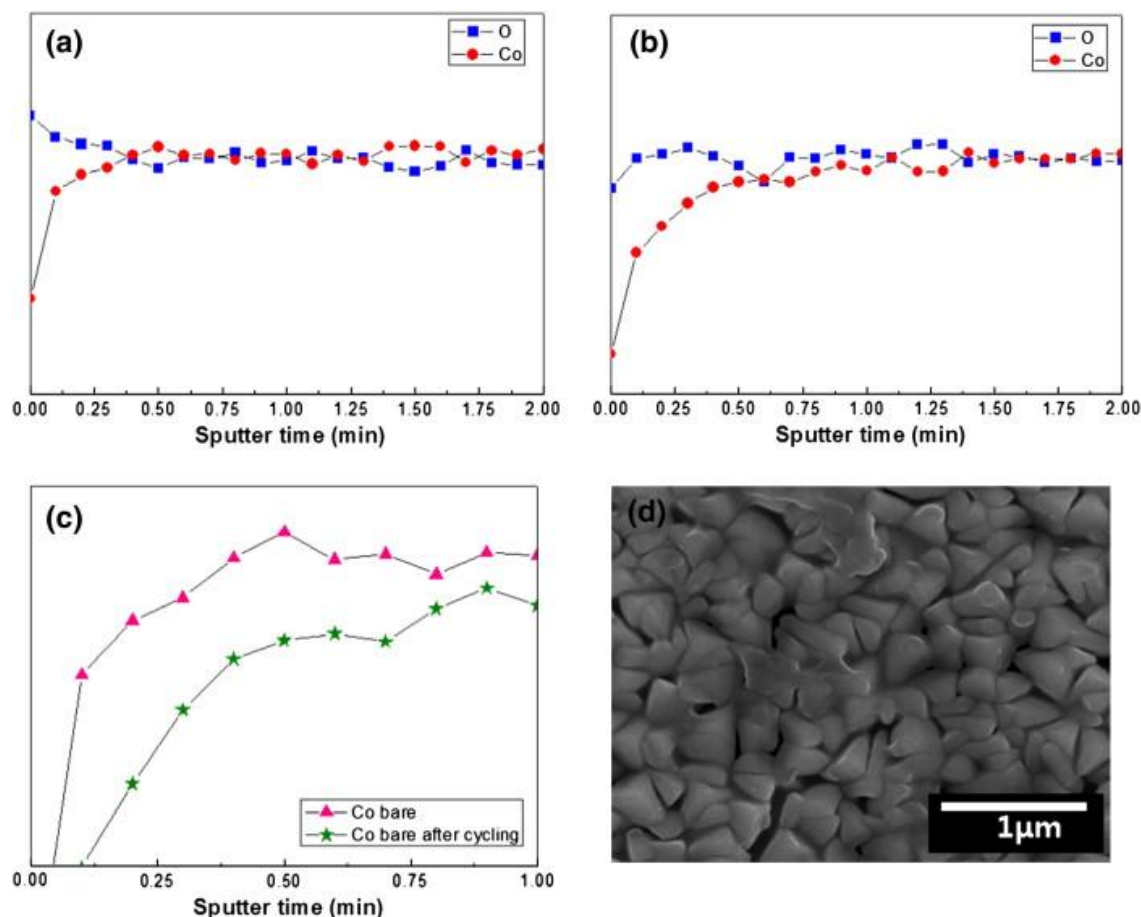
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Fig.3. Cyclic performance of the pristine and MgF<sub>2</sub>-coated LiCoO<sub>2</sub> film electrodes (a) measured at 30°C in the voltage range 4.5–3.0V at a current density of 0.4 mA·cm<sup>-2</sup>, and (b) measured at 45°C in the voltage range 4.25–3.0V at a current density of 0.2 mA·cm<sup>-2</sup>.

As reported previously [9], [10], [11], [12], [13], [14], the deterioration of the electrochemical properties of the “cycled electrode” is attributed to surface damage due to the interface reaction with the reactive electrolyte. An efficient method for identifying the deterioration is direct observation of the damaged surface of the electrode. However, it has been very difficult to directly observe the surface of a “cycled electrode” because of the small particle size of the cathode powder and the thin coating layer (approximately 10–100nm). Moreover, the conducting agent and binder, which are contained in a bulk-type electrode, may disturb characterization of the surface when using various surface analysis tools. Some analysis methods, such as transmission electron microscopy (TEM), have been used to characterize the interface layer of the electrode [6]. However, these tools offer only limited information because, for example, TEM experiments involve preparation of the sample, which can destroy or modify the interface layer. In this study, through the introduction of the film electrode, the surface of the cycled electrode was directly observed using SEM, and the concentration-depth profile was analyzed using XPS, which is one of the efficient surface analysis tools.

Fig.4a-c show the concentration profile of the pristine film before and after cycling (50 times) at 45°C. As shown in Fig.4a, except for a slight deviation in the surface region, the concentrations of Co and O were nearly homogeneous within the measured depth before cycling. Whereas, the significant decrease in Co concentration near the surface was notable after 50cycles at 45°C, as shown in Fig.4b. Fig.4c compares the Co concentration profile in the surface region before and after cycling at 45°C. This clearly shows that surface Co levels were seriously depleted on cycling due to the acidic electrolyte. Moreover, SEM image after cycling in Fig.4d presents that the surface of the LiCoO<sub>2</sub>

