Bulk-Type All-Solid-State Lithium Secondary Battery with $\text{Li}_2\text{S-P}_2\text{S}_5$ Thin-Film Separator

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ABSTRACT

Bulk-type all-solid-state batteries currently use a compressed powder pellet with the thickness of several hundred micrometers as a solid electrolyte separator. In this study, all-solid-state lithium secondary batteries (In/LiCoO_2) with a thin $\text{Li}_2\text{S-P}_2\text{S}_5$ solid electrolyte separator were constructed; their charge-discharge performance was investigated. The all-solid-state batteries using the $\text{Li}_2\text{S-P}_2\text{S}_5$ separator with a thickness of 3 μm were charged and discharged with the capacity of 93 mAh g^{-1} . This result suggests that bulk-type all-solid-state batteries were successfully prepared with the solid electrolyte separator with several micrometer thicknesses.

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1. Introduction

Development of all-solid-state lithium secondary batteries using nonflammable inorganic materials as a solid electrolyte is desired. Two types of all-solid-state batteries have been studied. One is thin-film batteries and the other is bulk-type batteries. Thin-film batteries are composed of electrode and solid electrolyte films [Fig. 1(a)]. The thin-film batteries are expected as a power source for microdevices. In most cases, the thickness of electrode films is less than 10 micrometers. Thin-film batteries with thin electrodes and thin solid electrolytes showed good cycle performance.^{1–6} Bulk-type batteries are composed of composite electrodes of active material and solid electrolyte powders [Fig. 1(b)]. For application as a power source for large machines, bulk-type all-solid-state batteries are favorable. In the bulk-type batteries, lithium-ion conduction in the composite electrode strongly affects the battery performance.⁷ Therefore, solid electrolytes with high conductivity are required for bulk-type batteries. Sulfide-based solid electrolytes are a potential candidate as solid electrolytes for bulk-type batteries since they have remarkably high lithium-ion conductivity over $10^{-3} \text{ S cm}^{-1}$ at room temperature.^{8–13}

Bulk-type all-solid-state batteries typically use a compressed powder pellet with a thickness of several hundred micrometers as a solid electrolyte separator [Fig. 1(b)]. Figure 1(c) shows the schematic of all-solid-state batteries aimed in this study. Reduction of the thickness of the solid electrolyte separator is required for the improvement of the battery performance. The use of thin-film solid electrolyte will lead to the increase of energy density. For the authors' knowledge, there are no reports about bulk-type all-solid-state batteries based on thin solid electrolyte separator of several micrometer thicknesses. Thin $\text{Li}_2\text{S-P}_2\text{S}_5$ solid electrolyte films were prepared by the pulsed laser deposition (PLD) method and the obtained films showed a high lithium-ion conductivity of ca. $10^{-4} \text{ S cm}^{-1}$.¹⁴ From the fundamental point of view, the PLD films are useful to achieve a favorable solid-solid interface

between electrode and electrolyte in laboratory-scale all-solid-state batteries.

In this paper, the construction of all-solid-state lithium secondary batteries with a $\text{Li}_2\text{S-P}_2\text{S}_5$ thin-film separator and their charge-discharge tests are reported.

Figure 1. (Color online) Schematic illustrations of (a) thin-film and (b) bulk-type all-solid-state lithium secondary batteries, and (c) bulk-type all-solid-state lithium secondary battery with a solid-electrolyte thin-film separator.

Figure 2. (Color online) SEM images and EDX mappings for P, S, and Co elements of the cross section of compressed composite positive electrode (PE) coated with $\text{Li}_2\text{S-P}_2\text{S}_5$ solid-electrolyte thin-film separator (SE separator).

2. Experimental

The mixture of a LiNbO_3 -coated LiCoO_2 electrode¹⁵ and an $80\text{Li}_2\text{S-}20\text{P}_2\text{S}_5$ solid electrolyte¹⁰ with the weight ratio of 70:30 was pressed into a pellet to obtain pelletized composite electrodes. A surface of the pelletized composite electrodes was coated with an $80\text{Li}_2\text{S-}20\text{P}_2\text{S}_5$ (mol%) solid electrolyte thin-film. The thin films of the $80\text{Li}_2\text{S-}20\text{P}_2\text{S}_5$ solid electrolyte were fabricated using PLD with a KrF excimer laser ($\lambda = 248 \text{ nm}$, LPXPro, Lambda Physik).¹⁴ The pulse energy was 200 mJ/pulse and the repeating frequency was 10 Hz. The energy density of the focused laser beam was estimated as about 2 J/cm^2 at the target. Argon gas (99.99%) was used as an ambient gas; the argon gas pressure was 5 Pa. The distance from the target to the substrate was 7 cm. The pelletized mixture of Li_2S (99.9%, Idemitsu Kosan) and P_2S_5 crystalline powder (99%, Aldrich) with a molar ratio of 80:20 was used as a target without sintering. Deposition was conducted at room temperature. An indium negative electrode foil was attached to the solid-electrolyte thin-film separator to construct all-solid-state batteries.

