Short communication

Lithium-ion transfer on a Li$_x$CoO$_2$ thin film electrode prepared by pulsed laser deposition—Effect of orientation-

Izumi Yamada, Yasutoshi Iriyama, Takeshi Abe*, Zempachi Ogumi

Graduate School of Engineering, Kyoto University, Kyotodaigaku-katsura, Nishikyo-ku, Kyoto 615-8510, Japan

Abstract

LiCoO$_2$ thin films with different orientations were fabricated by pulsed laser deposition, and Li-ion transfer at the interface between the electrolyte and a LiCoO$_2$ thin film electrode was investigated. This study particularly focused on the effect of orientation on Li-ion transfer. The thin films were shown to be highly crystallized by X-ray diffraction. Charge transfer resistance ascribed to Li-ion transfer at the interface was observed by ac impedance spectroscopy. While charge transfer resistance was strongly influenced by the preferred orientation of LiCoO$_2$ thin film, the activation energy evaluated from the temperature-dependence of Li-ion transfer resistance appeared to be independent of the orientation.
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Keywords: Thin film electrode; Orientation; Pulsed laser deposition; Interface

1. Introduction

The increase in worldwide energy consumption has led to the depletion of natural resources and an increased environmental burden, which are urgent problems to be solved. One practical approach to increased energy consumption is to increase the utilization efficiency. In this sense, secondary batteries have attracted much attention since hybrid electric vehicles (HEV) that use nickel hydrogen batteries show dramatic increase in gas mileage. Recently, Li-ion batteries have attracted much attention as power sources for next-generation EV and HEV.

If they are to be used as power sources for EV and HEV, fast charge and discharge reactions are required. Therefore, the internal resistance in Li-ion batteries should be decreased as much as possible. In Li-ion batteries, the charge and discharge reactions are based on Li-ion transfer between the positive and negative electrodes through an electrolyte. In this reaction, three Li-ion transfer processes should be considered: Li-ion diffusion through the electrode materials, Li-ion (solvated Li-ion) transport and migration in the electrolyte, and Li-ion transfer at the electrode/electrolyte interface. To attain fast charging and discharging, the reaction rates in these processes must be increased. Among these processes, the former two can be made faster by shortening the diffusion and migration paths using thinner electrode and electrolyte layers [1]. The use of fine active materials can also be used to decrease the diffusion path of Li-ion and to increase the number of reaction sites for Li-ion to insert and extract [2]. Li-ion transfer at the interface also plays an important role in the total rate of the battery reaction. However, this important process of Li-ion transfer at the interface is not yet well understood. Elucidation of the fundamental mechanism of Li-ion transfer at the interface should be important for the further development of higher-performances Li-ion batteries.

A detailed study of Li-ion transfer at the interface requires a structurally ordered interface consisting of pure active materials without any additives. Bouwman et al. [3] have first reported the effect of LiCoO$_2$ thin films with different orientations by using pulsed laser deposition and RF sputtering on electrical properties. This report motivated us to prepare the LiCoO$_2$ thin films with different orientation and then we aim to obtain the correlation between interfacial Li-ion transfers and the orientations of LiCoO$_2$. In this study, we prepared LiCoO$_2$ thin films with different orientations by pulsed laser deposition, and then examined Li-ion transfer at the electrode/electrolyte interface.

2. Experimental

Positive thin film electrodes of LiCoO$_2$ with different orientations were prepared by pulsed laser deposition using a

* Corresponding author.
E-mail address: abe@elech.kuic.kyoto-u.ac.jp (T. Abe).

KrF eximer laser with a wavelength of 248 nm (Japan Storage Battery, EXL-210), with polished Pt plates as substrates. The substrate was kept at 873 K under a stream of oxygen. $LiCoO_2$ thin films with different orientations were prepared by changing the deposition time (range 1–3 h). The resulting $LiCoO_2$ thin films were characterized by X-ray diffraction (XRD) and Raman spectroscopy. XRD was measured with a RINT-2200 (Rigaku) equipped with a graphite monochromator with a scintillation detector. Typical working conditions were 40 kV and 40 mA with a scanning speed of 1 s. Raman spectroscopy was conducted with a triple monochromator (Jobin-Yvon, T-64000) with a multi-channel charge-coupled device (CCD) detector. A 515.4-nm line (50 mW) from an argon ion laser (NEC, GLG3280) was used as a light source.

