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Electrochemical properties of an all-solid-state lithium-ion battery with an in-situ formed electrode material grown from a lithium conductive glass ceramics sheet

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HIGHLIGHTS

- Lithium insertion reaction into a lithium ion conductive solid electrolyte (LATP) sheet is investigated.
- Lithium insertion reaction into the LATP sheet occurs at 2.35 V (vs. Li/Li$^+$), which becomes in-situ formed electrode material.
- Charge transfer resistance at the in-situ formed electrode/LATP-sheet is less than 100 Ω cm^2.
- A multilayer of Pt/LATP-sheet/LiCoO$_2$/Au works as a battery operating at 1.5 V.
- The battery shows redox peak in the potential sweep curve even at 100 mV s^{-1} and stable charge-discharge reaction.

ARTICLE INFO

ABSTRACT

A lithium insertion reaction in a Li$^+$ conductive glass ceramics solid electrolyte (lithium aluminum titanium phosphate: LATP) sheet produces an in-situ formed electrode active material, which operates at 2.35 V vs. Li/Li$^+$ in the vicinity of the LATP-sheet/current–collector interface. Electron energy loss spectroscopy clarifies that titanium in the LATP sheet in the vicinity of the current collector/LATP-sheet interface is preferentially reduced by this lithium insertion reaction. Charge transfer resistance between the in-situ-formed-electrode and the LATP-sheet is less than 100 Ω cm^2, which is smaller than that of the common LiPON/LiCoO$_2$ interface. A thin film of LiCoO$_2$ is deposited on one side of the LATP-sheet as a Li$^+$ source for developing the in-situ formed electrode material. Eventually, a Pt/LATP-sheet/LiCoO$_2$/Au multilayer is fabricated. The multilayer structure successfully works as an all-solid-state lithium-ion battery operating at 1.5 V. A redox peak of the battery is observed even at 100 mV s^{-1} in the potential sweep curve. Additionally, charge–discharge reactions are repeated stably even after 25 cycles.

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1. Introduction

All-solid-state rechargeable lithium batteries (SSBs) using incombustible inorganic solid electrolytes are expected to be the next generation rechargeable batteries with greater safety and high energy density. However, a drawback of SSBs is their low power densities. One reason originates from the large interfacial resistances at the electrode/solid–electrolyte interfaces. Because electrodes and solid electrolytes are hard materials in general, they tend to have point contacts with each other, which inevitably reduce the number of electrochemical active sites at interfaces, thereby increasing interfacial resistance. Moreover, even if they have large contact areas, for example, using soft materials such as sulfide-based solid electrolytes, in some cases they react with each other, and a resistive mutual diffusion layer forms at the interfaces. An effective method to prevent the formation of a mutual diffusion layer is surface coating at the interface. Several coating materials have been proposed in various SSBs [1–4].

An alternative approach to remedy the interface problem is to directly grow electrode active materials from a solid electrolyte. Although lithium insertion reaction into a solid electrolyte is generally recognized as a reductive-side potential window for the solid electrolyte, it can also be considered as a formation of an electrode active material from a solid electrolyte. If an electrode active material can grow from a solid electrolyte and coexist, they should have a well-connected heterogeneous interface without a resistive mutual diffusion layer, leading to the formation of a low resistive electrode/solid−electrolyte interface.

Lithium insertion reaction process into solid electrolytes depends on the species of solid electrolytes. For example, perovskite-structured lanthanum lithium titanate (LLT) is well-known high Li^+ conductive solid electrolyte [5], but fast coloration of the entire LLT pellet occurs when a partial lithium insertion reaction into the LLT pellet is carried out [6]. Hence, it is difficult to create the coexistence of a parent solid electrolyte with a lithium inserted region. On the other hand, in the case of a Li^+ conductive glass ceramics solid electrolyte sheet based on NASICON-type structure $LiTi_2(PO_4)_3$ (LATP sheet; manufactured by OHARA Inc. Kanagawa, Japan) [7], lithium insertion reactions preferentially take place around solid-electrolyte/current−collector interface. Because the lithium inserted-regions (electrode active material) do not spread easily inside the parent LATP sheet (solid electrolyte) [8,9], this approach is regarded as more feasible compared to a method using LLT.

In previous work, we have focused on this latter case to date and have reported that an SSB using a partially lithium inserted LATP sheet as an electrode active material works as a battery [8,9]. However, because this electrode active material initially required a large irreversible capacity to be developed, our past works focused on the battery manufacturing process to prevent and/or apply this irreversible capacity. The aim of this work is to investigate the lithium insertion/extraction reaction into the LATP sheets. We especially focus on charge transfer reaction. We show that the in-situ-formed electrode/LATP-sheet interfacial resistance is reduced to less than $100 \ \Omega \ cm^2$, which is smaller than that of the common $LiCoO_2/LiPON$ interface ($\sim 150 \ \Omega \ cm^2$) [10]. Moreover, lower electronic conductivity of the in-situ-formed electrode active material tends to prevent the excessive growth of electrode material toward the LATP sheet, which restrains the irreversible capacity loss after the second cycle. Additionally, electrochemical properties of the Pt/LATP-sheet/$LiCoO_2$/Au multilayer are investigated.

