

## Investigation of $\text{LiCoO}_2$ Thin-Film Electrode Using Redox Reaction of Metal Cation

Jun-ichi Inamoto,<sup>a</sup> Kohei Miyazaki,<sup>a</sup>  
Tomokazu Fukutsuka,<sup>a</sup> Takeshi Abe<sup>a,b</sup>

<sup>a</sup>Department of Energy and Hydrocarbon Chemistry,  
Graduate School of Engineering, Kyoto University  
Kyoto-Daigaku Katsura, Nishikyo-ku,  
Kyoto 615-8510, Japan

<sup>b</sup>Japan Science and Technology Agency, 4-1-8, Honcho,  
Kawaguchi-shi, Saitama 332-0012, Japan

### Introduction

Lithium-ion batteries (LIB) have been expected as the power source of electric vehicles, and therefore, longer cycle life of LIB is required. To understand the degradation mechanism of LIB has been one of the important issues for a practical use in EV. In particular, solid electrolyte interface (SEI) of graphite negative electrode has been extensively studied since the growth of SEI leads to the capacity loss of LIB.

The degradation mechanism of positive electrodes has been also studied by many researchers. Similar to the graphite electrode, surface film has been observed on various positive electrodes, but it has not been understood in detail.

We focused on the electron-transfer reaction rates at the surface of positive electrodes. If surface film is electronic insulating, it would influence the electron-transfer reaction between electrode and electrolyte solution and this surface film may impair the lithium-ion extraction/insertion reaction at positive electrodes. Therefore, it is important to investigate the surface properties from the view of electron transfer. By using the outer-sphere redox reaction such as the redox of  $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ , electron-transfer rate between electrode and electrolyte solution can be evaluated [1]. In this study, we report the surface properties of  $\text{LiCoO}_2$  thin-film electrode by using outer-sphere redox reaction of metal cation [1], [2].

### Experimental

$\text{LiCoO}_2$  thin-film electrode was prepared by pulsed laser deposition. Three-electrode cell was used for electrochemical measurements of  $\text{LiCoO}_2$  thin-film electrode. Lithium-ion deintercalation/intercalation was conducted in 1 mol  $\text{dm}^{-3}$   $\text{LiClO}_4$ /propylene carbonate (PC) by cyclic voltammetry (0.1 mV  $\text{s}^{-1}$ , 3.5 – 4.2 V vs.  $\text{Li}^+/\text{Li}$ ). Before and after the lithium-ion de-intercalation/intercalation process, redox reaction of ferrocene was measured in 1 mol  $\text{dm}^{-3}$   $\text{LiClO}_4$ /PC containing 1 mmol  $\text{dm}^{-3}$  ferrocene by cyclic voltammetry (10 mV  $\text{s}^{-1}$ , 2.9 – 3.7 V vs.  $\text{Li}^+/\text{Li}$ ). From the cyclic voltammograms of redox reaction of ferrocene, standard rate constants of ferrocene were calculated.

### Results

X-ray diffraction pattern and Raman spectrum indicated that high crystalline  $\text{LiCoO}_2$  thin-film electrode was prepared. Figure 1 shows the cyclic voltammograms (CV) of  $\text{LiCoO}_2$  thin-film electrode in  $\text{LiClO}_4/\text{PC}$ . Around 3.9 V, peaks of lithium-ion de-intercalation/intercalation were observed. With cycling, redox currents gradually decreased. This result indicated the degradation of  $\text{LiCoO}_2$ . Figure 2 shows the CVs of redox reaction of ferrocene on  $\text{LiCoO}_2$  thin-film electrode before and after the lithium-ion de-intercalation/intercalation process.

Reversible redox peaks of ferrocene were observed in the CVs. Compared to CV before cycling, CV after cycling showed small peak separation. Standard rate constant of ferrocene was obtained after cycling. It indicates that the electron conductivity on the surface of  $\text{LiCoO}_2$  thin-film electrode increased after lithium-ion de-intercalation/intercalation process. Nishizawa et al. reported that de-intercalation of lithium ion from  $\text{LiCoO}_2$  led irreversible increase in its electron conductivity. Thus, we concluded that electronic passivation arisen from surface film formation did not occur but electron conductive layer, which consisted of lithium-deficit phase  $\text{Li}_x\text{CoO}_2$ , was formed on the surface of  $\text{LiCoO}_2$ . The effect of surface modification of  $\text{LiCoO}_2$  with  $\text{ZrO}_2$  on its surface electron conductivity will be discussed in the conference.

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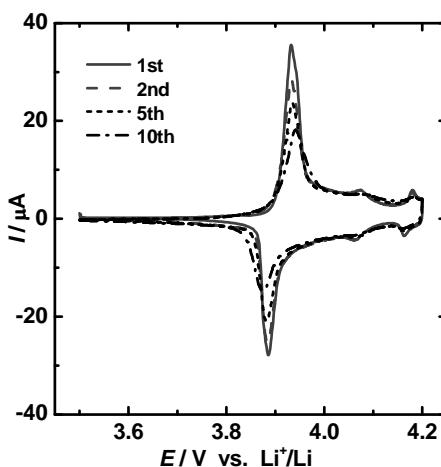


Fig. 1 CVs of  $\text{LiCoO}_2$  thin-film electrode in 1 mol  $\text{dm}^{-3}$   $\text{LiClO}_4/\text{PC}$ . Sweep rate was 0.1 mV  $\text{s}^{-1}$ .

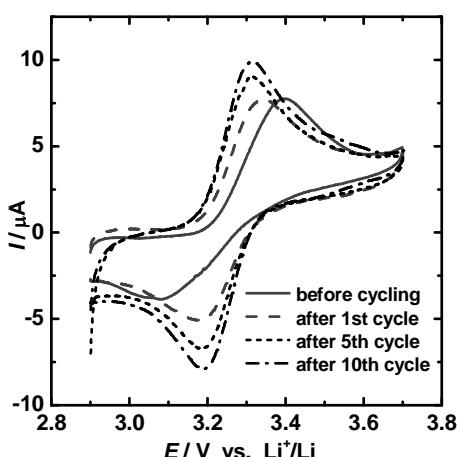


Fig. 2 CVs of redox reaction of ferrocene on  $\text{LiCoO}_2$  thin-film electrode. Electrolyte was 1 mol  $\text{dm}^{-3}$   $\text{LiClO}_4/\text{PC}$  containing 1 mmol  $\text{dm}^{-3}$  ferrocene. Sweep rate was 10 mV  $\text{s}^{-1}$ .

### Reference

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