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Microstructure and electrochemical properties of the HT-LiCoO₂/La_{2/3-x}Li_{3x}TiO₃ solid electrolyte interfaces

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Three different types of HT-LiCoO₂/lithium lanthanum titanate (LLT) assemblies were produced by depositing an HT-LiCoO₂ cathode on polycrystalline LLT with various surface finishes, to investigate the effects of the HT-LiCoO₂/LLT interface structure on the electrochemical properties of the assemblies. An amorphous layer is confirmed to be introduced by Ar ion irradiation to crystalline LLT. The HT-LiCoO₂/LLT assembly composed of the ion-irradiated LLT exhibits good cycle stability and relatively low apparent interface resistivity. These results indicate that the introduction of an amorphous LLT layer by surface modification of crystalline LLT is very effective in improving the structural stability and lithium-ion conductivity of the interface between HT-LiCoO₂ and crystalline LLT.

I. INTRODUCTION

All-solid-state lithium secondary batteries have great advantages over currently-used lithium secondary batteries containing flammable liquid electrolyte in terms of safety, thermal stability, and resistance to shock and vibration.¹⁻⁶ Because of such attractive properties, they have been considered as promising candidates for future application fields including large scale batteries used in electrical vehicle and power load leveling applications. In the case of the all-solid-state batteries, the interface structure between the electrode and solid electrolyte is considered to have a great influence on battery performance such as resistivity and mechanical stability of the interface between solid-electrode and solid-electrolyte upon charging and discharging. However, the relationship between the microstructures of the interface and electrochemical properties has not been investigated in detail. Recently, we have investigated the influence of the microstructure of the solid cathode/solid electrolyte interface on electrochemical properties using model

assemblies composed of a high-temperature modification of LiCoO₂ (HT-LiCoO₂) cathode with a layered rock-salt type rhombohedral structure and a perovskite-based lithium lanthanum titanate (LLT: La_{2/3-x}Li_{3x}TiO₃) solid electrolyte.^{7,8} Our previous results suggest that the resistivity as well as the mechanical stability of the interface can be controlled mainly by two factors, namely the introduction of nanoscale defect regions such as amorphous LLT at the interface; and the geometrical configuration of Li layers in the crystal structure of HT-LiCoO₂ with respect to the interface plane.^{7,8} In the present study, we prepare various model assemblies each composed of HT-LiCoO₂ cathode thin film deposited on polycrystalline LLT solid electrolyte with different types of surface finishes. We investigate microstructures of the HT-LiCoO₂/LLT interfaces and their influence on the electrochemical properties of the model assemblies to get insight into ways to improve battery performance by surface modification of the crystalline solid electrolyte.

II. EXPERIMENTAL PROCEDURE

Polycrystalline specimens of LLT were prepared by conventional solid-state reaction. High purity reagents

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of La₂O₃ (99.99%), Li₂CO₃ (99.99%), and TiO₂ (99.9%) were mixed in the metal ratio of La:Li:Ti = 0.5:0.5:1 in a planetary ball mill with acetone for 2 h. The mixed reagent was calcined at 800 °C for 4 h and heat-treated at 1150 °C for 12 h. The calcined material was then ground up, pressed into rods, and sintered at 1350 °C for 6 h in air. The metal ratio of the as-sintered material was determined by induction coupled plasma (ICP) analysis to be La:Li:Ti = 0.483:0.490:1.00. Thin-plate specimens with a thickness of 1 mm were cut from the as-sintered materials. Three different types of HT-LiCoO₂/LLT assemblies (positive-side half-cells) were prepared by depositing HT-LiCoO₂ cathode on one side of sintered LLT with various surface finishes, (i) cleaved, (ii) mechanically polished with 1 μm diamond paste, and (iii) Ar-ion-irradiated under various conditions with Gatan PECS. These three types of assemblies are hereafter assigned as cleaved, polished, and ion-irradiated specimens, respectively. The deposition of HT-LiCoO₂ was made by the pulsed laser deposition (PLD) method using the target material of Li_{1.4}CoO₂, with an LLT substrate temperature of 700 °C, and an oxygen pressure of 27 Pa. Pt coating was finally made by RF magnetron sputtering on top of the HT-LiCoO₂ cathode for measurements of electrochemical properties.

