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Short communication

Impedance analysis of PLD $LiNi_{0.8}Co_{0.2}O_2$ film electrode

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Abstract

The kinetics of intercalation are discussed using a pulsed laser deposition (PLD) film electrode and electrochemical impedance analysis. Films of $LiNi_{0.8}Co_{0.2}O_2$, deposited on single crystal substrates, were used for the study. The films have intercalative or blocking orientations on different crystal surfaces of the substrates. Impedance spectra show that there are at least three elemental processes in intercalation. Two processes at higher frequencies suggest that they occur at the electrode surface and are influenced by the orientation of the film. The third process appearing at low frequencies below 1 Hz indicates lithium motion in the bulk structure and shows the largest resistance among the three processes. This lithium conduction in a thin PLD film shows a semicircular response and is considered to be influenced more by the structure due to the nanometer-scale thickness.

Keywords: Intercalation; Impedance; Pulsed laser deposition; Epitaxial film

1. Introduction

Enhancement of electrode reaction speed is important in lithium ion batteries in order to develop novel high-power devices and to achieve high energy conversion efficiencies. Growing consciousness of safety concerns is also promoting research and development of all solid-state batteries. Since the reaction speed at the solid–solid interface is significantly slow, kinetic studies of the electrode reaction are gaining in importance.

The problem in kinetic studies using ceramic electrodes lies in the complexity of precisely describing structures of the electrode and the interface with the electrolyte. Structural parameters include the crystal structure of the material, the size of the primary particles, agglomeration of particles, distribution of electrode components, conduction paths of electrons and ions, and morphology of the interface. These parameters have an effect on each other and the reaction speed is determined as a total response including all of these parameters. The analysis of individual parameters is practically impossible and kinetic studies in many cases become empirical.

As one approach towards solving this problem, preparation of a pulsed laser deposition (PLD) film is beneficial under the concept of simplification or idealization of the electrode system. It is possible to prepare oxides epitaxially on a single crystal substrate by laser ablation deposition [1–4]. The film forms as a single crystal or an oriented polycrystal, depending on the mismatch between the film and substrate. In both cases, however, the structure is much simpler and more appropriate for kinetic study than a conventional electrode system. The crystal orientation of the film can be controlled by the surface atomic structure of the substrate [1,4–6]. In this article, kinetic parameters of intercalation for a $LiNi_{0.8}Co_{0.2}O_2$ PLD electrode were measured by the electrochemical impedance method [7–11], and the effects of crystal orientation on these parameters are discussed.

2. Experimental

Atomic proportions of Li_2CO_3, $Ni(OH)_2$ and Co_3O_4 in 15:24:2, were weighed for the preparation of $LiNi_{0.8}Co_{0.2}O_2$. This mixture was calcined at 600 °C for 6 h. After milling the resultant material, it was fired again at a temperature of 725 °C for 24 h to complete the reaction. The structure was confirmed by XRD, and a sintered pellet of the material was used as a target for laser ablation deposition.

A single-crystal of Nb-doped $SrTiO_3$ (STO) was used as the substrate. The substrate also functions as a current collector for the working electrode. Flat square plates with dimensions of 10 mm × 10 mm × 0.5 mm were sliced from the ingot for (1 1 0)

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or (1 1 1) crystal planes of STO to appear. The flatness of the surface was less than 15 angstroms.

The ablation of $LiNi_{0.8}Co_{0.2}O_2$ was performed using a KrF excimer laser (248 nm). The laser power was adjusted to 250 mJ and the pulse irradiation frequency was 10 Hz. The substrate temperature was held at 600 °C during deposition. The oxygen pressure in the ablation chamber was maintained at 3.3 Pa. The distance between the substrate and the target was 7.5 cm. The deposition was carried out for 60 min.

The preparation and structural characterization of the epitaxial PLD films were carried out by Kanno and co-workers of Tokyo Institute of Technology. A paper giving details on the preparation and structural characterization is in preparation and will be published in the near future.

Impedance spectra were measured, in order to obtain kinetic information, using a Solartron 1260 Frequency Response Analyzer with a 1287 Electrochemical Interface. Three electrode test cells with lithium reference and counter electrodes were used for the measurements. The impedance measurements were carried out by applying 10 mV of ac current in the range of 10^6–10^{-3} Hz.

3. Results and discussion

Thin-film X-ray diffraction patterns were measured, as shown in Fig. 1, to discuss the crystal structure of the ablated films. The $LiNi_{0.8}Co_{0.2}O_2$ electrode on STO(1 1 0) shows a 110 diffraction peak near 60° in 2θ. The active material in this case has intercalative orientation for lithium ions in the electrolyte. Another $LiNi_{0.8}Co_{0.2}O_2$ electrode on STO(1 1 1) shows a series of 00ℓ diffractions. Thus, the active material orders the basal planes parallel to the surface of the substrate. The film in this case shows a blocking effect against lithium intercalation. It was confirmed that these films are epitaxially grown on a single crystal substrate.

