Preparation of LiCoO₂ by Molten Salts on Li_{0.29}La_{0.57}TiO₃ Solid Electrolyte and Electrochemical Performances of the All-solid-state Li Secondary Battery

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ABSTRACT

An LiCoO₂ (LCO) phase is prepared on a perovskite type Li_{0.29}La_{0.57}TiO₃ (LLTO) solid electrolyte by heating mixed lithium salts of LiNO₃ and LiCl with Co(NO₃)₂·6H₂O at 700 °C for 1 h. The resultant LCO is evaluated as a positive electrode in an all-solid-state Li secondary battery. Liquid-phase sintering using molten salts has been effective for the formation of a favorable interface between oxides in which lithium ions migrate electrochemically with reversibility. The fracture surface revealed by field emission scanning electron microscopy observation shows that the microscopic texture of the LCO consists of a dense 1 to 2 μm thick layer closely attached to the solid electrolyte over a wide area, as well as LCO spherical particles with sizes of several micrometers. The former growth has superior electrochemical activity compared to the latter. Additionally, a preferential growth plane of the LCO on LLTO is analyzed by transmission electron microscopy and the process of formation with heating is described.

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1. Introduction

All-solid-state lithium secondary batteries (ASSBs) have received significant interest in recent years and challenging research is actively promoted in this field. ASSBs that use sulfide-based solid electrolytes are soon to come on the market as power sources for electrical vehicles.¹ ASSBs that use oxide-based electrolytes are in a different stage of development. The ionic conductivities of oxide-based electrolytes are a single or double magnitude lower than that of sulfide-based electrolytes and are confined around the range of $1 \times 10^{-4} \text{ S cm}^{-1}$ at room temperature. In addition, the formation of an interface between oxides requires heating at higher temperatures than sulfides due to an inevitable difference in the chemical bonding. Therefore, ASSBs that employ oxide-based electrolytes have been exclusively developed as thin film type and vapor deposition methods have been adopted for interface formation.^{2–5} However, the appearance of a solid electrolyte with a garnet type structure has again raised the expectations toward ASSBs with oxide-based electrolytes because of their excellent chemical stability and ease of

handling.^{6,7} Instead of physical vapor deposition methods, ceramic processing for the fabrication of a battery enables a wide range of applications for this type of battery.

Therefore, it is a challenging issue to form a rechargeable interface between oxides by wet-processing, along with a reduction of the interfacial resistance. One approach is to mix an active electrode material such as LiCoO₂ (LCO) with a low melting temperature compound such as Li₃BO₃.⁸ After preparation of a slurry that includes the electrode material, the solid electrolyte is then screen printed and sintered at 700 °C. The screen-printed LCO including Li₃BO₃ in the garnet-type solid electrolyte has exhibited good electrochemical performance and low interfacial resistance. Another approach is to use a solid electrolyte with thermoplasticity, such as the Li₃BO₃-Li₂SO₄ glass-ceramic.⁹ Even though the conductivity of the electrolyte is $1.4 \times 10^{-5} \text{ S cm}^{-1}$ at 25 °C, which is not high when compared to those of representative oxide-based electrolytes, a low heat treatment temperature such as 290 °C can be used, whereby favorable solid-solid contacts have been achieved. This work introduced a pivotal concept to obtain a chargeable interface in ASSBs.

However, both the electrodes mentioned include an ion-conducting assistant in the LCO positive electrode. The assistant material will affect the electrochemical properties, besides the interface between LCO and the solid electrolyte. Therefore, ASSBs

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that consist of only the LCO active material could provide critical information for further understanding of ASSBs.

An epitaxial LCO film on a SrTiO_3 substrate prepared by a sol-gel method has been reported.¹⁰ A solid-state cell of $\text{In-Li/Li}_{1.25}\text{Ge}_{0.25}\text{P}_{0.75}\text{S}_4/\text{LCO}$ showed a discharge capacity of ca. 80 mAh g^{-1} at C/50 rate and a similar result to that obtained by fabrication with pulsed laser deposition (PLD).⁴

