



Cycle stability increase by insertion of Li–La–Ta–O thin-film electrolyte between cathode and solid electrolyte for all-solid-state battery



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ABSTRACT

Recently, all-solid-state batteries (ASSBs) with an inorganic solid electrolyte have attracted significant interest because of their high potential for unique applications in space, deep sea, and radioactive environments. The inorganic solid electrolyte is one of the most fundamental parts since it determines the C rate and self-discharge properties. We prepared a series of ASSBs based on lithium lanthanum tantalum oxide (LLTO) solid-electrolyte thin films with thicknesses of 0, 100, and 200 nm by radio frequency (RF) magnetron sputtering. The microstructure and composition of the LLTO thin films were investigated by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and inductively coupled plasma atomic emission spectroscopy (ICP-AES). The results show that the LLTO thin films have a high ionic conductivity, and they reduce the contact resistance between the cathode and the solid electrolyte, and increase the ion path between the cathode and the bulk electrolyte. Thus, they can be applied to ASSBs as an interlayer between the cathode and the solid electrolyte.

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1. Introduction

The development of solid electrolytes for all-solid-state lithium ion batteries has received significant attention in the attempt to overcome the several problems presented by lithium ion batteries, such as flammability and self-discharge [1]. Recently, perovskite-structured $\text{Li}_{0.35}\text{La}_{0.55}\text{TiO}_3$ (LLT) [2,3], NASICON-structured $\text{LiTi}_2(\text{PO}_4)_3$ (LTP) [4,5], and garnet-structured $\text{Li}_7\text{La}_3\text{Ta}_2\text{O}_{12}$ (LLTO) [6,7] with a crystalline structure have been developed for the use in all-solid-state lithium ion batteries. However, these solid electrolytes have an ionic conductivity in the range of 10^{-4} – 10^{-5} S/cm, which is relatively low when compared with that of the liquid electrolytes (10^{-1} S/cm) [8]. Therefore, many studies on crystalline structured solid electrolytes have been conducted to increase the ionic conductivities in relation to their application in all-solid-state lithium ion batteries.

Solid electrolytes with a high ionic conductivity, low electronic conductivity, and good electrochemical stability are highly needed for all-solid state batteries (ASSBs). However, the titanium contained in the LLT or LTP solid electrolytes has a narrow electrochemical window and poor stability in relation to the energy and power densities of the ASSBs because of the reduction of Ti^{4+} at the interface between the solid electrolyte and the cathode [9].

In the last few decades, garnet-structured electrolytes have been investigated as super ionic conductors [10,11]. In particular, $\text{Li}_5\text{La}_3\text{Ta}_2\text{O}_{12}$ (LLTO) and $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) with high electrochemical stability in contact with lithium metal have been developed [12,13]. However,

bulk-type solid electrolytes, including garnet-structured electrolytes, still present a serious problem: the high contact resistance between the cathode and the electrolyte. Several studies have been conducted regarding the increase of ionic conductivity in solid electrolytes [14–16]. However, only a few studies have focused on the decrease of the contact resistance between the cathode and the bulk electrolyte. Recently, garnet-structured thin-film electrolytes fabricated by RF magnetron sputtering were investigated [17,18]. Bulk type solid electrolyte has relatively high ionic conductivity comparing with thin film electrolyte for ASSB. However, bulk type all-solid-state battery has high contact resistance at the interface between cathode materials and bulk electrolyte. This can make very serious problem to increase the irreversible capacity. On the other hand, thin-film electrolytes may exhibit a decrease of the contact resistance, due to covered a void of bulk materials and increased chemical bonding with bulk materials [19].

In this study, we show that an LLTO thin-film electrolyte between the cathode and the solid electrolyte can improve the cell performance by decreasing the contact resistance with the cathode.