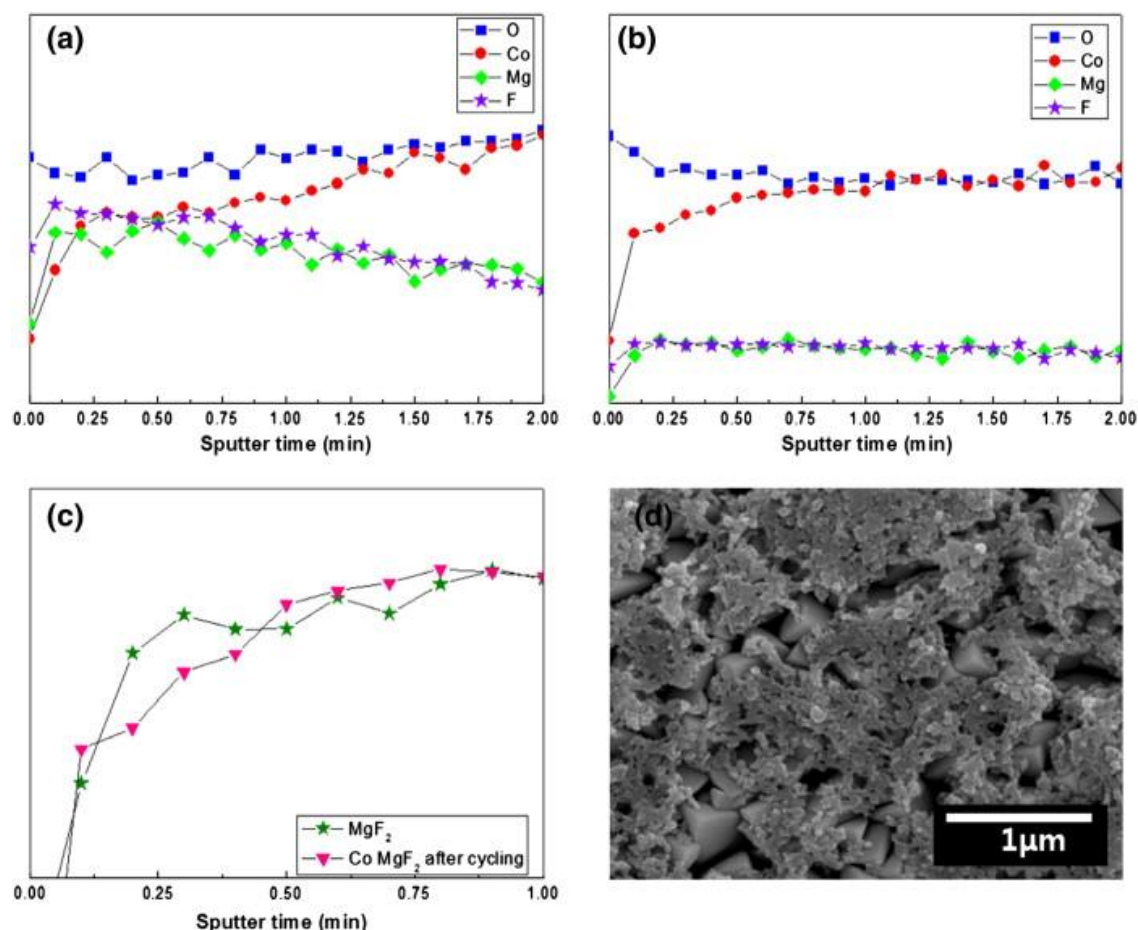
film was covered with an interface layer, which may be formed through the reaction of the electrode and electrolyte.



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Fig.4. (a) Concentration–depth profile of the pristine LiCoO<sub>2</sub> film measured by XPS before cycling. (b) Concentration–depth profile of the pristine LiCoO<sub>2</sub> film measured by XPS after cycling. (c) Comparison of Co concentration. (d) SEM image of the pristine LiCoO<sub>2</sub> film after cycling.

Fig.5a–c shows the concentration profile of the MgF<sub>2</sub>-coated LiCoO<sub>2</sub> film (coated using 0.1 M coating solution) before and after cycling. In the profile of the coated film before cycling (Fig.5a), Mg and F were detected in the near-surface region, while the Co concentration was slightly lower in the region compared to that of the pristine film. Considering the Fig.5b and c, it was evident that the Co concentration of the MgF<sub>2</sub>-coated film was nearly maintained on cycling at 45 °C, which implies that the coating layer efficiently prevented Co dissolution and successfully protected the surface of the electrode from the reactive electrolyte. However, the Mg and F concentrations were significantly decreased on cycling. This may indicate that the coating layer was sacrificed on cycling instead of the LiCoO<sub>2</sub> cathode, i.e., the MgF<sub>2</sub> coating layer seemed to react with acidic electrolyte and incur damage on cycling instead of the electrode material. As shown in the surface image of the coated film after cycle (Fig.5d), the MgF<sub>2</sub> coating layer of the film still remained after cycling. However, some parts of the coating layer seemed to be slightly removed (or damaged) on cycling. It was interesting that the LiCoO<sub>2</sub> grains, which were slightly visible through the coating layer, appeared clean and clear after cycling. These XPS and SEM analyses directly confirmed that the MgF<sub>2</sub> coating layer was effective as a protective layer to prevent the dissolution of the transition metal and the formation of an unwanted interface layer on the surface of the electrode, which may lead to enhanced electrochemical properties.



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Fig.5. (a) Concentration-depth profile of the MgF<sub>2</sub>-coated LiCoO<sub>2</sub> film measured by XPS before cycling. (b) Concentration-depth profile of the MgF<sub>2</sub>-coated LiCoO<sub>2</sub> film measured by XPS after cycling. (c) Comparison of Co concentration. (d) SEM image of the MgF<sub>2</sub>-coated LiCoO<sub>2</sub> film after cycling. The coating was performed using 0.1M coating solution.

## 4. Conclusions

Pristine and coated LiCoO<sub>2</sub> thin films were prepared to investigate the effect of coating and characterize the interface reaction between the surface of a cathode and the electrolyte on cycling. MgF<sub>2</sub>, a stable fluoride, was used as a new coating material in this work. The MgF<sub>2</sub> coating layer was very effective in improving the electrochemical properties of the LiCoO<sub>2</sub> film electrode. Based on the direct observation of the surface morphology using SEM, an unwanted interface layer, formed on the surface of the cycled electrode due to reaction with the electrolyte, was identified. Moreover, significant dissolution of Co on cycling was confirmed by XPS analysis. In contrast, the MgF<sub>2</sub>-coated film maintained a stable Co concentration on cycling. However, the MgF<sub>2</sub> coating layer seemed to be sacrificed on cycling instead of the cathode. This result directly shows the protective effect of the coating layer, which could explain the enhancement of electrochemical properties as a result of surface coating.