The electrochemical properties of $LiCoO_2$ thin film electrodes were studied by cyclic voltammetry with a three-electrode cell that used lithium metal as counter and reference electrodes (HSV-100, HOKUTO-DENKO Inc.). Unless otherwise stated, potentials are referenced to lithium metal. The electrolytes used were propylene carbonate (PC) containing 1 mol dm^{-3} $LiClO_4$ or 1 mol dm^{-3} $LiCF_3SO_3$.

Interfacial reactions between the electrode and electrolyte were studied by ac impedance spectroscopy using a Radiometer (VoltaLab40) over a frequency range of 100 kHz to 10 mHz with the same three-electrode cell.

All experiments were conducted under an Ar atmosphere.

3. Results and discussion

3.1. Structural characterization of $LiCoO_2$ thin films

Fig. 1(a) and (b) shows XRD patterns of $LiCoO_2$ thin films deposited on a Pt plate for 1 and 3 h, respectively. Numbers on peaks denote the index $h k l$. As shown in Fig. 1(a), only one peak $2\theta = 19.0$ is remarkable, other than peaks due to the substrate. This peak can be indexed as the reflection of the 0 0 3 plane of hexagonal $LiCoO_2$, indicating that the thin film deposited for 1 h is a c-axis-oriented film. In contrast, several peaks were observed
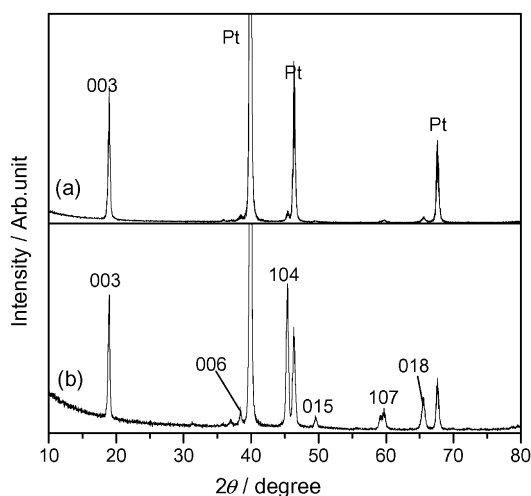

Fig. 1. X-ray diffraction patterns of $LiCoO_2$ thin films deposited on Pt for (a) 1 h and (b) 3 h.
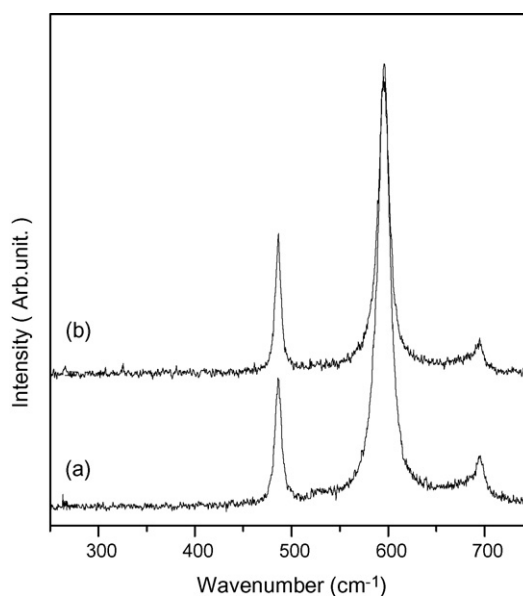

Fig. 2. Raman spectra of $LiCoO_2$ thin films deposited on Pt for (a) 1 h and (b) 3 h.

for the film deposited for 3 h, as shown in Fig. 1(b). In addition to 0 0 3, peaks indexed as the reflections of the 1 0 4, 0 1 5, 1 0 7, and 0 1 8 planes of hexagonal $LiCoO_2$ were also seen. The peak intensities of 0 0 3 and 1 0 4 were almost the same. Hence, the film deposited for 3 h should possess a random orientation.