2. Experimental procedure

The LLTO powder for the bulk solid electrolyte was prepared using LiOH (Aldrich, 99%, anhydrous), Ta_2O_5 (Aldrich, 99.9%), and La_2O_3 (Aldrich, 99.99%) as starting materials. The powder was mixed in stoichiometric amounts (20 wt.% LiOH excess was used) and then milled for 8–12 h in 2-propanol in a planetary ball mill with zirconia balls and grinding bowls. The annealing process for the crystallization of the LLTO was conducted at 900 °C for 12 h. The LLTO powder was annealed three times for 12 h alternating with ball milling steps. The

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LLTO powder was compressed by cold-press at 500 kg/cm² and sintered for 6 h at 1200 °C to prepare the LLTO target necessary to fabricate the LLTO thin film by sputtering process.

The LLTO thin film was deposited by an on-axis-type RF magnetron sputtering system using the LLTO target with a composition of Li₅La₃Ta₂O₁₂ in argon gas (Ar) with a purity of 99.999%. Before deposition, the LLTO target surface was pre-sputtered using Ar ion plasma at an RF sputtering power of 100 W to eliminate the oxide layer or any other contamination on the LLTO target surface. During the LLTO thin film deposition, the working pressure was 8×10^{-3} Torr and the applied RF power was 50 W.

X-ray diffraction (XRD, Rigaku RINT) measurements of LLTO target and thin films with Cu K α 1 radiation were performed to investigate the crystal structures and phases. The diffraction data were carried out over a 2 θ range from 20° to 80° at a scan rate of 2°/min. The composition of the LLTO film was analyzed by X-ray photoelectron spectroscopy (XPS, K-alpha, Thermo VG) and inductively coupled plasma atomic emission spectroscopy (ICP, Thermo Jarrell ASH, Polyscan 61E). The deposition rate of thin film was measured by scanning electron microscopy (FE-SEM, Hitachi S-4200). The measurement of the ionic conductivity was performed on a sandwich structure with top and bottom current collectors (CCs) (bottom CC/LLTO/top CC). Stainless steel (SUS: SS316) bottom and top CCs were deposited with SiO₂ coated Si substrates by direct-current (DC) magnetron sputtering with a 2-inch SUS target at room temperature. The SUS metal target had a purity of 99.99%. In addition, the Ar gas flow rate was maintained at a constant 30 sccm, the working pressure was 8×10^{-3} Torr and the DC power was 40 W (0.12 A). The deposition time and rate were 25 min and 23–24 nm/min, respectively. The final sandwich-structured cell was a multilayered structure of SUS/LLTO/SUS/SiO₂/Si and was measured at room temperature by electrochemical impedance spectroscopy (EIS, BioLogic EC-Lab VSP-300) analysis with frequency ranging from 1 MHz to 100 mHz. The stability of the interface between the cathode and the solid electrolyte was examined by high-resolution transmission electron microscopy (HR-TEM, JEM-2100 F, JEOL.) after current charge–discharge measurements.

The lithium cobalt oxide (LiCoO₂, LCO) cathode layer for the ASSB was fabricated using LCO powder (Sigma Aldrich) with a particle size of 10 μ m by a hot-press system at 250 °C under 500 kg/cm² for 1 h. The mold size is 12 π , and the thickness of LCO cathode layers was 120 μ m approximately. The SUS mesh current collector was used as the bottom current collector. The bulk LLTO electrolyte on the LCO layer with the LLTO thin-film electrolyte was also fabricated by hot-press method in the same conditions as the LCO cathode layer. Finally,

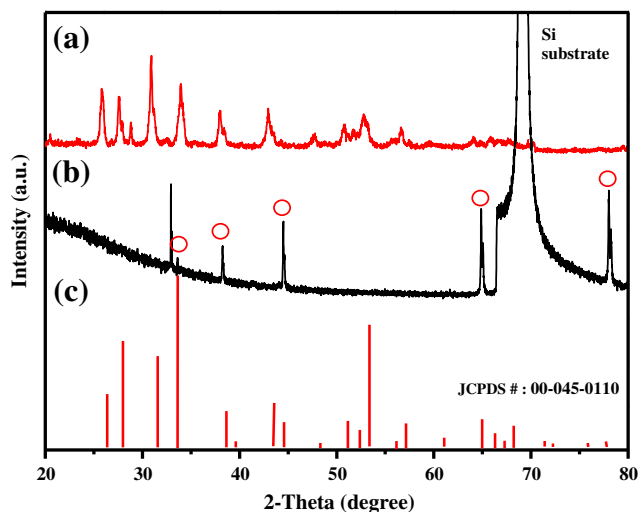


Fig. 1. X-ray diffraction patterns of the (a) LLTO target (b) LLTO thin film, and (c) JCPDS peaks of the LLTO (Li₅La₃Ta₂O₁₂).