The electrochemical properties were investigated by cyclic voltammetry (CV) performed at a constant scan rate of 0.1 mVs⁻¹ in the potential range of 3.2–4.3 V (for cleaved and polished specimens) and 3.5–4.2 V (for ion-irradiated specimens) versus Li/Li⁺ using a Hokuto Denko HSV-100 potentiometer (Tokyo, Japan). Three-electrode electrochemical cells with lithium metal sheets as reference electrode and counterelectrode were used for CV tests. A liquid electrolyte composed of 1 M LiClO₄ in propylene carbonate was used for the negative electrode side of the test cells. All electrochemical experiments were conducted in an argon-filled glove box at room temperature. Microstructures were investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) with JEOL JSM-5300 (Tokyo, Japan) and Philips CM200FEG (Eindhoven, The Netherlands), respectively.

III. RESULTS AND DISCUSSION

A. Microstructure of the finished surfaces of crystalline LLT

Figure 1 shows SEM micrographs of the finished surface of crystalline LLT. As seen in Fig. 1(a), the cleaved surfaces possess roughness comparable to the grain size of LLT (a few microns). In contrast to the cleaved surface, the polished surface is relatively flat and smooth with some minor scratches introduced during the mechanical polishing process [Fig. 1(b)]. Most of this minor damage on the polished surface can be removed by fur-

ther Ar-ion irradiation, which results in the greatest degree of flatness and smoothness among the three surface finishes, as shown in Fig. 1(c).

B. Interface microstructures between HT-LiCoO₂ cathode and LLT electrolyte

Figure 2 shows high-resolution TEM (HRTEM) images of the interface regions in cleaved and polished specimens. In the cases of the cleaved and polished specimens, the HT-LiCoO₂ thin film cathode is deposited epitaxially on LLT with orientation relationships of (110)_{LLT}//(11 $\bar{2}$ 0)_{LiCoO₂} and [111]_{LLT}//[0001]_{LiCoO₂}.^{7,8} In the HRTEM images for the cleaved and polished specimens, the lattice images are thus obtained clearly from both HT-LiCoO₂ and LLT phases. Of importance to note in the HRTEM image for the polished specimen [Fig. 2(b)] is that there are some amorphous regions formed at the interface, while neither amorphous regions nor intermediate phases are seen at the interface in the cleaved specimen [Fig. 2(a)]. Our preliminary experiment by energy-filtering TEM confirms the existence

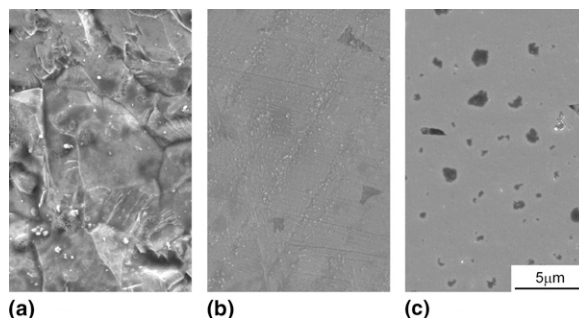


FIG. 1. SEM micrographs of (a) cleaved, (b) polished, and (c) ion-irradiated surfaces of crystalline LLT.

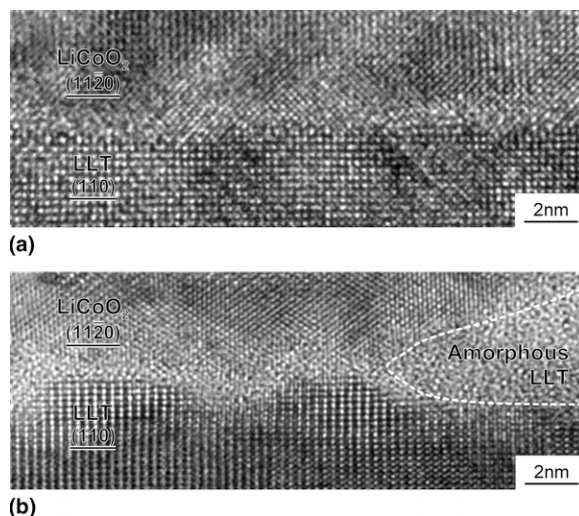


FIG. 2. High resolution TEM images of the interface between the HT-LiCoO₂ cathode and LLT electrolyte in (a) cleaved and (b) polished specimens.

of La and Ti but the absence of Co in the amorphous regions, which suggests that the amorphous regions are the LLT phase formed on the surface of crystalline LLT as a result of mechanical polishing. Since the amorphous LLT regions exist in places at the interface, HT-LiCoO₂ is considered to nucleate epitaxially on the remaining crystalline LLT regions.