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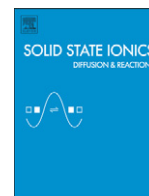
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# Interface characterization of $\text{MgF}_2$ -coated $\text{LiCoO}_2$ thin films

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## ABSTRACT

The electrochemical properties and interface reactions of pristine and coated  $\text{LiCoO}_2$  films were characterized.  $\text{MgF}_2$  was used as a new coating material to improve the electrochemical properties of the  $\text{LiCoO}_2$  film electrode. To directly observe the interface reaction between the surface of the cathode and the electrolyte, a film electrode with a wide, flat surface was introduced in this study. The rate capability, cyclic performance, and stability at high temperature of the  $\text{LiCoO}_2$  thin film were improved by  $\text{MgF}_2$  coating. The concentration–depth profile and surface image of the  $\text{LiCoO}_2$  film were investigated by SEM and XPS analyses before and after cycling. Pristine film showed significant Co dissolution and surface damage on cycling at high temperature (45 °C). However, both were efficiently depressed by the introduction of the  $\text{MgF}_2$  coating. These results confirm that the  $\text{MgF}_2$  coating layer successfully protected the surface of the cathode from the reactive electrolyte, leading to enhanced electrochemical properties for  $\text{MgF}_2$ -coated  $\text{LiCoO}_2$  films.

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## 1. Introduction

Lithium ion battery technology has developed rapidly as a result of the advances in and demand for electronic devices, electric vehicles, and energy storage devices [1–5]. The cathode is one of the key components in a lithium ion battery, affecting the discharge capacity, cyclic performance, rate capability, and thermal stability of the cell. One approach for improving the electrochemical properties of a cathode is surface modification by coating with stable materials, such as oxides [6–10], phosphates [11–15], or fluorides [16–19]. The interface between the cathode and electrolyte actively reacts during charge and discharge processes, which affects the electrochemical stability as well as the lithium ion exchange kinetics. The coating layer has been reported to stabilize the interface reaction and improve the electrochemical properties of the cathode. However, it has been difficult to characterize this interface reaction directly because of the small particle size of the pristine powder, the thinness of the coating layer, and the rough surface of the positive electrode. In this work, a  $\text{LiCoO}_2$  thin film electrode was introduced as a pristine cathode, to investigate in detail the interface reaction between the electrolyte and the coating layer of the pristine cathode. The surface of a thin film cathode is much wider and smoother, which may offer opportunity for careful observation of the interface reaction between the cathode and electrolyte. As a new fluoride coating material,  $\text{MgF}_2$  was introduced in this work. An inexpensive element, Mg has been used as a doping material to enhance the electrochemical properties of cathodes [20,21]. Moreover,  $\text{MgO}$  has already been used as

a coating material on  $\text{LiCoO}_2$  to improve cyclic stability [22,23]. In particular, our approach was inspired by the fact that other fluorides, such as  $\text{AlF}_3$ , were very effective in modifying cathode surfaces [16–19]. In this study, we investigated the interface reaction between a  $\text{MgF}_2$ -coated thin-film cathode and electrolyte, and characterized the reason for enhanced properties as a result of surface coating.

## 2. Experimental

The pristine  $\text{LiCoO}_2$  thin film, with a thickness of  $\sim 4 \mu\text{m}$ , was a commercial product from GS NanoTech Co. For the synthesis of the  $\text{MgF}_2$  coating solution, magnesium nitrate hexahydrate [ $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ], ammonium phosphate [ $(\text{NH}_4)_2\text{HPO}_4$ ] (Aldrich, 99%), and ammonium fluoride [ $\text{NH}_4\text{F}$ , Aldrich] were dissolved in 10 mL of a mixed solvent consisting of distilled water, 1-butanol, and acetic acid (wt. ratio of 1:2:2) with continuous stirring for 2 h at 25 °C. The effect of coating on the cathode electrochemical properties is significantly affected by the thickness of the coating material [24]. In this study, the concentration of the coating solution was adapted as a tool for controlling the thickness of the coating material: two  $\text{MgF}_2$  coating solutions at 0.05 and 0.1 M were prepared. A solution was coated onto a  $\text{LiCoO}_2$  thin film substrate using a spin-coater (K-359 model S-1, Kyowa Riken Co., Ltd.). The coated  $\text{LiCoO}_2$  thin films were heat-treated in a rapid thermal annealing (RTA) system at 400 °C for 30 min. The pristine  $\text{LiCoO}_2$  thin film was also heat-treated at 400 °C for 30 min before testing, to compare properties under the same fabrication conditions. The microstructures of the films were observed using field emission scanning electron microscopy (FE-SEM, Nova Nano 200).

The electrochemical characterizations of the coated  $\text{LiCoO}_2$  films were performed in non-aqueous half-cells. The active area of each film used for the electrochemical test was about  $1 \text{ cm} \times 1 \text{ cm}$ . Li foil

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was used as the counter electrode. The electrolyte was 1 M  $\text{LiClO}_4$  in propylene carbonate (PC). The cells were subjected to galvanostatic cycling using a WonAtech system. X-ray photoelectron spectroscopy (XPS, PHI 5000 VersaProbe (Ulvac-PHI)) analysis was used to obtain depth-concentration profiles of the elements (Co, O, Mg, and F) for the samples, which may offer good information about the interface reaction between the cathode and electrolyte.

### 3. Results and discussion

The surface morphologies of pristine and coated films were observed using SEM images. To obtain coating layers with different thicknesses, the concentration of the coating solution was controlled to 0.05 or 0.1 M. As shown in Fig. 1a, the pristine  $\text{LiCoO}_2$  film exhibited a smooth and clean surface without any hetero-particles. In contrast, numerous nanosized particles appeared on the surface of the  $\text{MgF}_2$ -coated film. In the cross-sectional image, the  $\text{LiCoO}_2$  film seemed to have a columnar structure. The coating layer was also observed clearly in the cross-sectional images of the coated film. As shown below Fig. 1e and f, Mg and F elements were distinctly detected via energy-dispersive X-ray spectroscopy (EDS), which confirmed the formation of a  $\text{MgF}_2$  coating layer on the surface of the  $\text{LiCoO}_2$  pristine film. Notably, the

coated film prepared from the 0.1 M coating solution exhibited larger EDS peaks indicative of Mg and F elements than the coated film prepared from the 0.05 M coating solution. This implies that the coated film prepared from the 0.1 M coating solution was thicker than that prepared from the 0.05 M solution, although it was difficult to exactly measure the thickness of the coating layer. Generally, the coating materials are likely to react with elements of the pristine cathode, such as Li and Co, because their small particle sizes lead to high surface free energy [15,19]. Therefore, it was anticipated that the  $\text{MgF}_2$  coating layer would react with the  $\text{LiCoO}_2$  surface and form a coating layer with a new composition, consisting of Mg, F, Co, and Li.

