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Characterization of electrode/electrolyte interface using *in situ* X-ray reflectometry and $LiNi_{0.8}Co_{0.2}O_2$ epitaxial film electrode synthesized by pulsed laser deposition method

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Abstract

An *in situ* experimental technique was developed for detecting structure changes at the electrode/electrolyte interface of lithium cell using synchrotron X-ray reflectometry and two-dimensional model electrodes with a restricted lattice plane. The electrode was constructed with an epitaxial film of $LiNi_{0.8}Co_{0.2}O_2$ synthesized by the pulsed laser deposition method. The orientation of the epitaxial film depends on the substrate plane; the 2D layer of $LiNi_{0.8}Co_{0.2}O_2$ is parallel to the $SrTiO_3$ (1 1 1) substrate ($(0\,0\,3)_{LiCo_{0.2}Ni_{0.8}O_2}//(1\,1\,1)SrTiO_3$), while the 2D layer is perpendicular to the $SrTiO_3$ (1 1 0) substrate ($(1\,1\,0)_{LiCo_{0.2}Ni_{0.8}O_2}//(1\,1\,0)SrTiO_3$). These films provided an ideal reaction field suitable for detecting structure changes at the electrode/electrolyte interface during the electrochemical reaction. The X-ray reflectometry indicated a formation of a thin-film layer at the $LiNi_{0.8}Co_{0.2}O_2$ (1 1 0)/electrolyte interface during the first charge–discharge cycle, while the $LiNi_{0.8}Co_{0.2}O_2$ (0 0 3) surface showed an increase in the surface roughness without forming the surface thin-film layer. The reaction mechanism at the electrode/electrolyte interface is discussed based on our new experimental technique for lithium batteries.
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Keywords: Epitaxial thin film; Lithium battery; Cathode materials; SEI layer; Reflectivity

1. Introduction

Since the lithium-ion configuration composed of carbon anodes and intercalation cathodes has been widely accepted for lithium secondary batteries, significant efforts have been devoted to attain high energy and power densities to produce an excellent energy storage system [1]. In particular, recent progress in pure electric vehicles (EV) and hybrid electric vehicles (HEV) require high power density operation for the current battery systems. Power characteristics of the battery systems are closely related to the nature of electrode reaction, which is composed of several steps proceeded in series: lithium diffusion in the electrolyte, adsorption of solvated lithium on the cathode surface, de-solvation, surface diffusion, charge-transfer reaction, intercalation from the surface to the bulk, and the bulk diffusion of lithium in the electrode material. Recent electrochemical studies have claimed that the de-solvation process was proposed to be a rate-determining step of the whole electrode reaction [2,3].

The chemical and electrochemical side reactions, which are detrimental to the safety, calendar life, and cycle life of lithium-ion batteries also occur at the electrode/electrolyte interface. It is well known that electrode surfaces are almost covered with a passive surface layer, which is generally called the solid electrolyte interface (SEI). The idea of the SEI layer was originally introduced on the alkali and alkaline earth metal in organic electrolytes [4]. The formation of the SEI phase on negative

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electrodes that are polarized below electrolyte reduction potential is a well-known phenomenon for lithium-ion batteries [4,5]. Inactive surface films have also been observed on the positive electrode; but less is known about the formation mechanisms of these films [6,7]. Although surface layers on both positive and negative electrodes can protect the electrode from further reactions with the electrolyte, they create a barrier for Li^+ ions during electrochemical charge/discharge cycling. This barrier increases cell impedance and decreases cycling efficiency of the battery.

Among the materials proposed for positive electrodes, lithium nickel–cobalt oxide with the layered rocksalt structure is a current electrode candidate for a HEV system [8]. Previous studies on lithium-ion batteries using lithium nickel cobalt oxide indicated that the positive electrode impedance was the main component of cell impedance rise during room-temperature storage [9], and charge-transfer resistance at the electrode/electrolyte interface was identified as the main contributor to the impedance increase. Surface characterization such as X-ray photoelectron spectroscopy indicated a formation of the SEI phase composed of a mixture of organic species that included polycarbonates and lithium fluoride, lithium phosphorus-type and lithium phosphorus fluoride oxide-type compounds [10,11]. From these observations, charge-transfer resistance at the positive-electrode/electrolyte interface, has been shown to be the main contributor to impedance rise in lithium-ion cells.