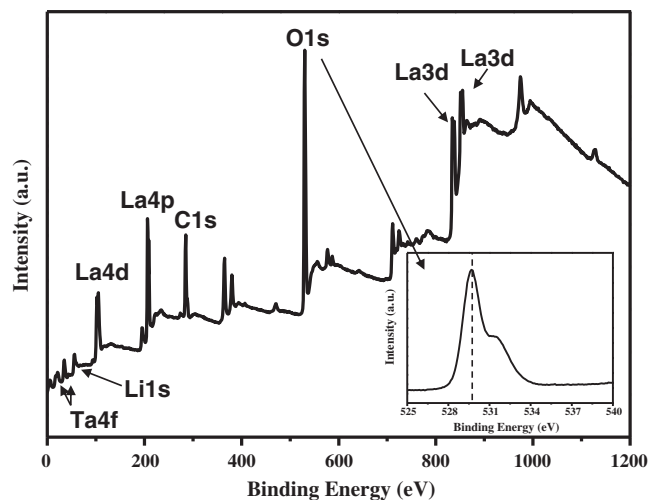


Fig. 2. XPS wide scan spectra of the LLTO thin film.

the lithium anode was deposited by thermal evaporation. This full cell was measured in a glove box filled with Ar gas. The cross-section of the full cell was examined with an optical microscope (OM, BIT-M). Constant current charge–discharge measurements were performed using a battery cycler system (WBC-3000, Wonatech).

3. Results and discussion

Fig. 1 shows the XRD spectra of the (a) LLTO target and (b) LLTO thin film, and (c) the JCPDS peaks of the LLTO with a composition of Li₅La₃Ta₂O₁₂. The LLTO target, as shown in Fig. 1(a), shows some sharp diffraction peaks belonging to the garnet-structured LLTO phase (Fig. 1(c)). Fig. 1(b) shows the XRD spectrum of the LLTO thin film and silicon wafer substrate. LLTO thin film except peak of the substrate generated at 70° can be observed as the microcrystalline peaks. The stoichiometry was changed due to the rearrangement of the atoms during the sputtering. The XRD spectrum of the LLTO thin film includes the peaks of the (332) facet (33.6°), (521) facet (38.2°), (620) facet (44.5°), (840) facet (64.8°), and (765) facet (78°). However, no sharp diffraction peaks belonging to the crystal are present. Therefore, the LLTO thin film obtained by RF magnetron sputtering presents a microcrystalline structure. Fig. 2 shows the XPS spectrum of the LLTO thin film. The spectrum consists of a series of peaks assigned to Li, La, Ta, and O. The peak at 284.8 eV was assigned to the adventitious C 1s as a

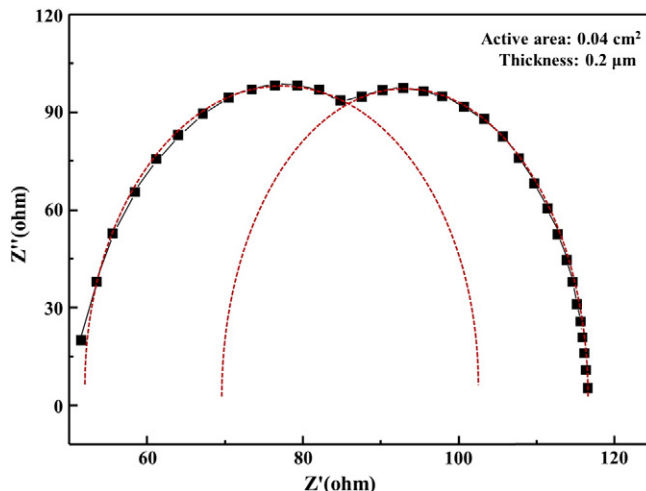


Fig. 3. Electrochemical impedance spectroscopy of the LLTO thin film.

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