We have focused on liquid-phase sintering using molten salts to form a charge/dischargeable interface between LCO and a sintered $\text{Li}_{0.29}\text{La}_{0.57}\text{TiO}_3$ (LLTO) solid electrolyte using conventional labware. This preparation method is expected to produce LCO with high crystallinity at lower temperatures on the solid electrolyte. Moderate reaction conditions are desirable, such as low temperature and short heating time, to suppress interdiffusion between the electrode and electrolyte materials. Therefore, starting materials with low melting points were adopted. The preparation of LCO with various molten salts on metals and the resultant electrochemical properties in liquid electrolytes have been reported in the literature.^{11–14} A thin film LCO electrode with a thickness of ca. $0.3 \mu\text{m}$ on an Au substrate was prepared by the oxidation of Co in molten carbonates at 650°C .¹¹ LCO powders were prepared from a eutectic mixture of LiCl and Li_2CO_3 salts with $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ at 800°C .¹² LCO with excess lithium was produced from the molten-salt of the LiNO_3 - LiCl eutectic at 850°C for 8 h and the electrochemical properties in a liquid electrolyte showed a reversible capacity of 167 mAh g^{-1} in the range 2.5–4.4 V.¹³ A dense-packed and idiomorphic LCO crystal layer was formed on a Pt substrate by flux coating with a LiNO_3 - LiOH mixed flux.¹⁴ All of these produced LCO electrodes were washed with distilled water to remove excess lithium salts.

The present paper describes the preparation of LCO from molten salts on an LLTO solid electrolyte and the resultant electrochemical properties for an all-solid-state Li secondary battery. The molten salts are used as a lithium source to obtain stoichiometric LCO, i.e., excess lithium salts are not used in the preparation, so that washing is not required. To focus on the interface of LCO and the LLTO oxide electrolyte, a Li ion-conducting sulfide electrolyte is inserted between the LLTO solid electrolyte and In-Li as a negative electrode to protect the reduction of LLTO by Li.

2. Experimental

The starting materials employed were LiNO_3 (>99.9%, Fujifilm Wako Chem.), LiCl (>99.9%, Fujifilm Wako Chem.), and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (>99.9%, Fujifilm Wako Chem.). A eutectic

mixture of LiNO_3 : LiCl in a molar ratio of 0.88 : 0.12 was used as the Li-source. The melting point of the Li salt eutectic mixture is 244°C . A stoichiometric mixture of the Li and Co salts was placed on a LLTO solid electrolyte (Toho Titanium Co., Ltd.) and was heated at temperatures from 500 to 700°C for 1 h in air. This procedure was repeated to obtain a thicker LCO. The ionic conductivity of the LLTO solid electrolyte is $6.8 \times 10^{-4} \text{ S cm}^{-1}$ at 27°C and $1.7 \times 10^{-3} \text{ S cm}^{-1}$ at 50°C , and the latter value corresponding to the temperature of the LLTO solid electrolyte is used for the present evaluation of all-solid-state batteries.¹⁵ X-ray diffraction (XRD) measurements were performed using $\text{CuK}\alpha$ radiation to identify the crystal phases (XRD-6100, Shimadzu Co., Ltd.). Raman spectra for the LCO surface were collected using laser Raman microscopy (RAMAN Touch, Nanophoton Co.). Field-emission scanning electron microscopy (FE-SEM; JSM-6700, JEOL) and transmission electron microscopy (TEM; JEM-ARM200F, JEOL) observations of the LCO surface and the interface of LCO with LLTO were conducted at 200 kV. The electrochemical properties of the LCO electrode on a 10 mm diameter LLTO solid electrolyte was examined with an all-solid-state cell tester. The weight of samples was measured by analytical balance (Balance XPE20, METTLER TOLEDO). The error is within 0.03 mg. The loading weight of LCO was obtained by the difference of the weight of LLTO and that of the sample including LCO and LLTO. The experimental error of specific capacity was in the range 1–2 mAh g^{-1} . Here, an In-Li alloy was used as the anode electrode. The electrode potential of the alloy is 0.62 V vs. Li^+/Li . $\text{Li}_{1.25}\text{Ge}_{0.25}\text{P}_{0.75}\text{S}_4$ powder was inserted between LLTO and Li-In to prevent the reduction of LLTO by Li and to assure the mobility of Li ions.¹⁶ Charge-discharge testing was conducted galvanostatically, with the current density fixed at C/100 rate, where a current of 137 mA g^{-1} was defined as 1 C-rate, in voltage ranges from 2.0 to 3.6 V or from 2.0 to 4.2 V. All measurements were conducted at 50°C .