An amorphous layer is also confirmed to exist at the interface of the ion-irradiated specimen, as shown in Fig. 3. The thickness of the amorphous layer varies with irradiation condition. If Ar ion irradiation is made perpendicular to the surface of crystalline LLT, an amorphous layer with a relatively uniform thickness of about 10 nm is formed, as shown in Fig. 3(a). Because of the thick amorphous layer, the orientation relationships between HT-LiCoO₂ and LLT phases no longer exist in this case. If Ar ion irradiation is made at an inclined angle (30°) for the surface of the LLT electrolyte for a short period of time (1 min), an amorphous layer with a thickness of a few atomic widths is observed and the exact same orientation relationships between HT-LiCoO₂ and LLT phases are observed [Fig. 3(b)]. Our preliminary surface analysis by x-ray photoelectron spectroscopy (XPS) confirms that the chemical composition of the Ar-ion irradiated surfaces after heat treatment at 700 °C for 2 h, which is comparable to the condition of PLD deposition of HT-LiCoO₂, is almost identical to that of the cleaved LLT surface. This indicates that the amorphous layers introduced by Ar ion-irradiation are also of the LLT phase. It is important to note that the amorphous LLT layer is maintained without crystallization after heat treatment, which is comparable to the condition of PLD deposition of the HT-LiCoO₂ phase. This indicates a relatively high thermal stability of the amorphous LLT

introduced by the surface treatment of crystalline LLT by Ar-ion irradiation.

C. Cyclic voltammetry

Figure 4 compares cyclic voltammograms (CV) measured for the cleaved, polished, and ion-irradiated specimens. The ion irradiated specimen corresponds to that shown in Fig. 3(b) with a thin amorphous LLT layer. In each voltammogram, three anodic peaks (denoted as A, B, and C) and corresponding cathodic peaks are observed. The major anodic peak A at around 3.9 V has been reported to correspond to a first-order phase transition between two different types of rhombohedral phases.⁹ The minor anodic peaks B and C correspond to a phase transition from rhombohedral to monoclinic phases and from monoclinic to another rhombohedral phase, respectively.⁹ The cleaved specimen exhibits the anodic and cathodic peaks shifting to higher and lower potentials, respectively, with the number of cycles. This indicates the low cyclic stability resulting from the increasing interface resistance with charge-discharge cycles [Fig. 4(a)]. SEM observations for the cleaved specimen revealed that some parts of HT-LiCoO₂ thin film had peeled off from the LLT electrolyte after three CV cycles, resulting in an increase in the apparent LLT/LiCoO₂ interface resistance and low cyclic stability.⁷ In contrast, the peak potentials for the anodic and cathodic reactions observed in the cyclic voltammograms for the polished and ion-irradiated specimens do not change much during three cycles of potential sweeps [Figs. 4(b) and 4(c)], indicating that these two specimens have higher stability upon insertion and extraction of lithium ion through the HT-LiCoO₂/LLT interface than the cleaved specimen does. As can be clearly seen from the figure, the peak separation between the major anodic and cathodic peaks in the CV for the ion-irradiated specimen is smaller than the peak separation for the polished specimen. Since both the crystalline LLT electrolytes and HT-LiCoO₂ cathodes in these two specimens are virtually identical from the viewpoint of microstructure, such a difference in the peak separation is likely to correspond mainly to the difference in the apparent interface resistivity between the HT-LiCoO₂ cathode and LLT electrolyte, that is, the apparent interface resistivity for the ion-irradiated specimen with a thin amorphous LLT layer is expected to be lower than that for the polished specimen. As confirmed by HRTEM observations, morphology and amount of amorphous LLT are the major differences between these two specimens.