Considering interface between $LiCoO_2$ thin films and the electrolyte, c-axis-oriented thin film deposited for 1 h has very few sites of Li ion transfer at defects on the surface and planes other than 0 0 3. On the other hand, the random thin film deposited for 3 h has more sites because the Li-ion layer faces the interface vertically.

Raman spectroscopy measurements were also carried out to study the orientation of surface of $LiCoO_2$ thin films in addition to bulk information from XRD. Fig. 2 shows Raman spectra of $LiCoO_2$ thin films deposited for (a) 1 h and (b) 3 h. Stoichiometric $LiCoO_2$ shows two Raman bands at 486 cm^{-1} (E_g mode) and 596 cm^{-1} (A_{1g} mode) [4]. As shown in Fig. 2, both E_g and A_{1g} peaks were observed in each thin film. In addition to the E_g and A_{1g} peaks, a small peak was observed at 690 cm^{-1}, which was assigned to Co_3O_4. Fig. 2(a) and (b) showed similar spectra. However, the ratio of the peak intensity of E_g to that of A_{1g} varies with a change in the degree of c-axis-orientation of $LiCoO_2$ thin films [5].

3.2. Electrochemical properties of $LiCoO_2$ thin films

The electrochemical properties of $LiCoO_2$ thin film electrodes were examined in liquid electrolyte of 1 mol dm^{-3} $LiClO_4$/PC. Fig. 3 shows cyclic voltammograms of the c-axis-oriented $LiCoO_2$ thin film deposited for 1 h. A large peak at 3.92 V and very small peaks at 4.08 and 4.18 V appeared in the cathodic direction. These peaks correspond to the phase transition of $LiCoO_2$, suggesting that the resultant $LiCoO_2$ thin film showed electrochemical properties almost identical to those in the literature [6]. The peak separation of the redox cou-
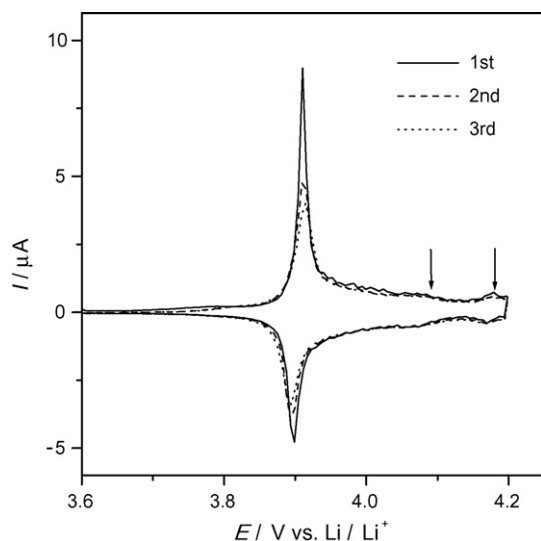
Fig. 3. Cyclic voltammogram of LiCoO$_2$ thin film electrode deposited for 1 h in 1 mol dm^{-3} LiClO$_4$/PC. Scanning rate = 0.1 mV s^{-1}.

Fig. 5. Nyquist plots of LiCoO$_2$ thin film deposited for 1 h in 1 mol dm^{-3} LiCF$_3$SO$_3$/PC at potentials of 3.60, 3.80, 3.92, 4.00, 4.20, and 4.40 V.

ple at around 3.9 V was about 40 mV, which suggests a small ohmic drop, and therefore the electric conductivity of the c-axis-oriented LiCoO$_2$ thin film is high enough for electrochemical measurements. In addition, the peak height at 3.92 V decreased with cycles. The decrease upon cycling is probably because of isolation of some grains by crack formation during charging and discharging.