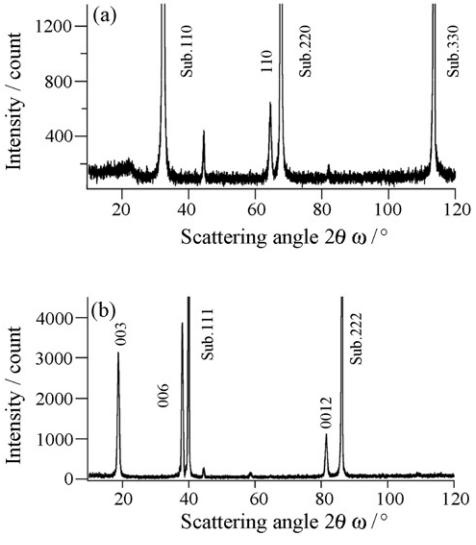

Fig. 1. XRD patterns of ablation films deposited on Nb-doped $SrTiO_3$ substrate. (a) $LiNi_{0.8}Co_{0.2}O_2$ film on (1 1 0) crystal plane of STO and denoted as an intercalative film. (b) $LiNi_{0.8}Co_{0.2}O_2$ film on (1 1 1) crystal plane of STO and denoted as a blocking film.

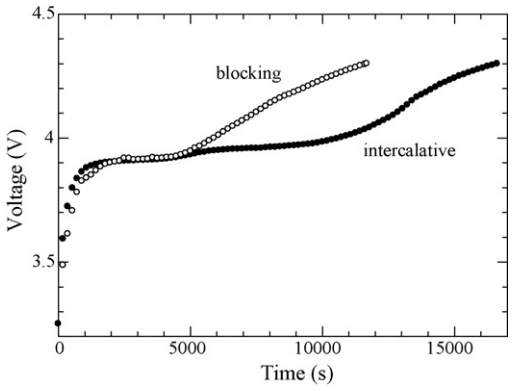

Fig. 2. Constant current charge curves of $LiNi_{0.8}Co_{0.2}O_2$ films on STO(1 1 0) and (1 1 1) substrates. The former is indicated as intercalative and the latter is indicated as blocking.

The charge profiles at a constant current density are shown in Fig. 2. The shapes and potentials of these curves are similar to those of the powder $LiNi_{0.8}Co_{0.2}O_2$ electrode. The difference in coulombic capacities is considered to occur by the different crystal orientations of the $LiNi_{0.8}Co_{0.2}O_2$ films.

Impedance spectra of $LiNi_{0.8}Co_{0.2}O_2$ electrodes on STO(1 1 0) and STO(1 1 1) in Fig. 3 shows similar profiles,

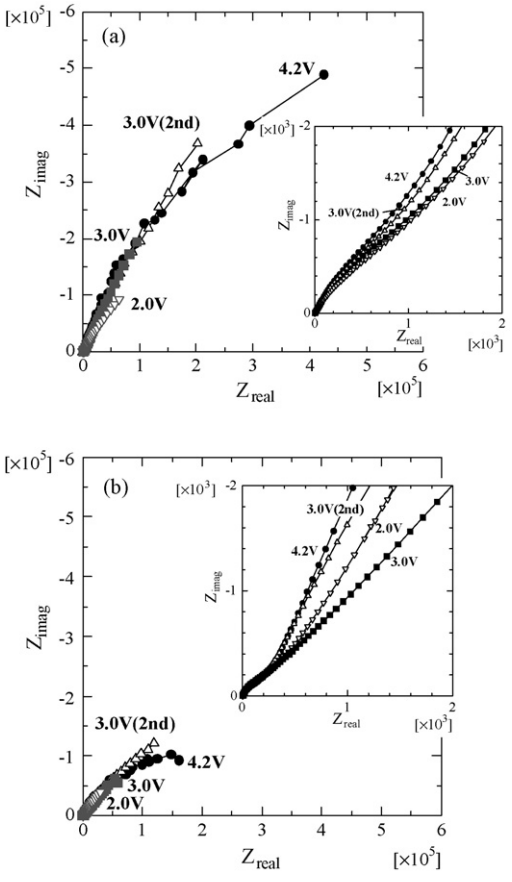

Fig. 3. Complex plane impedance plots for (a) $LiNi_{0.8}Co_{0.2}O_2$ films on STO(1 1 0) and (b) (1 1 1) substrates. The whole spectra show frequencies ranging from 10^6 to 10^{-3} Hz. The insets show the enlarged high frequency region. The numbers beside the curves show the potentiostatic equilibrated cell voltage.