

# Dynamic behavior of surface film on $\text{LiCoO}_2$ thin film electrode

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## Abstract

Electrochemical oxidation behavior of non-aqueous electrolytes on  $\text{LiCoO}_2$  thin film electrodes were investigated by *in situ* polarization modulation Fourier transform infrared (PM-FTIR) spectroscopy, atomic force microscopy and X-ray photoelectron spectroscopy (XPS).  $\text{LiCoO}_2$  thin film electrode on gold substrate was prepared by rf-sputtering method. *In situ* PM-FTIR spectra were obtained at various electrode potentials during cyclic voltammetry measurement between 3.5 V vs.  $\text{Li/Li}^+$  and 4.2 V vs.  $\text{Li/Li}^+$ . During anodic polarization, oxidation of non-aqueous electrolyte was observed, and oxidized products remained on the electrode at the potential higher than 3.75 V vs.  $\text{Li/Li}^+$  as a surface film. During cathodic polarization, the stripping of the surface film was observed at the potential lower than 3.9 V vs.  $\text{Li/Li}^+$ . Depth profile of XPS also showed that more organic surface film remained on charged  $\text{LiCoO}_2$  than that on discharged one. AFM images of charged and discharged electrodes showed that some decomposed products deposited on charged electrode and disappeared from the surface of discharged one. These results indicate that the surface film on  $\text{LiCoO}_2$  is not so stable.

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## 1. Introduction

Rechargeable lithium battery has high energy density, so that it is attractive as power source for hybrid electric vehicle (HEV). This is accomplished by high cell voltage owing to highly oxidative and reductive active materials used in this battery [1,2]. To realize this high voltage, aprotic non-aqueous solvents have been utilized for electrolyte solutions. In general, propylene carbonate (PC), ethylene carbonate (EC) and diethyl carbonate (DEC), that are popular non-aqueous solvents for rechargeable lithium battery, have wider electrochemical window than operation voltage of this battery [3–5]. However, some research groups have proposed that non-aqueous electrolytes are likely to be oxidized and form surface film on cathode active material like SEI layer on graphite anode [6,7]. Our group also has analyzed electrochemical oxidation of PC or EC and DEC binary solvent on  $\text{LiCoO}_2$  thin film electrode occurring around 3.8 V vs.  $\text{Li/Li}^+$  by *in situ* FTIR measurement and XPS analysis [8–11].

In the case of graphite anode, SEI layer plays an important role for lithium intercalation/de-intercalation. By using EC-based electrolyte solution, SEI layer is usually formed during the first cycle and stably remained on the surface during intercalation/de-intercalation processes continuing in further cycles [12,13]. On the other hand, in the case of PC-based electrolyte, co-intercalation of the solvent molecules occurs, and this phenomenon causes an exfoliation of graphene layers [14]. This exfoliation prevents smooth intercalation/de-intercalation of lithium ion into/from graphite anode. So far, some inorganic and organic compounds have been proposed as electrolyte additives, to improve the stability of SEI layer. Vinylene carbonate (VC) is one of the most popular electrolyte additives for graphite anode. It has been supposed that polymerized VC makes stable SEI layer and improves a cycle performance of batteries [15,16].

Recently, a surface of cathode material has been investigated in order to improve a life performance of rechargeable lithium ion batteries. For instance, a surface of active materials has been covered with non-conducting oxides, such as alumina and zirconia to suppress degradation of cathodes [17,18]. On the other hand, surface analysis on cathode material has been also done to observe a dynamic behavior of cathode material surface [8–11].

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In these studies, only anodic polarization behavior of  $\text{LiCoO}_2$  and  $\text{LiMn}_2\text{O}_4$  has been discussed by using *in situ* FTIR measurement and XPS analysis. In these studies, an electrochemical oxidation of solvents has been detected from 4.0 V vs.  $\text{Li/Li}^+$ .

In the present study, we also investigated surface film formation process on  $\text{LiCoO}_2$  thin film electrode by using *in situ* PM-FTIR, XPS and AFM to discuss the stability of the surface film on  $\text{LiCoO}_2$  during charge and discharge processes. In this study, we focused on organic surface films formed on  $\text{LiCoO}_2$ , so that we selected  $\text{LiClO}_4$  as the Li-salt to avoid the decomposition of Li-salt. In this work, we employed PM-FTIR in order to realize higher sensitivity for organic compounds formed on  $\text{LiCoO}_2$  electrode and dynamic behavior of surface film during discharge and charge processes.

## 2. Experimental

In this study,  $\text{LiCoO}_2$  thin film electrodes were prepared by rf-sputtering (SPK-301, Tokki). Sputtering conditions were the same with that reported in our previous paper [10,11], and sputtering duration was 90 min. The as-sputtered film was in an amorphous state, so that the thin film was heated at  $700^\circ\text{C}$  for 5 h, in order to improve its crystallinity.

The prepared thin film was analyzed by X-ray diffraction method (RINT-2000, Rigaku) with  $\text{Cu K}\alpha$  (40 kV and 40 mA) at a scan rate of  $1^\circ\text{min}^{-1}$  in  $2\theta$  range from  $10^\circ$  to  $100^\circ$ . Raman spectroscopy (NRS-1000, Jasco) with 532 nm laser radiation was also utilized to detect hexagonal and cubic phases of  $\text{LiCoO}_2$ .