Fig. 4 shows the cyclic voltammogram of the random-oriented LiCoO$_2$ thin film deposited for 3 h. As shown in Fig. 4, a large peak and two small peaks were observed, and the peak height decreased upon cycling in a similar way as shown in Fig. 3 due to crack formation as stated above. The peak separation of the redox couple was again about 40 mV, indicating that the electronic conductivity is high enough for electrochemical measurements. The cyclic voltammograms in Figs. 3 and 4 are very similar except for the current intensities. This difference in current intensity is principally due to the difference in inser-
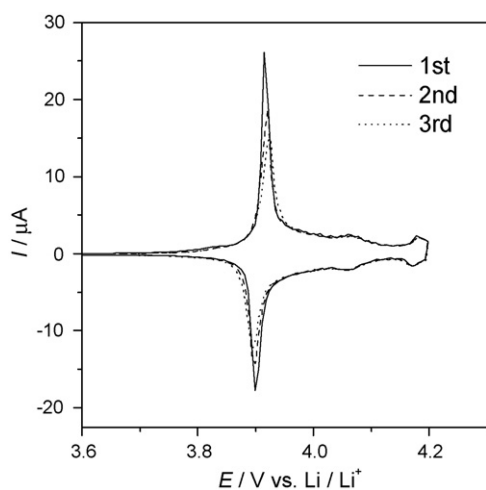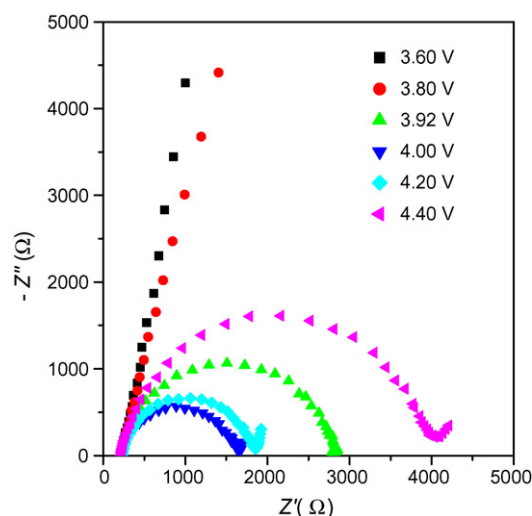
tion/extraction sites for Li-ion. The details will be discussed later.

3.3. ac impedance spectroscopy

AC impedance measurements were carried out by a three-electrode cell using LiCF$_3$SO$_3$ as a Li-salt for safety reasons. As shown in Fig. 5, Nyquist plots gave one semi-circle and a linear line for the c-axis-oriented LiCoO$_2$ thin film electrode at potentials between 3.92 and 4.40 V. Since the electric conductivity of LiCoO$_2$ was sufficiently high as described above, the semi-circle can be ascribed to charge (Li-ion) transfer resistance at the LiCoO$_2$/electrolyte interface at the given potentials. Below 3.8 V, only blocking-electrode-type behavior was observed. As is clear from the cyclic voltammograms in Figs. 3 and 4, little current is observed at potentials below 3.8 V. Therefore, this blocking-electrode-type behavior is quite valid.