The existence of regions or a layer of amorphous LLT at the interface introduces three different types of interfaces, namely (i) HT-LiCoO₂/crystalline LLT, (ii) HT-LiCoO₂/amorphous LLT, and (iii) crystalline LLT/amorphous LLT. The apparent interface resistivity appeared as the

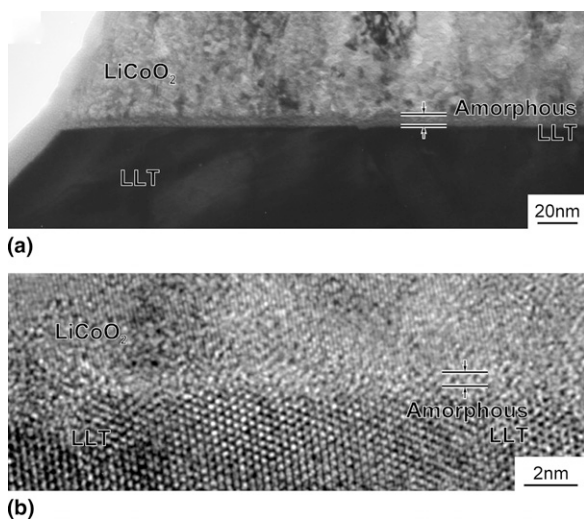


FIG. 3. Microstructure of the interface between the HT-LiCoO₂ cathode and LLT electrolyte in ion-irradiated specimens. Ar ion irradiation is made (a) perpendicular and (b) inclined at an angle of 30° to the surface of crystalline LLT.

