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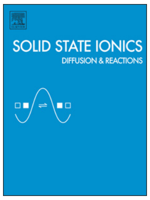

Preparation and *in-situ* characterization of well-defined solid electrolyte/electrode interfaces in thin-film lithium batteries

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ABSTRACT

An all-in-vacuum (*in-vacuo*) fabrication and evaluation system for thin-film all-solid-state lithium batteries was designed and constructed. To prepare clean solid electrolyte/electrode interfaces, ultra-high-vacuum (UHV) chambers for the deposition of cathode, electrolyte, and anode thin films were directly connected to each other. Thus, throughout the fabrication and evaluation, the samples were maintained under UHV conditions, not exposed to air. The thin-film lithium battery, with a clean and well-defined solid electrolyte/electrode interface, exhibited very good electrochemical properties even without post-deposition annealing. This performance is attributed to the clean solid electrolyte/electrode interface prepared in the vacuum.

1. Introduction

All-solid-state lithium batteries using an inorganic solid electrolyte are expected to become next-generation batteries owing to their safety, large capacity, and high potential window compared with present lithium-ion batteries based on liquid organic electrolytes [1,2]. One of the largest drawbacks for the practical use of all-solid-state batteries is the large internal resistance at the solid electrolyte and electrode interfaces, which strongly influences the electrochemical properties of the batteries. Although the improvement of the ionic conductivity at the electrolyte/electrode interface by coating the electrode materials with buffer layers has been reported in bulk-type all-solid-state batteries [3–5], the origin of the interface resistance during the Li-ion conduction has not yet been clarified. This is because quantitative microscopic analysis of the ionic conduction across the interface is extremely difficult, as the interface area, crystal structures, and orientations have not been defined for bulk-type batteries composed of powders.

A well-defined thin-film-stack Li/solid electrolyte/electrode interface, i.e., an all-solid-state thin-film lithium battery, is an ideal platform for fundamental studies [6–14], particularly for examining the Li-ion conductivity at electrolyte/electrode interfaces in batteries. Investigations of the origin of the interface resistance at solid electrolyte/electrode interfaces become possible with the controlled crystal orientation and/or a defined interface area provided by thin-film growth techniques. Kuwata et al. fabricated thin-film lithium batteries and estimated the charge-transfer resistance at a $Li_3PO_4/LiCoO_2$ (LCO) interface [10]. Furthermore, Iriyama et al. reported that annealing treatment drastically reduced the interface resistance [8,9]. These works clearly demonstrate the validity of thin-film batteries for the quantitative analysis of the ionic conductivity at electrolyte/electrode interfaces. However, even for thin-film lithium batteries, the details of the ionic conductivity mechanism at the electrolyte/electrode interface are not understood. This is because in previous studies, thin-film batteries were exposed to air during the fabrication process and subjected to annealing treatment, yielding ambiguity regarding the atomic structure of the interface. If a surface of the electrode was exposed to air before the deposition of the solid electrolyte, contaminants such as hydrocarbon and reacted layers should function as a resistive layer or non-active interface for the Li-ion conduction. To gain further insight into the intrinsic Li-ion-conducting mechanism, the preparation of a "clean" and "well-defined" electrolyte/electrode interface is crucial. To this end, the fabrication of the electrolyte/electrode interface in an ultra-high vacuum (UHV) is required to prevent adsorption or reaction with H_2O, N_2, or CO_2 at the surface and interface of thin films.

In the present paper, we report the fabrication and *in-situ* characterization of clean and well-defined solid electrolyte/electrode interfaces in thin-film lithium batteries using an all-in-vacuum (*in-vacuo*) system. To ensure clean interfaces, all the UHV chambers for film deposition and evaluation were directly connected to each other, and thus, the batteries

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were not exposed to air at any time during the preparation or evaluation processes. We first report details regarding the set-up of our apparatus and then describe the fabrication process for the batteries used. Subsequently, we discuss the electrochemical properties of the batteries, which indicate a stable battery operation with a superior cyclability. The most significant part of our work is that we successfully prepared clean electrolyte/electrode interfaces and investigated the chemical states at the interfaces. These studies of ideal clean interfaces using an all-in-UHV deposition/evaluation system provide a deeper understanding of the ionic conductivity at the electrolyte/electrode interface, which is a key concern for advanced all-solid-state batteries.

2. Results and discussions

2.1. Construction of in-vacuo thin-film lithium battery fabrication/evaluation system

We first report the construction of the *in-vacuo* thin-film lithium battery fabrication/evaluation system. Fig. 1(a) shows the system set-up of our apparatus. The thin-film deposition system is composed of four chambers: a pulsed-laser-deposition (PLD) system for the electrode materials (LCO, in this study), RF and DC magnetron sputter deposition systems for the $Li_3PO_{4-x}N_x$ (LiPON) electrolyte and Au current collector, respectively, and a Li metal thermal evaporation system. The deposition chambers were maintained in a high vacuum; the background pressure of the PLD chamber was $\sim 1 \times 10^{-7}$ Pa. All the deposition chambers were connected to a UHV ($\leq 10^{-8}$ Pa) chamber equipped with a linear sample transfer system. The transfer system, capable of metal mask exchange, carries six samples with metal masks, which can be transferred to evaluation chambers (a four-probe electrical measurement system and a photoemission system; $\leq 10^{-8}$ Pa) through a vacuum. A sample substrate was fixed onto a substrate holder compatible with an Omicron sample holder; the substrate holder was then placed onto the mask holder. When changing masks in a vacuum chamber, the substrate holder was set to different mask holders stored in the linear transfer chamber.

