

In situ FT-IR measurement for electrochemical oxidation of electrolyte with ethylene carbonate and diethyl carbonate on cathode active material used in rechargeable lithium batteries

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Abstract

LiCoO₂ thin-film electrodes were prepared by rf-sputtering and sol-gel methods. The prepared thin films contained different amounts of Co₃O₄ as an impurity depending on the preparation conditions. In situ FT-IR spectroscopic analyses on electrochemical oxidation of ethylene carbonate (EC) and diethyl carbonate (DEC) containing LiClO₄ on the LiCoO₂ thin-film electrodes were carried out. The electrochemical oxidations of EC and DEC occurred even at 3.8 V versus Li/Li⁺ on the fresh LiCoO₂. The solvents EC and DEC were oxidized to some compounds with carboxylic groups. In situ FT-IR spectra obtained for the LiCoO₂ thin films prepared by different methods were compared each other.

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1. Introduction

Rechargeable lithium battery has high energy density [1]. This high energy density is accomplished by high cell voltage owing to highly oxidative and reductive abilities of active materials used in this battery [1–3]. This is realized by utilizing wide electrochemical window of nonaqueous electrolytes, which provides stable operation of batteries [4–6]. However, non-aqueous electrolytes are likely to be oxidized on cathode active materials, due to high working potential, especially in the course of rapid charging process [7]. Therefore, the electrochemical oxidation of non-aqueous electrolytes has been investigated by many researchers using in situ and ex situ methods [8–10]. LiCoO₂ has been used as cathode active material in commercialized lithium batteries. We have already analyzed the electrochemical oxidation of propylene carbonate (PC) containing lithium salts on LiCoO₂ with in situ FT-IR spectroscopy [11,12].

In this work, the electrochemical oxidations of the mixed solvent of ethylene carbonate (EC) and diethyl carbonate (DEC) containing LiClO₄ on LiCoO₂ thin-film electrodes were analyzed by in situ FT-IR. LiCoO₂ has a layered structure, however, it has been reported that some other phases could be formed during charge-discharge cycles or depending on preparation conditions [13,14], which would affect the surface state of LiCoO₂. In the present study, LiCoO₂ thin films were fabricated by rf-sputtering [11] and sol-gel [15] methods, and their activities for the electrochemical oxidation of a nonaqueous electrolyte were compared each other.

2. Experimental

2.1. Preparation of LiCoO₂ thin film by sol-gel process

A precursor solution for LiCoO₂ was prepared from CH₃COOLi, Co(CH₃COO)₂·4H₂O, CH₃COOH, 2-C₃H₇OH, poly-vinyl pyrrolidone (PVP, molecular weight: 55,000), and H₂O, and the mixed ratio was *x*:1:1:10:20:50

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($x=0.8$ and 1.1) [15]. The precursor was deposited on Au substrates by using spin coat method, and it was converted to gel simultaneously. The gel film was heated at $800\text{ }^{\circ}\text{C}$ for 10 min. This process was repeated four times to increase the film thickness. Finally, the film was heat-treated at $800\text{ }^{\circ}\text{C}$ for 1 h. The thickness of the prepared thin films were $0.25\text{ }\mu\text{m}$ confirmed by scanning electron microscope observation.

2.2. Preparation of LiCoO_2 thin film by rf-sputtering

LiCoO_2 thin film was also prepared on a gold substrate by rf-sputtering (13.56 MHz). LiCoO_2 powder synthesized by normal solid-state reaction was used as a target. The sputtering gas was a mixture of O_2 and Ar (2:1 in volume), and the chamber pressure was maintained at 5×10^{-3} Torr. LiCoO_2 was deposited using a radio frequency power supply operating at 150 W. The Au substrate was heated at $300\text{ }^{\circ}\text{C}$, and the sputtering duration was 30 min. The as-deposited film was amorphous state, and then the thin film was followed by heat treatment at $700\text{ }^{\circ}\text{C}$ in air for 5 h. The thickness of the prepared thin films were $0.25\text{ }\mu\text{m}$ confirmed by scanning electron microscope observation.

2.3. Characterization of LiCoO_2 thin films

The LiCoO_2 thin films were characterized by X-ray diffraction (XRD, RINT-UltimaII, Rigaku Co.) measurements with $\text{Cu K}\alpha$ radiation, and micro-Raman spectroscopy (NRS-1000, Jasco) with 532 nm laser radiation. The electrochemical properties of LiCoO_2 thin-film electrodes were characterized by cyclic voltammetry with three-electrode system in propylene carbonate containing 1.0 mol dm^{-3} LiClO_4 , and lithium metal was used as reference and counter electrodes.