The electrochemical properties of the pristine and coated  $\text{LiCoO}_2$  thin films were characterized to investigate the effectiveness of the  $\text{MgF}_2$  surface modification. Fig. 2a presents the discharge capacities of the pristine and  $\text{MgF}_2$ -coated  $\text{LiCoO}_2$  thin films as a function of current density between 3.0 and 4.25 V. The current density was increased stepwise, from 0.2 to 0.4 to 0.6  $\text{mA}\cdot\text{cm}^{-2}$ . The cell was cycled 20 times at a given current density, and then increased to a higher current density. As observed in Fig. 2a, the pristine and coated films showed similar discharge capacities during the initial cycle. However, as the increase of current densities, the discharge capacity of the pristine film was significantly decreased. As the film electrodes do not contain a

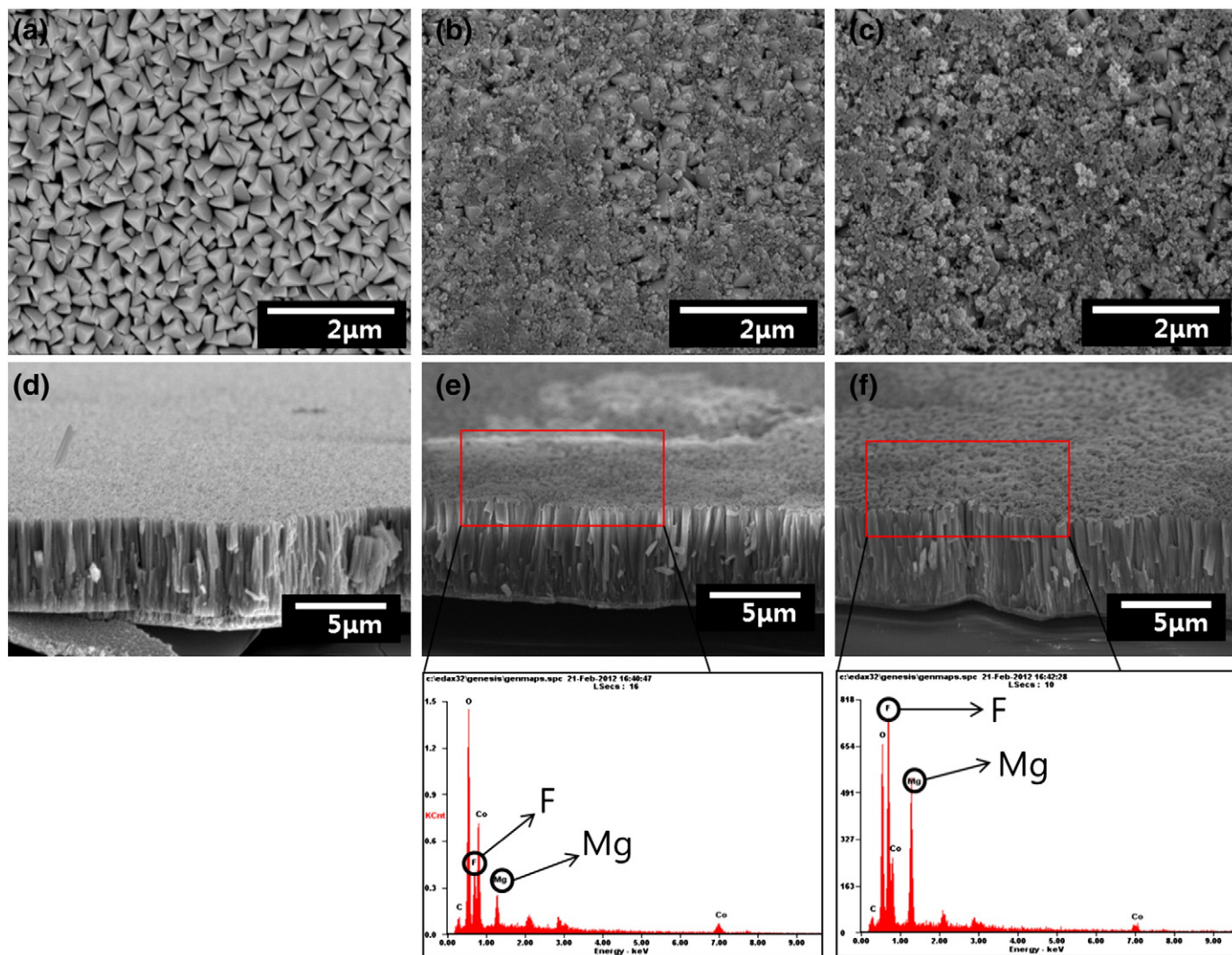


**Fig. 1.** SEM images of the pristine and coated  $\text{LiCoO}_2$  thin film electrodes. (a) Surface of the pristine film; (b) surface of the  $\text{MgF}_2$ -coated film using 0.05 M coating solution; (c) surface of the  $\text{MgF}_2$ -coated film using 0.1 M coating solution; (d) cross-sectional image of the pristine film; (e) cross-sectional image of the  $\text{MgF}_2$ -coated film using 0.05 M coating solution; and (f) cross-sectional image of the  $\text{MgF}_2$ -coated film using 0.1 M coating solution (EDS spectra of coating layers are shown below Fig. 1e and f).