3. Results and Discussion

Figure 2 shows SEM images and EDX mappings for P, S, and Co elements of the cross section of the compressed composite electrode coated with $\text{Li}_2\text{S-P}_2\text{S}_5$ solid electrolyte films. The composite electrode is the mixture of a LiCoO_2 active material and a $\text{Li}_2\text{S-P}_2\text{S}_5$ solid electrolyte. The dispersion of the LiCoO_2 active material and the $\text{Li}_2\text{S-P}_2\text{S}_5$ solid electrolyte was observed in the EDX mappings of the composite electrode. A layer of the thickness of about $3 \mu\text{m}$ was observed in the magnified SEM image. The layer is composed of P and S, indicating that the layer is the $\text{Li}_2\text{S-P}_2\text{S}_5$ solid electrolyte. The thickness of the solid electrolyte separator of conventional bulk-type all-solid-state batteries [Fig. 1(b)] was approximately several hundred micrometers. The thickness of the solid electrolyte separator is reduced to ca. 1/100 in this study. The SEM images also show that the thickness of the composite positive

Figure 3. (Color online) Charge-discharge curves for the 1st and 10th cycles of the all-solid-state batteries (In/ LiCoO_2) using the $\text{Li}_2\text{S-P}_2\text{S}_5$ solid electrolyte separator with the thickness of $3 \mu\text{m}$. The used current density was 0.25 mA cm^{-2} (0.2 C).

electrode is approximately $50 \mu\text{m}$. It was also confirmed that the surface of the pellets was covered with the solid electrolyte film by SEM-EDX observation (not shown here). The $\text{Li}_2\text{S-P}_2\text{S}_5$ solid electrolyte film was uniformly formed on the composite electrode layer.

An all-solid-state cell was constructed by attaching an indium foil as a negative electrode on the $\text{Li}_2\text{S-P}_2\text{S}_5$ thin-film separator. The current collectors for both positive and negative electrodes were stainless steels. Figure 3 shows charge-discharge curves for the 1st and 10th cycles of the all-solid-state batteries using the $\text{Li}_2\text{S-P}_2\text{S}_5$ separator with the thickness of $3 \mu\text{m}$. A current density for charging

and discharging was 0.25 mA cm^{-2} and an operation temperature was 25°C . The all-solid-state batteries reversibly charged and discharged with the capacities of 93 mAh g^{-1} for the 1st cycle and 88 mAh g^{-1} for the 10th cycle. The capacity was calculated from the weight of LiCoO_2 particles. The coulomb efficiencies for the 1st and 10th cycles were 93 and 97%, respectively. As shown in Fig. 1(b), usual bulk-type all-solid-state cells typically use a compressed powder pellet as a solid electrolyte separator with a thickness of several hundred micrometers. This is the first report on achievement of charge and discharge in bulk type all-solid-state cells using a solid electrolyte separator with several micrometer thicknesses.

The volumes of the LiCoO_2 particles and the indium sheet change during charge and discharge process. The volume change of the composite electrode layer in the bulk-type batteries is larger than that in the thin-film batteries because the bulk-type ones have larger amounts of active materials. It is noted that the bulk-type battery with thin $\text{Li}_2\text{S-P}_2\text{S}_5$ separator worked without short circuit. The $\text{Li}_2\text{S-P}_2\text{S}_5$ thin-film separator had an enough mechanical property to avoid crack-formation caused by the stress from the volume changes. This result shows the possibility that bulk-type all-solid-state batteries are obtainable using the solid electrolyte separator with several micrometer thicknesses. Decreasing the thickness of solid electrolyte separator leads to the improvement of energy density of batteries because an occupied volume with solid electrolyte decreases. The cell in this study has more than 5 times larger energy density than usually studied bulk-type all-solid-state cells using solid electrolyte with several hundred micrometers thickness, when the energy density was calculated from the total weight of the composite electrode and the solid electrolyte separator. The all-solid-state batteries have a strong possibility to be next generation secondary batteries with a large energy density.

The capacity of 93 mAh g^{-1} is small and needs to increase. To improve the battery performance, optimization of electronic and lithium-ion conductivity in the composite electrode would be needed. For example, mixing conductive additives into the composite electrode would bring about the increase of electronic conductivity in the composite electrode.

4. Conclusion

In this paper, bulk-type all-solid-state batteries based on $\text{Li}_2\text{S-P}_2\text{S}_5$ solid-electrolyte separators with several micrometer thicknesses were reported. The thickness of the LiCoO_2 composite positive electrode was approximately $50 \mu\text{m}$; that of the solid electrolyte separator was $3 \mu\text{m}$. The all-solid-state In/LiCoO_2 cell using a solid electrolyte separator of micrometer thickness worked with the reversible capacity of 93 mAh g^{-1} without short circuit. The all-solid-state batteries with the thin solid electrolyte separator have a strong potential to be a next generation secondary battery with a large energy density.

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