2. Experimental

Mirror-polished LATP sheets [7] (150 μm in thickness) were used as solid electrolytes in this study. The Li^+ conductivity of the LATP sheet is $1 \times 10^{-4} \ S \ cm^{-1}$ at room temperature. The crystalline phase presented in the LATP sheet is a mixture of $Li_{1+x}Al_xGe_yTi_{2-x-y}P_2O_{12}$ (main-phase), $Li_{1+x+3z}Al_x(Ge,Ti)_{2-x}(Si_zPO_4)_3$ (sub-phase), and $AlPO_4$. The former two phases have been indexed using $LiTi_2(PO_4)_3$ with a NASICON-type structure in XRD. Details on this sheet have been precisely reported in other papers [11,12]. Thin films of $LiCoO_2$ were deposited on one side of the LATP sheet by pulsed laser deposition at 873 K for 1, 3, 5, and 8 h (the deposition rate is ~ 0.1 μm per hour). Then, thin films of platinum (Pt) or gold (Au) were covered on these film electrodes as current collectors by RF magnetron sputtering. The opposite side of the LATP sheet was covered with a Pt thin film. As will be described below, partial Li^+ insertion reaction into the LATP sheet near the Pt/LATP-sheet interface produces the in-situ-formed Li^+ insertion electrode active material. Thus, any electrode active material is not presented at Pt/LATP-sheet interface in pristine state.

Electrochemical properties of the two kinds of half-cells, that is, Pt/LATP-sheet and LATP-sheet/$LiCoO_2$/Pt, were measured by cyclic voltammetry (CV), charge-discharge reaction, and AC impedance spectroscopy at room temperature using a three-electrode cell. The bare side of the LATP sheet in each half cell was immersed in propylene carbonate containing $1 \ mol \ dm^{-3} \ LiClO_4$ (EL-PC), while the opposite Pt or $LiCoO_2$ side was mounted on a stainless steel substrate. Reference and counter electrodes were lithium (Li) immersed in the EL-PC. The electrochemical apparatus used in these experiments is schematically shown in Fig. 1. The LATP sheet is a liquid-tight sheet, and this cell configuration includes an interfacial Li^+ transfer reaction at the EL-PC/LATP-sheet interface. This interfacial resistance was investigated using a Li/EL-PC/LATP-sheet/EL-PC/Li symmetrical non-blocking electrode cell [13]. Hereafter, electrode potential of electrochemical properties using half cells will be referred to as the Li/Li^+. The electrochemical properties of a multilayer of Pt/LATP-sheet/$LiCoO_2$/Au (SSLIB) were measured in the same manner, but, in this case, the voltage of the SSLIB was measured. The electrode area of the Li/EL-PC/LATP-sheet/EL-PC/Li cell is $0.4 \ cm^2$, and that of other cells is $0.785 \ cm^2$.

Electron energy loss spectroscopy (EELS) analysis with a 200 kV transmission electron microscope (TEM, JEM-2100F) was performed to evaluate the electronic state of a transition metal element Ti included in the cycled LATP sheet. The Pt/LATP side of the SSLIB was partially thinned with a focused ion beam system (FIB, FB-2100), and the potential sweep measurement (sweep rate: $0.67 \ mV \ s^{-1}$) of the TEM sample was carried out in the TEM [14]. After the initial cycle, the TEM sample was maintained by a short circuit, and then the EELS spectra of Ti $L_{2,3}$-edge were obtained from the two points; one is approximately 1.5 μm apart from the Pt/LATP interface and the other is near the interface where the lower electric-potential was previously observed by electron holography [15].

3. Results and discussions

3.1. Electrochemical properties of the Pt/LATP-sheet half cell

Fig. 2(a) shows the CV of the lithium insertion/extraction reactions of the Pt/LATP-sheet half-cell:, a couple of redox peaks were observed at 2.35 V. This indicates that part of the LATP sheet works as an electrode active material [8,9]. This redox potential is nearly the same with $LiTi_2(PO_4)_3$ (LTP) where lithium insertion/extraction reactions take place at 2.5 V (vs. Li/Li^+) via a two-phase reaction between LTP and $Li_3Ti_2(PO_4)_3$ [16,17]. Fig. 2(b) shows initial lithium insertion/extraction curves of the LATP sheet. A potential plateau was observed near 2.35 V, and large irreversible capacity was observed. This indicates that the lithium-inserted region does not recover to the original solid electrolyte, thus, the LATP sheet is
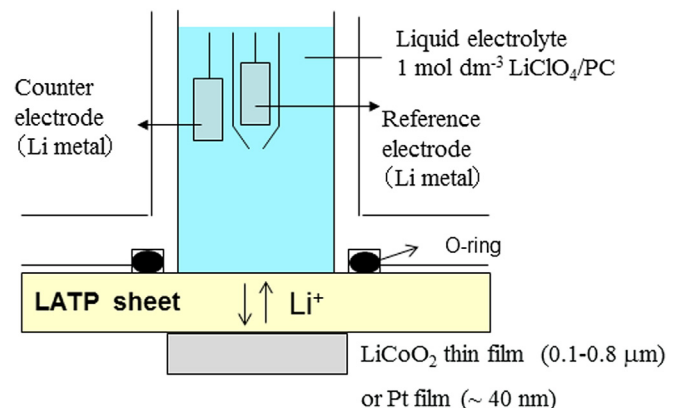

Fig. 1. Schematic image of an electrochemical measurement system for half-cells.