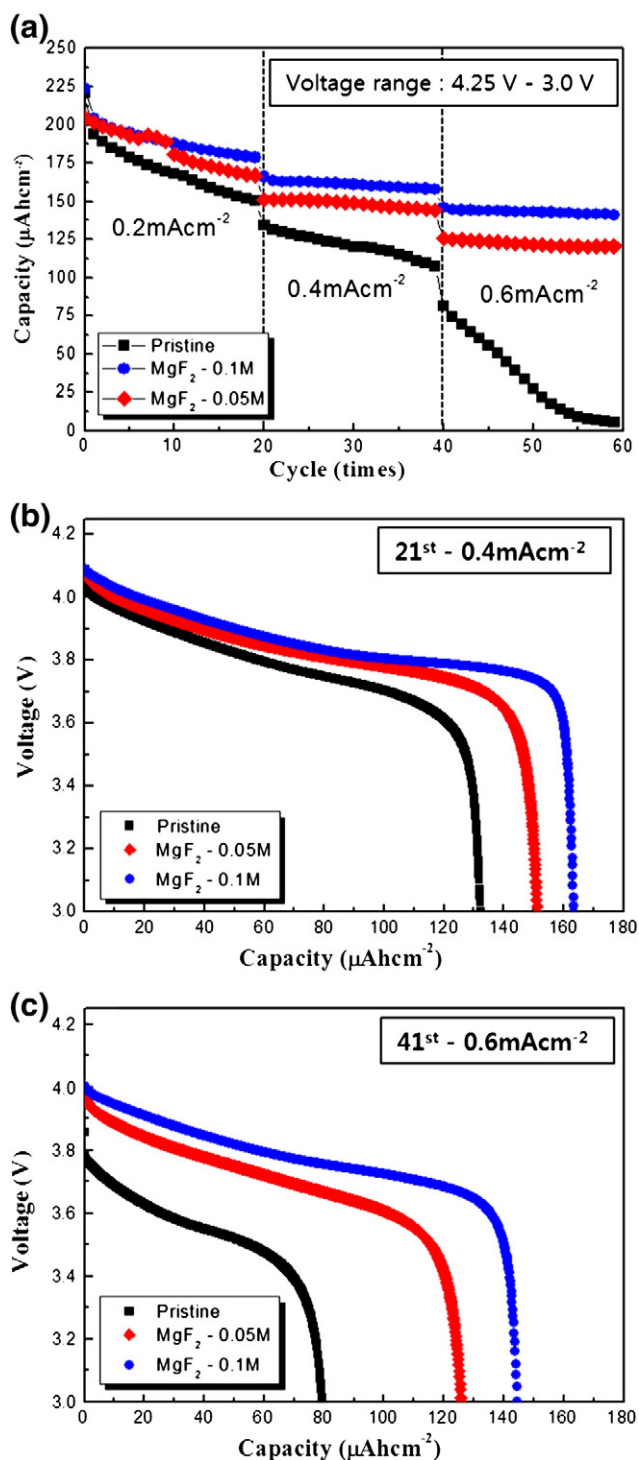


**Fig. 2.** (a) Discharge capacities and cyclic performance of the pristine and  $\text{MgF}_2$ -coated  $\text{LiCoO}_2$  thin films; (b) discharge profiles of the pristine and  $\text{MgF}_2$ -coated films at a current density of  $0.4 \text{ mA} \cdot \text{cm}^{-2}$  (21st cycle of Fig. 2a); (c) discharge profiles of the pristine and  $\text{MgF}_2$ -coated films at a current density of  $0.6 \text{ mA} \cdot \text{cm}^{-2}$  (41st cycle of Fig. 2a).

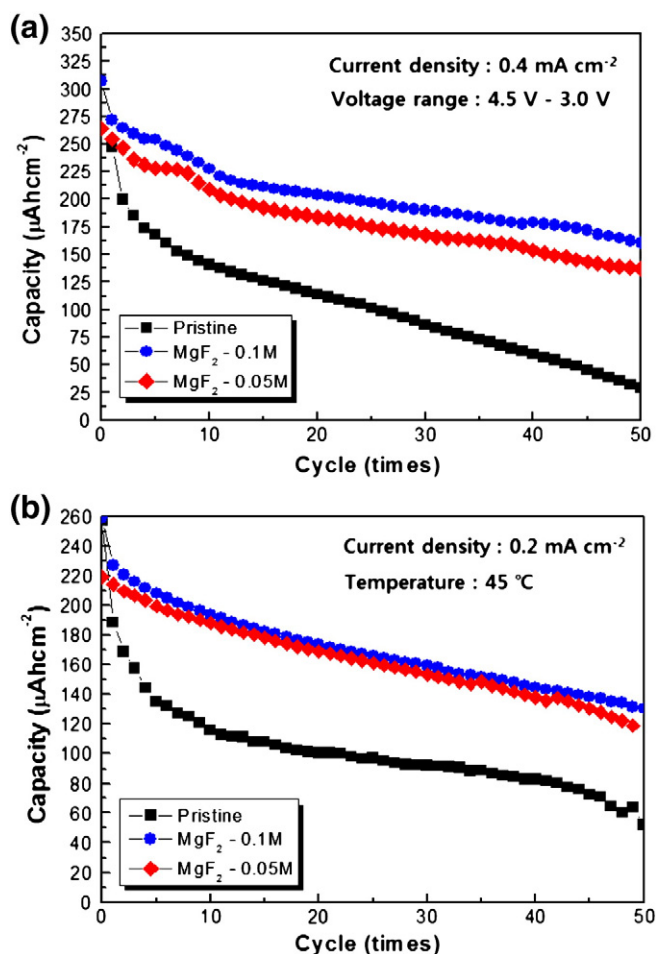


**Fig. 3.** Cyclic performance of the pristine and  $\text{MgF}_2$ -coated  $\text{LiCoO}_2$  film electrodes (a) measured at  $30^\circ\text{C}$  in the voltage range 4.5–3.0 V at a current density of  $0.4 \text{ mA} \cdot \text{cm}^{-2}$ , and (b) measured at  $45^\circ\text{C}$  in the voltage range 4.25–3.0 V at a current density of  $0.2 \text{ mA} \cdot \text{cm}^{-2}$ .