An oxidation of non-aqueous electrolytes was analyzed by *in situ* PM-FTIR spectroscopy (Nicolet 6700, Thermo Electron). The *in situ* spectroelectrochemical cell for external reflectance method [19] and the optical system for *in situ* PM-FTIR

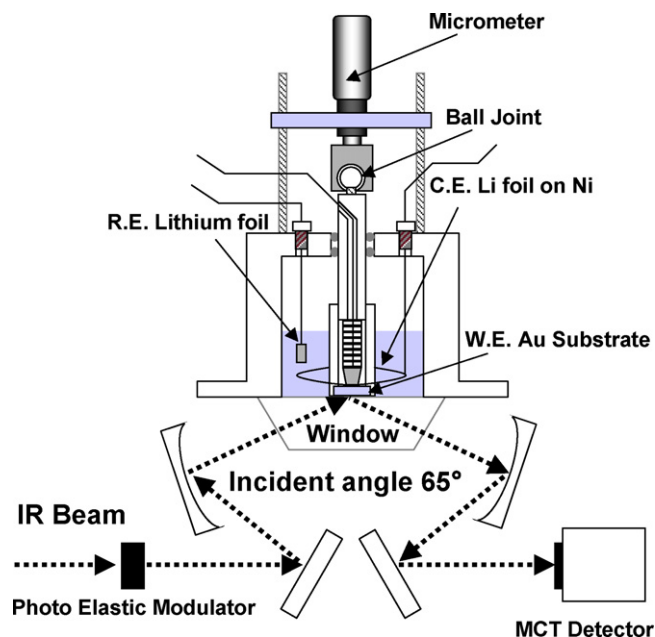


Fig. 1. Schematic illustration of *in situ* PM-FTIR cell and optical system.

spectroscopy were shown in Fig. 1. *In situ* PM-FTIR spectroscopy was performed using p-polarized and s-polarized IR beam modulated by a photoelastic modulator (PEM-90, Hinds) with Dual-channel Synchronous Sampling Technique Module. A sum-spectrum of p-polarized and s-polarized IR beam was collected by A channel as a background spectrum, and a differential spectrum was collected by B channel as a sample spectrum (Fig. 2). When the IR beam is reflected from electrode, p-polarized beam is strongly absorbed by molecules on the electrode surface, more than s-polarized beam. Therefore, spectrum of the electrolyte solution between window and

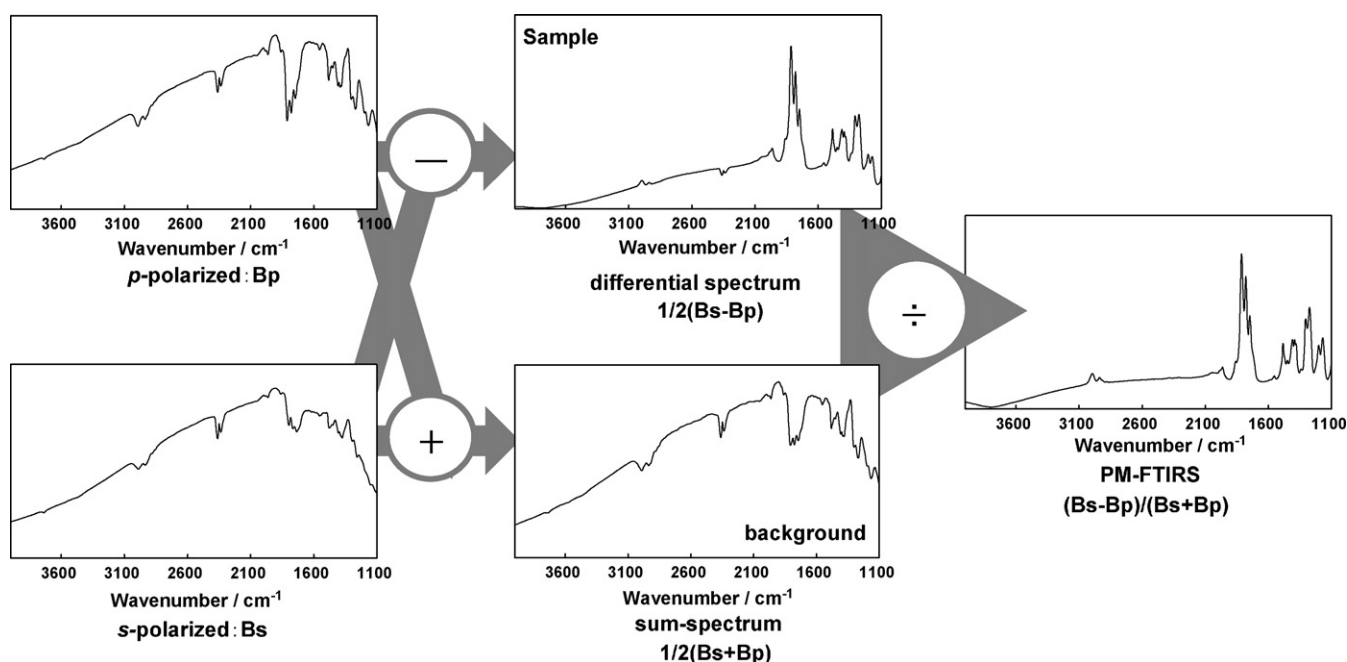


Fig. 2. Spectrum calculation for PM-FTIR.

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