3. Results and Discussion

The samples on LLTO were obtained by heating the starting materials at temperatures ranging from 500 to 700°C for 1 h and the XRD patterns are shown in Fig. 1. The Bragg peaks corresponding to the Co_3O_4 , low-temperature spinel-type phase of LCO (LT-LCO) and high-temperature LCO (HT-LCO) phases are overlapped due to their analogous lattice parameters.^{17–19} Except for the LLTO phase as a solid electrolyte, the Co_3O_4 phase was present in the sample heated at 500°C . The samples heated at 600 and 700°C contained a

Figure 1. XRD patterns for the samples prepared by heating the starting material at various temperatures, for used $\text{Li}_{0.29}\text{La}_{0.57}\text{TiO}_3$ substrate for solid electrolyte and for HT-LiCoO₂, LT-LiCoO₂ and Co_3O_4 collected from International Crystal Structure Database.^{17–19}

Figure 2. Raman spectra for LiCoO_2 on $\text{Li}_{0.29}\text{La}_{0.57}\text{TiO}_3$ prepared from molten salts at (a) 700 °C for 1 h and (b) 600 °C for 3 h.

high-temperature LCO (HT-LCO) phase and that at 700 °C had a single phase of HT-LCO. The calculated trigonal lattice parameters in a hexagonal setting were $a = b = 2.8174(12)$, $c = 14.0590(99)$ Å. Combined with the result of a sample heated at 900 °C, the relative intensity ratio of the Bragg peaks for I_{003}/I_{104} of LCO tended to increase with the sintering temperature.

To confirm the obtained phase from the local structure view point, microscopic Raman spectra were collected from the LCO surface on LLTO heated at 700 °C for 1 h and at 600 °C for 3 h, as shown in Figs. 2a and 2b, respectively. The entire region for both spectra corresponded to the HT-LCO phase. However, in the latter LCO a small amount of Co_3O_4 phase and LT-LCO were present in some places, which were not identified by XRD measurements. The bands at 450 and 685 cm^{-1} which correspond to LT-LCO and Co_3O_4 , respectively, can be seen clearly (Fig. 2b).²⁰ Co_3O_4 forms a dense layer before reacting with the decomposition products of the lithium salts. Subsequently, the lithium source may diffuse with a lithium concentration gradient and then react with Co_3O_4 , so that compositional deviation may be present on the LCO surface. For subsequent investigations, the mixture of $\text{LiNO}_3 : \text{LiCl} = 0.88 : 0.12$ and a heating condition of 700 °C for 1 h were employed.

Figures 3a and 3b show FE-SEM fracture surface and surface images for the sample heated at 700 °C for 1 h, respectively. The microstructure of LCO on LLTO is made up of two distinctive types; a dense 1 to 2 μm thick layer attached to LLTO and 3–4 μm diameter spherical particles next to the layer. The former dense layer consists of pillar-shaped particles that are closely bonded with each other. The heating of only $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ on LLTO at 300 °C produced a texture analogous to the dense layer. Consequently, the starting materials in the liquid state possibly lead to the formation of a dense layer below 300 °C. On the other hand, the spherical particles are aggregates comprised of primary particles with diameters of 0.1 μm , which form textures with plentiful porosity. Therefore, these two

Figure 3. FE-SEM images of (a) the fracture surface of the $\text{LiCoO}_2/\text{Li}_{0.29}\text{La}_{0.57}\text{TiO}_3$ interface and (b) the surface of LiCoO_2 prepared by molten salts at 700 °C for 1 h.

types of microstructures are attributable primarily to the fluidity of the molten salts of the starting materials. The LCO prepared from the molten salts was examined as a positive electrode material in an ASSB to evaluate the electrochemical activity. A LGPS powder was inserted between LLTO and the Li-In negative electrode to prevent the reduction of LLTO by Li. Electrochemical charge and discharge tests were conducted galvanostatically at 50 °C. The weight of LCO obtained by this preparation method is dependent on the amount of starting materials and the number of films formed. Figures 4a and 4b show charge and discharge curves for ASSBs with 2.3 and 7.0 mg cm^{-2} of LCO, respectively. The former showed a distinctive curve for LCO, except for the first cycle, with a reversible capacity of around 50 mAh g^{-1} . On the other hand, the thicker LCO electrode showed significant polarization, although a discharge capacity of 0.52 mAh cm^{-2} was obtained at 9.6 $\mu\text{A cm}^{-2}$; the thickness of the LCO was calculated to be ca. 14 μm based on the weight, surface area and density of LCO. Further investigation is required to clarify the large irreversible capacity observed at the 1st cycle.

The observed specific capacity increased with a decrease in the weight of LCO, which suggests that not all LCO participates in the electrochemical reactions, but that some of the LCO may have electrochemical activity. The optimized preparation conditions led to the development of a dense layer of LCO. LCO at 1.0 mg cm^{-2} could be obtained by removal of the LCO aggregates from the dense LCO layer. The results of charge and discharge testing are shown in

Figure 4. Charge-discharge curves for LiCoO₂ prepared from molten salts at 700 °C for 1 h in an ASSB at a current density of C/100 rate at 50 °C for LiCoO₂ at (a) 2.3 and (b) 7.0 mg cm⁻².