conducting agent such as carbon, their electrochemical properties may be vulnerable under fast charge-discharge conditions. Considering that the average capacity of the  $\text{LiCoO}_2$  thin film was  $\sim 50 \mu\text{Ah} \cdot \text{cm}^{-2} \cdot \mu\text{m}^{-1}$ , the current densities of 0.2, 0.4, and  $0.6 \text{ mA} \cdot \text{cm}^{-2}$  could be converted into 1, 2, and 3 C rates, respectively, which seemed to be fast cycling conditions for the film electrode. In contrast, the  $\text{MgF}_2$ -coated  $\text{LiCoO}_2$  thin film delivered a higher discharge capacity than did the pristine film at current densities of 0.4 and  $0.6 \text{ mA} \cdot \text{cm}^{-2}$ , which showed that surface modification with  $\text{MgF}_2$  coating enhanced the rate capability of the  $\text{LiCoO}_2$  film electrode. Theoretically, the  $\text{MgF}_2$  layer is a non-conducting material for Li ions and electrons. Thus, it might be supposed that the coating layer would block the intercalation of Li ions and the movement of electrons, which would decrease the discharge capacity and rate capability. However, the actual capacity being measured is limited by various hindrances, such as the unwanted interface layer formed by the reaction between the cathode and electrolyte. It is well known that acid (such as HCl and HF) can be generated from the

**Table 1**  
Discharge capacities and capacity retention values of pristine and  $\text{MgF}_2$ -coated  $\text{LiCoO}_2$  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  $0.2 \text{ mA} \cdot \text{cm}^{-2}$ .)

|                                       | Pristine ( $\mu\text{Ah} \cdot \text{cm}^{-2}$ ) | %    | 0.05 M $\text{MgF}_2$ coated $\text{LiCoO}_2$ film ( $\mu\text{Ah} \cdot \text{cm}^{-2}$ ) | %    | 0.1 M $\text{MgF}_2$ coated $\text{LiCoO}_2$ ( $\mu\text{Ah} \cdot \text{cm}^{-2}$ ) | %    |
|---------------------------------------|--------------------------------------------------|------|--------------------------------------------------------------------------------------------|------|--------------------------------------------------------------------------------------|------|
| $0.2 \text{ mA} \cdot \text{cm}^{-2}$ | 190.7                                            | 100  | 204.8                                                                                      | 100  | 203.9                                                                                | 100  |
| $0.4 \text{ mA} \cdot \text{cm}^{-2}$ | 132.3                                            | 69.4 | 151.2                                                                                      | 73.8 | 163.5                                                                                | 80.2 |
| $0.6 \text{ mA} \cdot \text{cm}^{-2}$ | 79.5                                             | 41.7 | 125.7                                                                                      | 61.3 | 144.5                                                                                | 71.0 |

reaction between water and salts (such as  $\text{LiClO}_4$  and  $\text{LiPF}_6$ ) in the electrolyte. An extremely small amount of water (less than few tens of ppm) is enough to initiate this reaction. The acid-containing 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 deteriorates the electrochemical properties of the “pristine” cathode. However, when the surface of the cathode is covered with a coating layer, the coating material serves as a protective layer, preventing direct contact with the reactive electrolyte. This may suppress the dissolution of the transition metal and the formation of an unwanted interface layer. Therefore, a coating layer does not just hinder lithium intercalation and electron movement, but rather, it functions as protection from the reactive electrolyte, which drives the enhancement of the electrochemical properties such as discharge capacity and rate capability.

Fig. 2b and c shows the voltage profiles of the pristine and  $\text{MgF}_2$ -coated film at current densities of 0.4 and 0.6  $\text{mA}\cdot\text{cm}^{-2}$  (21st and 41st cycles of Fig. 2a). The rate capability of the  $\text{LiCoO}_2$  film was significantly enhanced by  $\text{MgF}_2$  surface coating. In particular, the coated film prepared from the 0.1 M coating solution exhibited better rate capability than that prepared from the 0.05 M coating solution, which implied that too thin of a coating layer was insufficient to obtain a suitable coating effect. Table 1 summarizes the discharge capacity and capacity retention values at the various current densities (the values of the initial cycles at the respective current densities). Pristine film showed a capacity retention of ~41.67% at a current density of 0.6  $\text{mA}\cdot\text{cm}^{-2}$ , compared with that at a current density of 0.2  $\text{mA}\cdot\text{cm}^{-2}$ . In contrast,

the capacity retentions of the coated samples were ~61.35% (0.05 M coating solution), and ~70.96% (0.1 M coating solution).

The pristine and  $\text{MgF}_2$ -coated  $\text{LiCoO}_2$  films were cycled in the voltage range 4.5–3.0 V (at a current density of 0.4  $\text{mA}\cdot\text{cm}^{-2}$ ) to characterize the coating effect under more severe conditions. It has been reported that  $\text{LiCoO}_2$  experiences structural instability in the high voltage range (i.e., above 4.25 V), which leads to rapid capacity fading on cycling [25]. As shown in Fig. 3a, the discharge capacity of the pristine film rapidly dropped to ~10% of the initial value during 50 cycles due to structural degradation. In contrast, the  $\text{MgF}_2$ -coated film showed much enhanced cyclic performance under the same conditions, which encouraged us to believe that the  $\text{MgF}_2$  coating layer was effective in inhibiting structural degradation on cycling at a high cut-off voltage. The enhancement of the structural stability of  $\text{LiCoO}_2$  by surface modification has been reported previously [26]. Cho et al. proposed that coating materials can suppress structural degradation on cycling at high cut-off voltage because coatings can protect the cathode against the reactive electrolyte to prevent Co dissolution [26]. The protective effect of the  $\text{MgF}_2$  coating layer was also confirmed by a cycling test at high temperature. Fig. 3b shows the cyclic performance of pristine and  $\text{MgF}_2$ -coated  $\text{LiCoO}_2$  films at 45 °C (voltage range was 4.25–3.0 V). High temperature promotes chemical reactions between the electrolyte and the electrode surfaces; thus, it was expected that the electrode would undergo significant surface damage. As anticipated, the cyclic performance of the pristine film seemed to deteriorate at high temperature (Fig. 3b). However, it was clear that the  $\text{MgF}_2$  coating layer improved the cyclic performance of the film electrode at 45 °C. This