2.4. In situ FT-IR measurements

The spectro-electrochemical cell for in situ FT-IR measurements was similar to that reported elsewhere [12]. The external reflectance method was employed to collect the FT-IR data using a standard FT-IR spectrometer (FT-IR-230, Jasco). CaF_2 was used as the IR window. Nickel wire was used as the counter electrode, and lithium metal was used as the reference electrode. The electrolyte was 1.0 mol dm^{-3} $\text{LiClO}_4/\text{EC-DEC}$ (1:1 in volume). The electrode potential was stepped with a potential width of 0.3 V from 3.5 to 5.0 V versus Li/Li^+ . At each potential, the external reflectance spectrum was measured. In situ FT-IR measurement was performed with p-polarized IR beam in order to investigate the interfacial reaction between electrolyte and electrode. From two reflectance spectra obtained before and after a potential step, a subtractively normalized interfacial FT-IR (SNIFT-IR) was calculated according to the following equation [12]:

$$\frac{\Delta R}{R} = \frac{R_1 - R_0}{R_0} \quad (1)$$

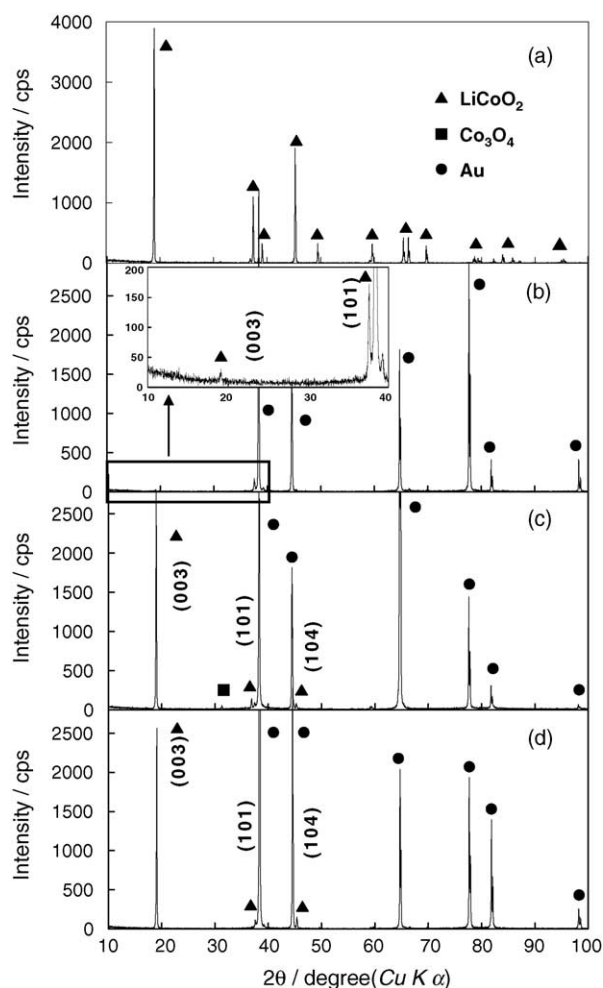


Fig. 1. X-ray diffraction patterns of LiCoO_2 samples: (a) solid-state synthesized powder, (b) thin film deposited by rf-sputtering followed by heat treatment, (c) thin film prepared by sol-gel process with $x=0.8$, and (d) $x=1.1$.

here R_0 is the reflectance spectrum before the potential step and R_1 is the reflectance spectrum after the potential step.

3. Results and discussion

Fig. 1 shows XRD patterns of LiCoO_2 samples. In the case of LiCoO_2 powder synthesized by normal solid-state reaction, no impurity phase was detected. The thin films prepared by sputtering and sol-gel process also exhibited the XRD pattern of LiCoO_2 besides the peaks of Au substrate. However, the sol-gel sample with Li molar ratio of 0.8 contained Co_3O_4 as an impurity. In the case of LiCoO_2 thin film prepared by sputtering followed by heat-treatment at $700\text{ }^{\circ}\text{C}$, the peak intensity of (1 0 1) was higher than that of (0 0 3) and (1 0 4). This indicates that the film had a preferred orientation (1 0 1) planes parallel to the Au substrate [16]. On the other hand, the LiCoO_2 thin films prepared by sol-gel process had a preferred Li orientation (0 0 3) parallel to the substrate.