To confirm the assignment of the semi-circle in Fig. 5 as charge transfer resistance, impedance measurements were carried out with different concentrations of Li salt. Liquid electrolyte of 0.125–1.00 mol dm^{-3} LiClO$_4$/PC was used and the potential was kept constant at 3.92 V. As shown in Fig. 6, the diameter of the semicircle increased as the salt concentration decreased. This indicates that these semi-circles are derived from the relaxation processes related to the reaction in which Li-ion plays as a carrier. The correlation between the Li salt concentration and the reciprocal of the charge transfer resistance was plotted in Fig. 7, and a linear relationship was observed. Generally, exchange current i_0 is expressed as $i_0 = FAk^0C$ (F: Faraday constant, A: area, k^0: standard heterogeneous rate constant, C: concentration of species) [7]. On the other hand, the charge transfer resistance is described as $R_{ct} = RT/nFi_0$ (R: gas constant, T: absolute temperature, n: stoichiometric number of electrons involved in an electrode reaction) [7]. These equations can be rewritten as $i_0 = (RT/nF) \times 1/R_{ct}$. Based on these equations, we obtain $i_0 = FAk^0C = (RT/nF) \times 1/R_{ct}$. Therefore, the reciprocal of charge transfer resistance is proportional to the Li salt con-
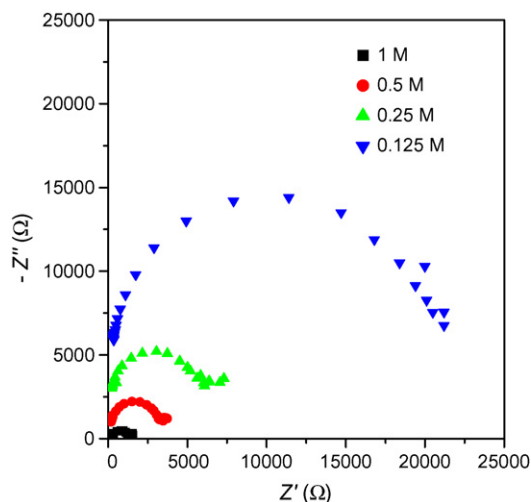

Fig. 4. Cyclic voltammogram of LiCoO$_2$ thin film electrode deposited for 3 h in 1 mol dm^{-3} LiClO$_4$/PC. Scanning rate = 0.1 mV s^{-1}.

Fig. 6. Nyquist plots of LiCoO$_2$ thin film deposited for 1 h in 1.0, 0.5, 0.25 and 0.125 mol dm^{-3} LiClO$_4$/PC.

Fig. 8. Variation of the charge transfer resistance of an electrolyte/LiCoO$_2$ thin film [deposited for (a) 1 h and (b) 3 h] interface with the electrode potential.

centration. From Fig. 7, the assignment in the Nyquist plot is considered to be reasonable.