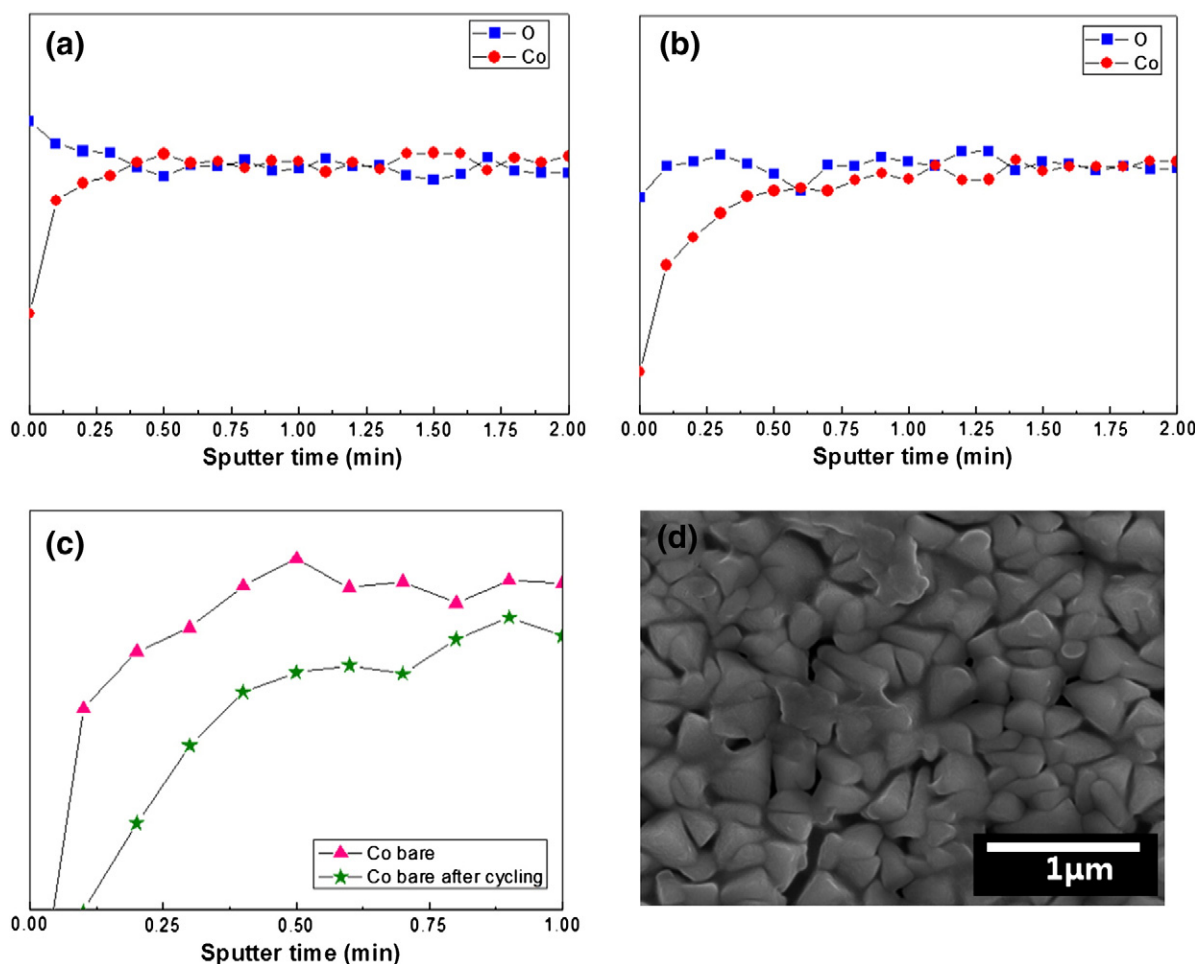


Fig. 4. (a) Concentration–depth profile of the pristine  $\text{LiCoO}_2$  film measured by XPS before cycling. (b) Concentration–depth profile of the pristine  $\text{LiCoO}_2$  film measured by XPS after cycling. (c) Comparison of Co concentration. (d) SEM image of the pristine  $\text{LiCoO}_2$  film after cycling.