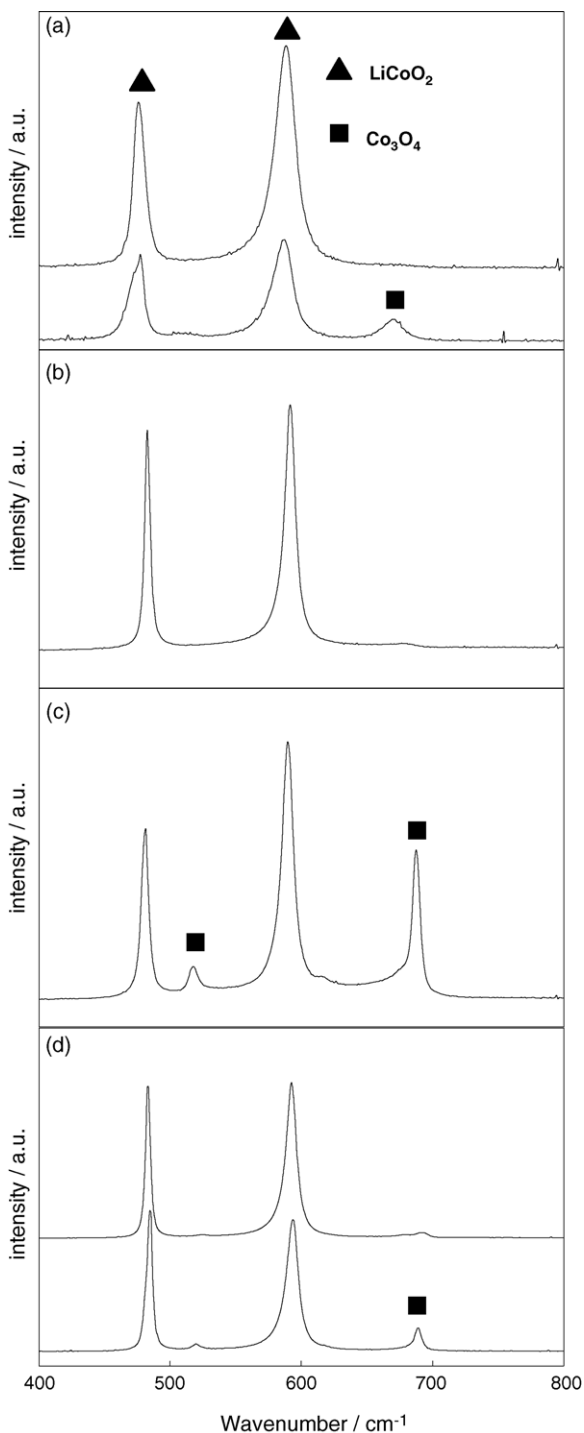


Fig. 2. Raman spectra of LiCoO₂ samples: (a) solid-state synthesized powder (the two spectra obtained from different spots of the sample), (b) thin film deposited by rf-sputtering followed by heat treatment, (c) thin film prepared by sol-gel process with $x=0.8$, and (d) $x=1.1$.

Fig. 2 shows the Raman spectra of LiCoO₂ prepared by solid-state synthesis, rf-sputtering, and sol-gel methods. The peaks at 482 and 592 cm⁻¹ were observed in the all spectra, those could be assigned as E_g and A_{1g} vibration modes in hexagonal LiCoO₂ (space group: $R\bar{3}m$), respectively [17,18]. The peaks at 518 and 686 cm⁻¹ observed for the film pre-

pared by the sol-gel process with $x=0.8$ (Fig. 2(c)) can be attributed to Co₃O₄ [19], which agrees to the XRD result shown in Fig. 1(c). These two peaks can be observed in the spectrum of $x=1.1$ (Fig. 2(d)) and even for the LiCoO₂ powder (Fig. 2(a)). This result suggested that a small amount of impurity, Co₃O₄, which were not detected by XRD, were included in the prepared sample. From the peak intensities of impurity phase, it can be seen that the amount of impurity depends on the preparation condition of LiCoO₂.

The cyclic voltammograms (CV) of LiCoO₂ thin-film electrodes prepared by sputtering and sol-gel process are shown in Fig. 3. As well known, the three reversible peaks at 3.9, 4.1 and 4.2 V were observed in the all CVs [2,3,15]. However, the symmetry of the voltammograms during anodic and cathodic scans depended on the preparation condition of the films. Apparently, the amount of the impurity phase affects the electrochemical properties of the films.