Figure 5. Charge-discharge curves for LiCoO₂ prepared from molten salts at 700 °C for 1 h in an ASSB at 50 °C with different cut-off voltages of (a) 2.0 to 3.6 V at 1.4 μA cm⁻² and (b) 2.0 to 4.2 V at 1.2 μA cm⁻².

Figure 6. Discharge curves for LiCoO₂ prepared from molten salts at 700 °C for 1 h in an ASSB at various current densities ranging from C/100 to C/2 rate at 50 °C.

close to the {104} plane. The faint spot that appears in between 102 and 000 is probably from 003 of the adjacent pillar, which may have rotated 180° in the {104} plane (that caused the same 104 spot). Several other SAED patterns all indicate that {104} is the preferential growth plane of the pillar-shaped LCO grains.

Previously reported preparations of LCO from molten salt have used a lithium salt as a flux and an excess amount of lithium.^{11–14}

Figure 7. (a, b) Cross-sectional BF TEM images of LiCoO₂ near the Li_{0.29}La_{0.57}TiO₃ interface, and (c) an SAED pattern of LiCoO₂.

However, in the present method, the lithium salts used as a lithium source were in stoichiometric amounts. It is likely that lithium is lost due to diffusion into the solid electrolyte or by vaporization. Based on the XRD measurements and thermochemical properties of each starting material, the mechanism for the formation of LCO by this preparation is proposed as follows. With heating, self-fluxing, dehydration and decomposition of Co-nitrate occur firstly and then Co₃O₄ is formed below 300 °C, whereas the same processes of the Li-salts occur at higher temperatures where Li₂O₂ is formed above 437 °C. Moreover, an apparent change was observed in the starting materials during heating from 25 to 500 °C using a hot plate. The liquid-state due to self-fluxing and melting disappeared at around 200 °C, and fluidity appeared again from 227 to 270 °C, which produced a froth or foam. A solid was then formed and it became black at around 462 °C. According to these changes, LCO is possibly formed by the following reaction:

However, this LCO is a low-temperature phase with a spinel type structure, which is known to be less electrochemically active than the high-temperature phase.^{20,21} Further heating causes LT-LCO to change into HT-LCO, a layered-NaCl type structure phase, as illustrated in Fig. 8.

Similarities between crystallographic axes for the crystal structures formed during heating may contribute to produce an interface between LCO and LLTO. The cubic lattice parameter of Co₃O₄ is $a = 8.072(3) \text{ \AA}$,¹⁹ and that of LT-LCO is $a = 7.994(1) \text{ \AA}$,¹⁸ whereas the tetragonal lattice parameters of LLTO are $a = b = 3.874 \text{ \AA}$, and $c = 7.746 \text{ \AA}$.¹⁵ By comparing with the c axis of LLTO and that of Co₃O₄, and that of LT-LCO, the difference is in the range 3.2–4.2 %. In addition, all these oxides are based on a close-packing of oxide ions. The molten salts in the liquid-state may support the

construction of a favorable interface between the oxides. As a result, an LCO layer with an electrochemically active phase is formed on the LLTO solid electrolyte. It can thus be concluded that liquid-phase sintering using molten salts is effective for the construction of a favorable interface between oxides in which lithium ions migrate electrochemically with reversibility.

4. Conclusions

A single phase of LCO was prepared on an LLTO solid electrolyte substrate by heating a starting material consisting of LiNO₃, LiCl, and Co(NO₃)₂·6H₂O at 700 °C for 1 h. The resultant LCO layer performed as a positive electrode in an all-solid-state Li secondary battery. The fracture surface revealed by FE-SEM observation showed that the microscopic texture of the LCO consisted of a dense 1 to 2 μm thick layer closely attached to the solid electrolyte over a wide range area and LCO spherical particles with sizes of several micrometers. A process for the formation of LCO was proposed, based on the oxides formed by decomposition of the salts.

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CRedit Authorship Contribution Statement

Naoto Katada: Data curation (Lead), Investigation (Lead), Writing – original draft (Lead)
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Yoshinori Arachi: Funding acquisition (Lead), Investigation (Supporting), Supervision (Lead), Writing – review & editing (Lead)
Kazutaka Mitsuishi: Data curation (Equal), Investigation (Equal)

Conflict of Interest

The authors declare no conflict of interest in the manuscript.

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Figure 8. Schematic illustration of the formation of LiCoO₂ by molten salts on Li_{0.29}La_{0.57}TiO₃ solid electrolyte.

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