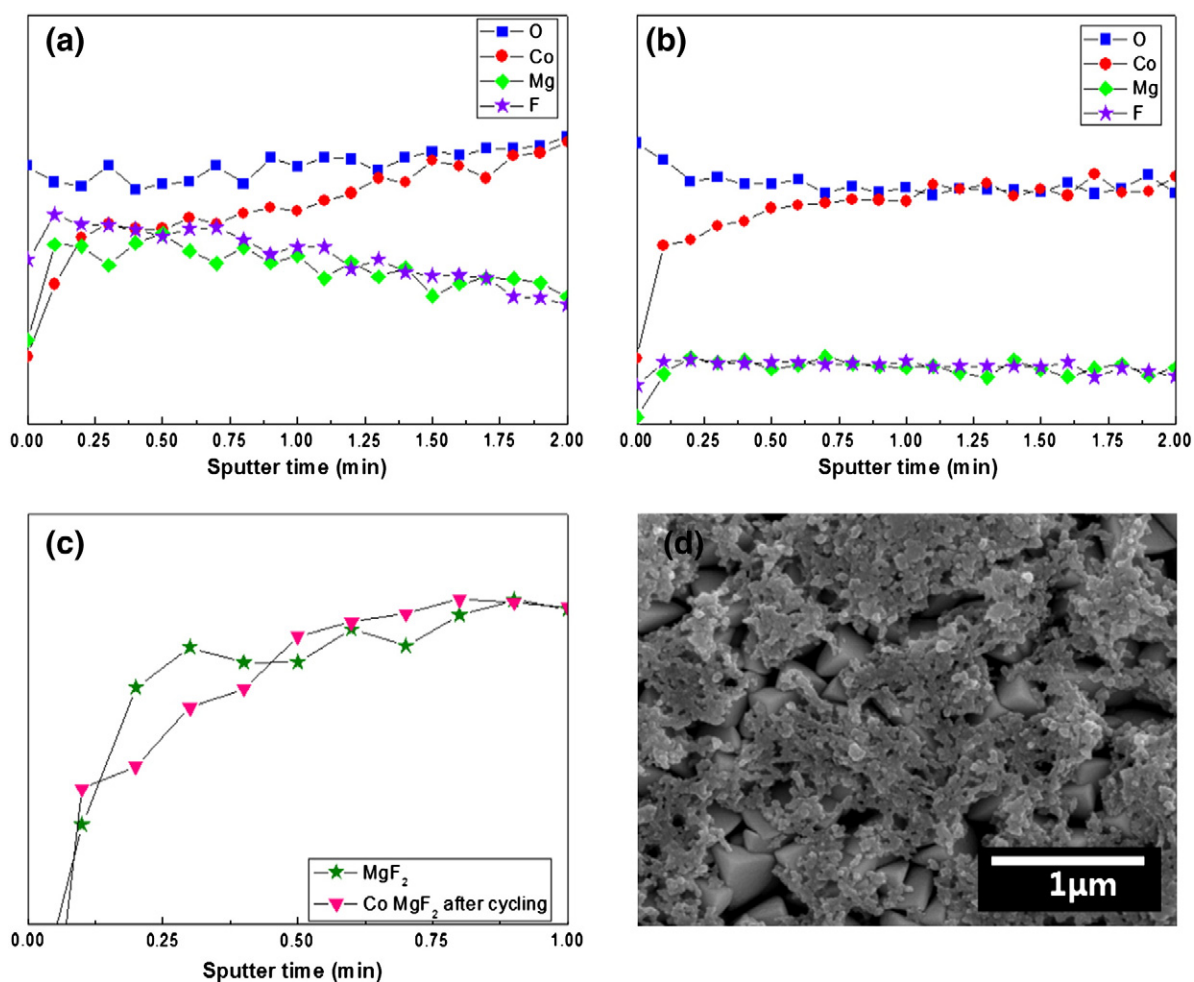


**Fig. 5.** (a) Concentration-depth profile of the MgF<sub>2</sub>-coated LiCoO<sub>2</sub> film measured by XPS before cycling. (b) Concentration-depth profile of the MgF<sub>2</sub>-coated LiCoO<sub>2</sub> film measured by XPS after cycling. (c) Comparison of Co concentration. (d) SEM image of the MgF<sub>2</sub>-coated LiCoO<sub>2</sub> film after cycling. The coating was performed using 0.1 M coating solution.

result also confirmed that MgF<sub>2</sub> was an effective coating layer for protecting the cathode surface from the reactive electrolyte on cycling.

As reported previously [9–14], the deterioration of the electrochemical properties of the “cycled electrode” is attributed to surface damage due to the interface reaction with the reactive electrolyte. An efficient method for identifying the deterioration is direct observation of the damaged surface of the electrode. However, it has been very difficult to directly observe the surface of a “cycled electrode” because of the small particle size of the cathode powder and the thin coating layer (approximately 10–100 nm). Moreover, the conducting agent and binder, which are contained in a bulk-type electrode, may disturb characterization of the surface when using various surface analysis tools. Some analysis methods, such as transmission electron microscopy (TEM), have been used to characterize the interface layer of the electrode [6]. However, these tools offer only limited information because, for example, TEM experiments involve preparation of the sample, which can destroy or modify the interface layer. In this study, through the introduction of the film electrode, the surface of the cycled electrode was directly observed using SEM, and the concentration-depth profile was analyzed using XPS, which is one of the efficient surface analysis tools.

Fig. 4a–c show the concentration profile of the pristine film before and after cycling (50 times) at 45 °C. As shown in Fig. 4a, except for a slight deviation in the surface region, the concentrations of Co and O were nearly homogeneous within the measured depth before cycling. Whereas, the significant decrease in Co concentration near the surface

was notable after 50 cycles at 45 °C, as shown in Fig. 4b. Fig. 4c compares the Co concentration profile in the surface region before and after cycling at 45 °C. This clearly shows that surface Co levels were seriously depleted on cycling due to the acidic electrolyte. Moreover, SEM image after cycling in Fig. 4d presents that the surface of the LiCoO<sub>2</sub> film was covered with an interface layer, which may be formed through the reaction of the electrode and electrolyte.

Fig. 5a–c shows the concentration profile of the MgF<sub>2</sub>-coated LiCoO<sub>2</sub> film (coated using 0.1 M coating solution) before and after cycling. In the profile of the coated film before cycling (Fig. 5a), Mg and F were detected in the near-surface region, while the Co concentration was slightly lower in the region compared to that of the pristine film. Considering the Fig. 5b and c, it was evident that the Co concentration of the MgF<sub>2</sub>-coated film was nearly maintained on cycling at 45 °C, which implies that the coating layer efficiently prevented Co dissolution and successfully protected the surface of the electrode from the reactive electrolyte. However, the Mg and F concentrations were significantly decreased on cycling. This may indicate that the coating layer was sacrificed on cycling instead of the LiCoO<sub>2</sub> cathode, i.e., the MgF<sub>2</sub> coating layer seemed to react with acidic electrolyte and incur damage on cycling instead of the electrode material. As shown in the surface image of the coated film after cycle (Fig. 5d), the MgF<sub>2</sub> coating layer of the film still remained after cycling. However, some parts of the coating layer seemed to be slightly removed (or damaged) on cycling. It was interesting that the LiCoO<sub>2</sub> grains, which were slightly visible through the coating layer, appeared clean and clear after cycling. These XPS and SEM

analyses directly confirmed that the  $\text{MgF}_2$  coating layer was effective as a protective layer to prevent the dissolution of the transition metal and the formation of an unwanted interface layer on the surface of the electrode, which may lead to enhanced electrochemical properties.

#### 4. Conclusions

Pristine and coated  $\text{LiCoO}_2$  thin films were prepared to investigate the effect of coating and characterize the interface reaction between the surface of a cathode and the electrolyte on cycling.  $\text{MgF}_2$ , a stable fluoride, was used as a new coating material in this work. The  $\text{MgF}_2$  coating layer was very effective in improving the electrochemical properties of the  $\text{LiCoO}_2$  film electrode. Based on the direct observation of the surface morphology using SEM, an unwanted interface layer, formed on the surface of the cycled electrode due to reaction with the electrolyte, was identified. Moreover, significant dissolution of Co on cycling was confirmed by XPS analysis. In contrast, the  $\text{MgF}_2$ -coated film maintained a stable Co concentration on cycling. However, the  $\text{MgF}_2$  coating layer seemed to be sacrificed on cycling instead of the cathode. This result directly shows the protective effect of the coating layer, which could explain the enhancement of electrochemical properties as a result of surface coating.

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