Fig. 4(a) shows SNIFT-IR spectra obtained for the LiCoO₂ thin-film electrode prepared by sputtering. The in situ FT-IR measurements were performed for the fresh thin-film electrode. A downward peak corresponds to the formation of new chemical compounds and an upward one shows consumption of chemical compounds originally existing in the measurement system. The signals of SNIFT-IR appeared even at 3.8 V, and the intensities of signals increased as the electrode potential increased. The upward peaks were observed at 1810, 1750, 1260 and 1160 cm⁻¹. These peaks suggested the decomposition of EC and DEC on the LiCoO₂ surface. The FT-IR measurements of pure EC and EC + DEC were carried out using a capillary thin film method, and the assignments of the peaks are shown in Table 1, which are similar to that reported in the literature [20]. The peaks at 1810 and 1750 cm⁻¹ were assigned to C=O stretching vibrations from EC and DEC, respectively. The downward peaks were observed at 1780, 1725, 1400, 1290, and 1185 cm⁻¹. It was considered that the peak at 1810 cm⁻¹ shifted to 1780 cm⁻¹, which could be ex-

Table 1
Assignment of each peak in FT-IR spectra

Upward peaks	1810 cm ⁻¹	C=O stretching vibration from EC
	1750 cm ⁻¹	C=O stretching vibration from DEC
	1260 cm ⁻¹	C–O–C asymmetric stretching vibration from DEC
	1160 cm ⁻¹	C–O–C symmetric stretching vibration from EC
Downward peaks	1780 cm ⁻¹	C=O stretching vibration
	1725 cm ⁻¹	C=O stretching vibration
	1400 cm ⁻¹	CH ₂ bending vibration
	1290 cm ⁻¹	C–O–C asymmetric stretching vibration
	1185 cm ⁻¹	C–O–C symmetric stretching vibration

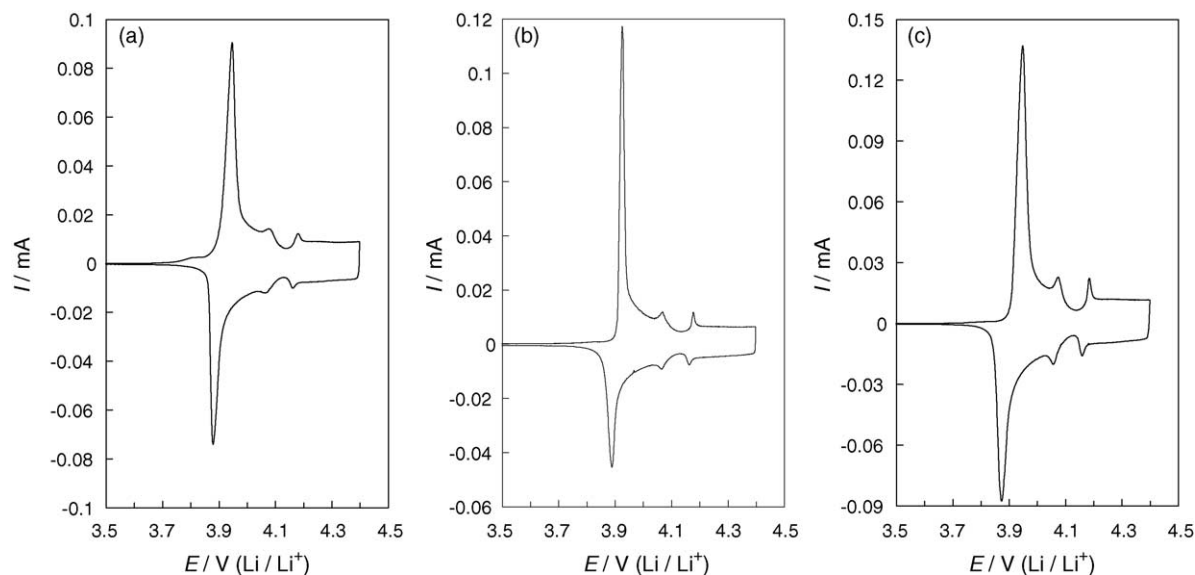


Fig. 3. Cyclic voltammograms of LiCoO₂ thin film electrodes: (a) sputtered film, (b) film prepared by sol-gel process with $x=0.8$, and (c) $x=1.1$. The scan rate was 10 mV min^{-1} and the electrolyte was propylene carbonate containing 1.0 mol dm^{-3} LiClO₄.