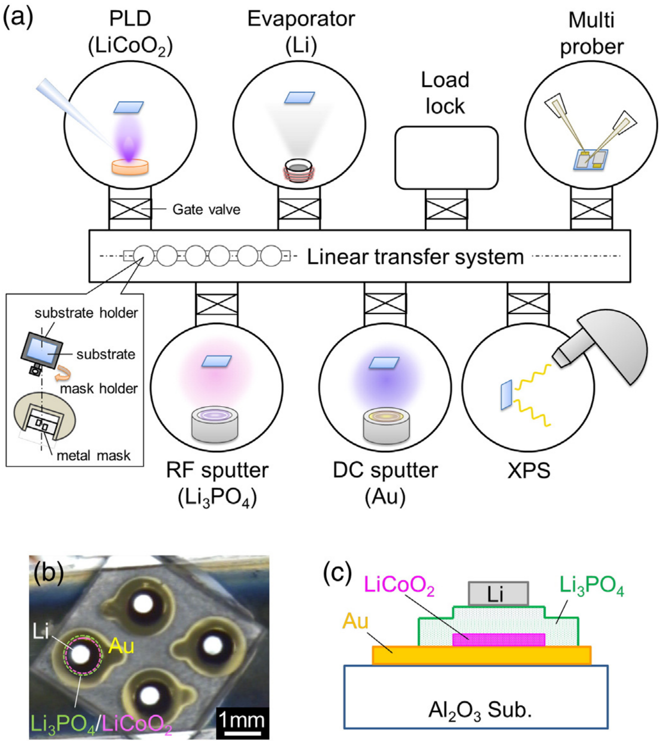

Fig. 1. (a) Schematic of all-in-vacuum fabrication/evaluation system and (b) microscope photograph and (c) schematic cross-sectional view of thin-film battery.

For the battery fabrication, we prepared four types of masks made of stainless steel (SUS 304) or Inconel 600. The Li anode pattern was designed to have a smaller area than the LCO cathode pattern (Fig. 1(b)) in order to evaluate the interface resistance even if the metal masks were misaligned. For the Li anode deposition, an Inconel mask annealed in air at 1000 °C was used. This annealing turned the surface of the mask into an insulator, and thus, the short circuiting of the Li with the cathode via the metal mask was avoided.

We typically used 5 × 5 mm substrates, on which four thin-film batteries with an active region of 0.2 mm^2 can be fabricated (circular shape with 0.25-mm diameter), as shown in Fig. 1(b). To minimize the probability of an internal short circuit originating from residual particles on the substrates, we employed a breakable substrate that could be cleaved along pre-existing breaking grooves (Shinkosha Co., Ltd. Japan). The breakable substrate prevented the adhesion of particles generated during the wheel-saw cutting process of the substrate.

The electrical property measurement system was configured to measure the charge/discharge curves, cyclic voltammetry (CV), and impedance spectra at sample temperatures ranging from 5 to 550 K. In this system, *x*, *y*, and *z* piezo linear actuators precisely positioned the probes on the thin-film device. Because the mechanical connections that conduct heat to the temperature-controlled sample region are minimal with the piezo-positioning device—that is, the connections are limited to electrical lines—the sample temperature could be reduced to 5 K. In order to avoid reactions between the probe tip and Li anode, we employed Ni-coated BeCu as probes.

Photoemission experiments were performed using a hemispherical electron spectrometer (VG Scienta R4000) with a wide-angle lens (WAL). Al Kα X-rays ($h\nu = 1486.8$ eV) were monochromatized by quartz single crystals and focused on a sample with a spot size of 1.5 × 3 mm. All X-ray photoelectron spectroscopy (XPS) data were taken using a transmission mode.

2.2. Preparation of thin-film lithium batteries

A schematic cross-sectional view of the fabricated thin-film lithium battery is presented in Fig. 1(c). A weakly (111)-oriented polycrystalline Au film as the current collector was first deposited on an unheated Al_2O_3(0001) single-crystal substrate using DC magnetron sputtering. To improve the orientation of the crystallites, the deposited Au film was transferred to the PLD chamber and then annealed at 600 °C for 10 min in a vacuum by heating the substrate holder using an infrared laser. The annealed Au film exhibited a (111) orientation with a rocking-curve full width at half maximum (FWHM) of 1.7°. The in-plane orientation was found to be randomly oriented, as confirmed by in-plane X-ray diffraction (XRD) measurements.

On this (111)-oriented Au layer, an LCO film was deposited as a cathode using PLD [15,16]. During the deposition of the LCO film, the substrate was maintained at 400 °C with an oxygen partial pressure of 0.13 Pa. A sintered ceramic target with a Li-rich composition of $Li_{1.2}CoO_2$ (Toshima Manufacturing Co., Ltd., Japan) was used to compensate for the loss of Li during the deposition. A KrF excimer laser (wavelength of 248 nm) was irradiated at a repetition rate of 5 Hz with an energy density of 1.0 J cm^{-2} on the target.

Subsequently, the LCO film was covered with a solid electrolyte layer of LiPON deposited using RF magnetron sputtering at room temperature. The LiPON was deposited in a N_2 atmosphere of 0.5 Pa using a 2-in. Li_3PO_4 target. The RF power was fixed at 100 W because the LiPON film was frequently peeled from the Al_2O_3 substrate with the removal of the LCO film above 200 W. The sputtering deposition was conducted in an off-axis configuration; the vertical distance between the target and substrate was 55 mm, and the horizontal distance was 45 mm [17].

Finally, a metallic Li film for the anode was deposited on the LiPON layer using a conventional evaporation method. We measured the thickness of the Au, $LiCoO_2$, and LiPON layers with a stylus profiler

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