The effects of orientation on charge transfer resistance are shown in Fig. 8(a) and (b). *c*-axis-oriented and random-oriented films were used for Fig. 8(a) and (b), respectively. As shown in Fig. 8(a), charge transfer resistance appeared at around 3.9 V and then decreased drastically. Charge transfer resistance then remained constant up to 4.2 V and increased gradually. As shown in Fig. 8(b), the behavior of the charge transfer resistance of the random-oriented film is almost similar to that of *c*-axis-oriented film, but the charge transfer resistance increased at a lower potential of 4.1 V. In addition to this difference in the onset potential when the charge transfer resistance increased, the values of the charge transfer resistance were also quite different. The minimum charge transfer resistance for *c*-axis-oriented film was 10-fold greater than that for random-oriented film. This large difference in charge transfer resistance was due to the orientation of LiCoO$_2$ thin films. In the present system, the resistance is affected by the number of active sites that Li-ions can inter-
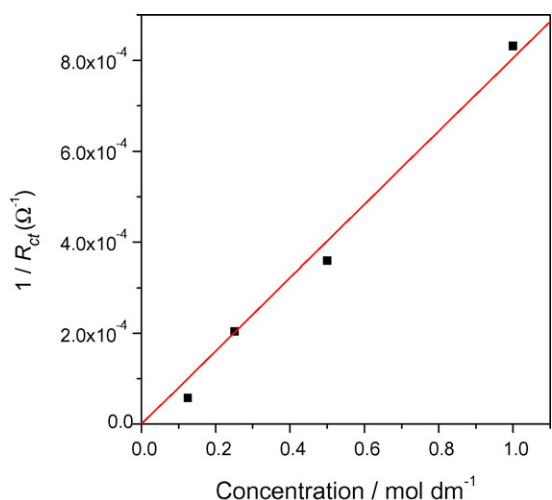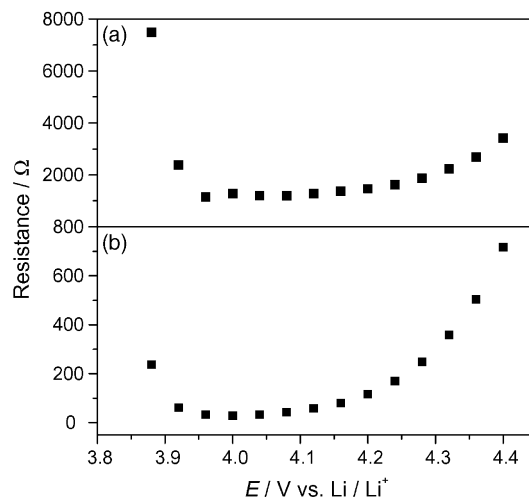
calate and de-intercalate at the LiCoO$_2$ thin film. Since the area of the working electrode is restricted by the o-ring, Li-ion can intercalate and de-intercalate only at defects on the film surface for *c*-axis-oriented film. On the other hand, random-oriented film has many active sites for Li-ion to intercalate/de-intercalate. Consequently, the charge transfer resistance of *c*-axis-oriented film was greater than that of random-oriented film. The number of active sites seems to influence the onset potential at which the charge transfer resistance increased. Once the charge transfer resistance increased at potentials above 4.2 V, the resistance did not decrease with a decrease in the electrode potential, indicating that an irreversible reaction such as electrolyte oxidation (decomposition) occurs at higher potentials [8]. This electrolyte decomposition should occur at active sites of LiCoO$_2$ thin film, and therefore electrolyte oxidation occurs more readily at more negative potentials when the random-oriented film is used.
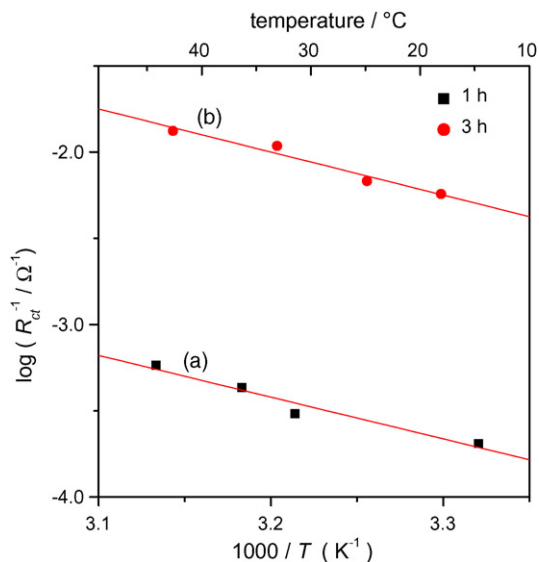

Fig. 9. Temperature-dependence of the charge transfer resistance of an electrolyte/LiCoO$_2$ thin film [deposited for (a) 1 h and (b) 3 h] interface vs. the electrode potential.

Fig. 7. Concentration-dependence of the reciprocal of charge transfer resistance.

Fig. 9 shows the temperature-dependence of the charge transfer resistance of *c*-axis-oriented $LiCoO_2$ thin film (squares) and random-oriented $LiCoO_2$ thin film (circles). By the least-squares method, the apparent activation energies for Li-ion transfer were determined to be 46 ± 7.3 kJmol^{-1} for *c*-axis-oriented thin film and 48 ± 6.1 kJmol^{-1} for random-oriented thin film at 4.10 V. The activation energies appeared to be almost the same regardless of the orientation of $LiCoO_2$. This result indicates that a high activation barrier exists at the $LiCoO_2$/electrolyte interface and the activation energy is not influenced by the orientation of the electrode materials. Our recent studies on large activation barriers at the electrode/electrolyte interface revealed that de-solvation is responsible for the activation energy [9–11]. Therefore, the present results seem to be quite valid.

4. Conclusion

Li-ion transfer at the interface between an electrolyte and $LiCoO_2$ thin films with different orientations was studied. The orientation of the $LiCoO_2$ thin film electrode strongly affects the charge transfer resistance, but does not affect the activation energy for charge transfer. These results indicate that the orientation may play an important role in decreasing the internal resistance in lithium ion batteries.

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