Previous studies on the electrode/electrolyte interface were based on polycrystalline materials, which contain the effects of many parameters; for example, surface structure, surface morphology, surface defect, grain boundary, and even a reaction between the electrode and electrolyte. Then, the system might not be suitable for clarifying electrode reaction mechanism. Furthermore, most of the experimental results on the interface were obtained by *ex situ* observation such as XPS [12–15], infrared spectroscopy [6,16], NMR [17], and ellipsometry [18], where the electrode surfaces were studied after the battery reactions. However, there are very few experimental techniques, which allow direct observation of the electrode/electrolyte interface during the electrochemical reactions.

X-ray reflectivity method is one of the best experimental techniques to detect the electrode surface during the electrochemical reactions. However, the electrode surface should be flat with a roughness of ∼1 nm, and it was only applied for ideal electrode system such as under potential deposition (UPD) process [19–21]. Our approach is to clarify the reactions at the interface of the intercalation electrode of lithium batteries with developing new experimental setup for ideal two-dimensional electrodes for practical battery systems.

In the present study, we tried to design an ideal electrode suitable for investigating interfacial reactions at the two-dimensional electrode surface. The epitaxial thin-films of cathode material, $LiNi_{0.8}Co_{0.2}O_2$, were successfully synthesized on single crystal substrates, $SrTiO_3$, by the pulsed laser deposition (PLD) method. These films were characterized by the thin-film X-ray diffraction method (XRD). We developed experimental techniques, *in situ* X-ray reflectometry, to investigate the surface reaction during the lithium (de)intercalation process. The relationship between the surface reaction and the electrochemical property is discussed based on our preliminary results of reflectivity data.

2. Experimental

$LiNi_{0.8}Co_{0.2}O_2$ films were grown using a KrF excimer laser with a wavelength of 248 nm under O_2 and a pulsed laser deposition (PLD) apparatus, PLD 3000 (PVD products, Inc.). The substrate used was single crystals of Nb-doped $SrTiO_3$ (0.5% Nb, 10 mm × 10 mm × 5 mm size). The conductivity of the substrate was $5.28 \times 10^{-3}\ \Omega$ cm at room temperature. The orientations of the substrate crystals were (1 1 1), (1 1 0), and (1 0 0) for $SrTiO_3$. The substrates were washed with ultra pure water and annealed at 1000 °C. The targets for the PLD process were synthesized by sintering starting materials at high temperatures. Li_2CO_3, NiO, and Co_3O_4 were used for the starting materials. The target had an excess lithium composition (Li/M = 1.0–1.3, M = 0.8Ni 0.2Co) to compensate a lithium loss during the PLD process. The lattice parameters of the targets were a = 2.8660(3) and c = 14.1666(8) Å, which are consistent with the ICSD (# 83302) values of a = 2.8676 and c = 14.1689 Å. For the PLD experiments, we changed oxygen pressure, laser power, laser frequency, distance between target and substrate, the substrate orientations, and synthesis temperatures. Thin-film X-ray diffraction data were recorded by a thin-film X-ray diffractometer, ATX-G (Rigaku) with Cu $K\alpha_1$ radiation. The orientation of the films were characterized both by the out-of-plane and in-plane techniques. The thickness, density, and roughness of the films were determined by X-ray reflectivity measurement using a thin-film X-ray diffractometer (ATX-G, Cu $K\alpha$) in air. The surface morphology and roughness of the films was investigated by atomic force microscopy (AFM, Digital Instruments Nanoscope IV).

The charge–discharge characteristics of the epitaxial films were examined with lithium cell using lithium metal as an anode. The cut-off voltages were 3.0 and 4.3 V. The electrolyte was EC (ethylene carbonate)–DEC (di-ethyl carbonate) with a molar ratio of 3:7 as a solvent and a supporting electrolyte of 1 M $LiPF_6$. The charge–discharge current was 100 nA.

The surface structure changes of the electrode were measured by *ex situ* X-ray reflectivity (XRR) measurements, after the film was soaked into the electrolyte, or after the lithium cell was constructed. The surface changes during the electrochemical reactions were observed by *in situ* XRR with synchrotron X-rays and an *in situ* X-ray/electrochemical cell in transmission geometry. The cell was mounted on the theta stage of a κ-type six-circle diffractometer (Newport) installed on a bending-magnet beamline BL14B1 at SPring-8. The X-rays were monochromated by the Si (1 1 1) double crystal system and focused by two Rh-coated bent mirrors. The beam size of the incident X-ray was 0.1 mm (vertical) × 0.4–1.0 mm (horizontal), which was adjusted by a slit placed in front of the sample. The angular acceptance of the receiving slit was 2 mrad for the 2θ direction and 20 mrad for the χ direction. A wavelength of 1.09886 Å was selected for penetrating X-rays through the organic solvent used

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