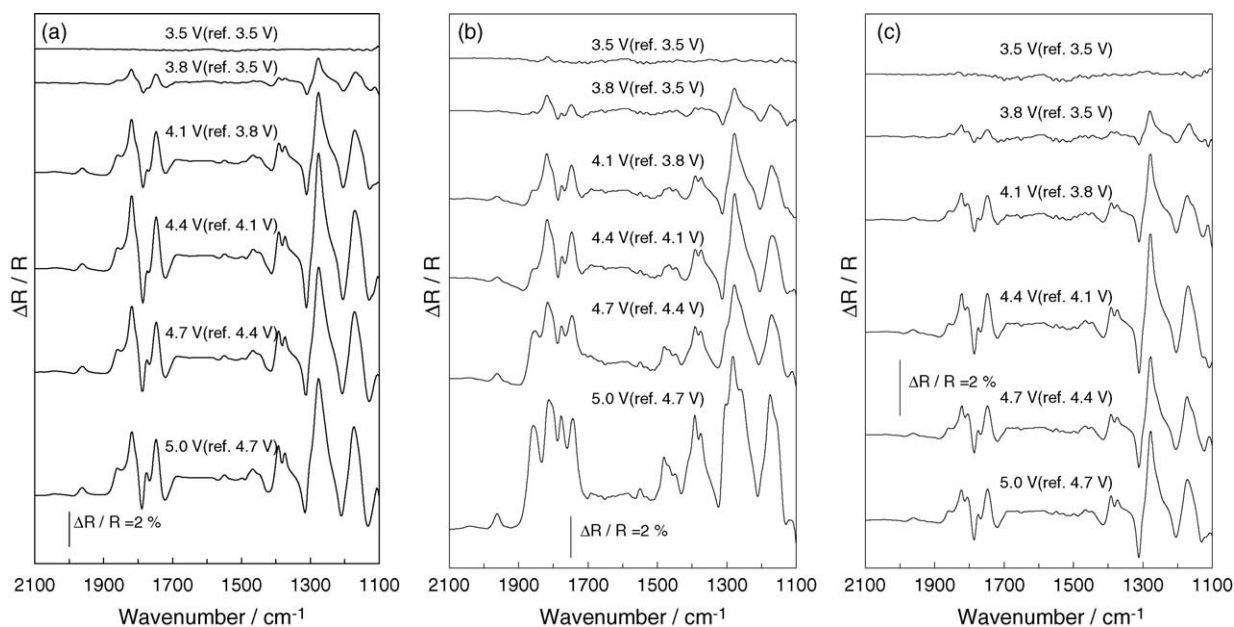


Fig. 4. SNIFT-IR spectra for electrochemical oxidation of 1.0 mol dm^{-3} LiClO₄/EC+DEC on the LiCoO₂ thin-film electrodes prepared by sputtering (a) and sol-gel process (molar ratios Li = 0.8 (b) and Li = 1.1 (c)).

plained as follows; a ring opening reaction of EC took place, and the product with a linear chain structure was accumulated on the electrode surface. Similarly, the peak at 1750 cm^{-1} shifted to 1725 cm^{-1} . Probably, the chains in DEC broke into a shorter linear chain via a radical species. Actually, a similar decomposition process was reported for the case of propylene carbonate-based electrolyte [11,12]. Fig. 4(b) and (c) show the SNIFT-IR spectra obtained for LiCoO₂ thin-film electrodes prepared by sol-gel process. In the case of the film of $x=0.8$, obtained spectra were apparently different from those of sputtered film, while the spectra of $x=1.1$

showed similar tendency to Fig. 4(a). The downward peaks can be scarcely observed in the spectra of Fig. 4(b), although the upward peaks can be observed. This means that the accumulation of the decomposition products does not occur on the film prepared with $x=0.8$, in spite of the oxidation of the electrolyte. The weak downward peaks would be attributed to weak interaction between carboxylic group (one of decomposition products) and electrode surface. The presence of Co₃O₄ phase may lower the interaction. Therefore, it can be said that the surface state of the cathode material has a significant influence on the oxidation process of the electrolytes.

4. Conclusions

LiCoO₂ thin-film electrodes were prepared by rf-sputtering and sol-gel methods. The prepared thin films contained different amounts of Co₃O₄ as an impurity depending on the preparation conditions. In situ FT-IR spectroscopic analyses of the electrochemical oxidation of EC and DEC containing LiClO₄ on the LiCoO₂ thin film electrodes were carried out. The measured SNIFT-IR spectra suggested that several possible reaction processes took place on the LiCoO₂ thin-film electrodes. The electrochemical oxidations of EC and DEC occurred even at 3.8 V versus Li/Li⁺ on the fresh LiCoO₂. The solvents EC and DEC were oxidized to some compounds with carboxylic groups. The surface state of LiCoO₂ has a significant influence on the stability of decomposition products on the electrode surface.

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