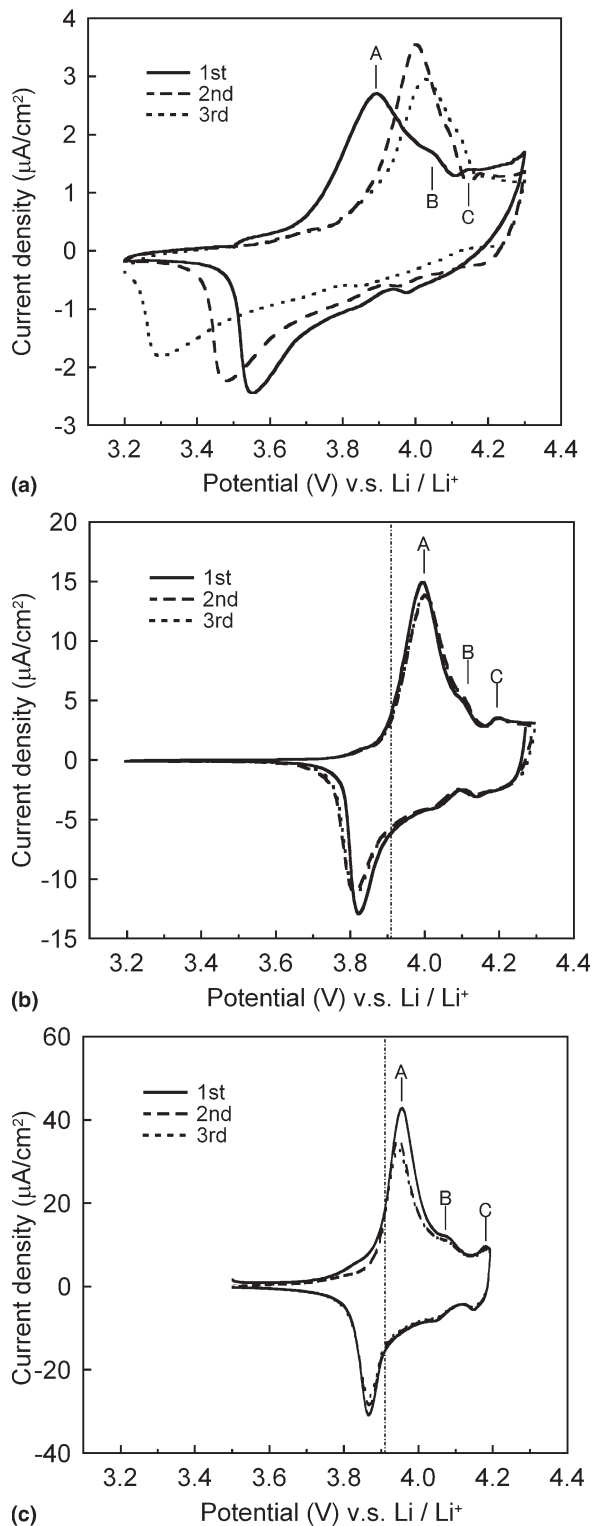


FIG. 4. Cyclic voltammograms for (a) cleaved, (b) polished, and (c) ion-irradiated specimens.

peak separation in CV test is then considered to reflect the lithium ion permeability through these three types of interfaces and also the lithium ion diffusivity in amorphous LLT. Although the exact values of the lithium ion perme-

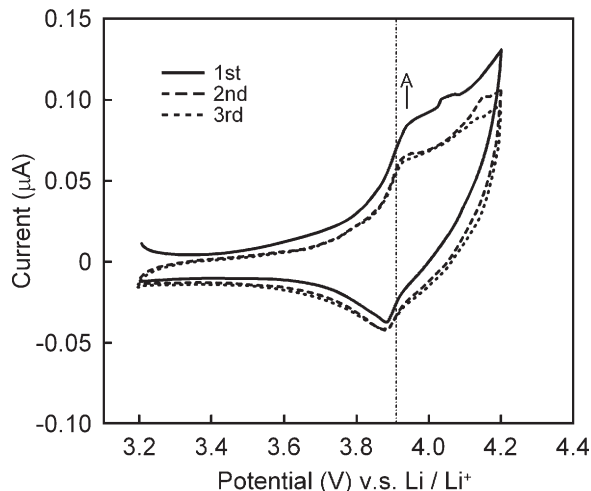


FIG. 5. Cyclic voltammograms for the cleaved specimen with an additional Ar-ion irradiation made perpendicular to the LLT surface.

ability for these interfaces were not able to be determined from the results of CV tests, the smaller peak separation observed for the ion-irradiated specimen with a thin amorphous LLT interface layer suggests that the actual lithium ion permeability across the latter two types of crystalline/amorphous interfaces is much lower than that across the first type of crystalline/crystalline interface. Thus, it can be concluded that the existence of the amorphous LLT regions at the interface plays a beneficial role in mechanically stabilizing the interface and reducing the apparent interface resistivity for the lithium ionic transport upon charge/discharge operations, when compared to the cleaved specimen. In order to further confirm the beneficial effects of Ar ion irradiation for improving interface stability, the surface of a cleaved specimen was treated by Ar-ion irradiation. Because of the roughness of the cleaved surface [Fig. 1(a)], Ar ion irradiation was made perpendicular to the surface so as to form an amorphous LLT layer on the whole surface. The irradiation condition was set identical to that used for the specimen shown in Fig. 3(a) so that the amorphous layer is relatively thick (~10 nm). Figure 5 shows the CV measurement for the cleaved specimen subjected to an additional Ar-ion irradiation. As seen from the figure, the separation between the major anodic and cathodic peaks is small, and the peak positions do not change much over three CV cycles, indicating successful improvement of interface stability as well as lithium-ion permeability through the interface. It can thus be concluded the surface modification of crystalline LLT by Ar-ion irradiation is quite effective in improving the interface properties between the HT-LiCoO₂ cathode and LLT electrolytes.

IV. CONCLUSIONS

The effects of the surface finishes of crystalline LLT on the electrochemical properties were studied using three different types of HT-LiCoO₂/LLT assemblies. In

the case of the polished and ion-irradiated specimens, an amorphous LLT layer exists on the interface between HT-LiCoO₂ and LLT. With the increase in the interface area covered with amorphous LLT, the separation of the major anodic and cathodic peaks in CV decreases, indicating that the formation of an amorphous LLT layer at the interface is beneficial to the decrease in the apparent resistance to lithium-ion permeation through the interface. The introduction of an amorphous layer by surface modification of crystalline LLT is thus found to be beneficial in improving the interface resistivity as well as the mechanical stability of the HT-LiCoO₂/LLT interface.

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