Sheet-Type Solid-State LIB

Atsushi Sakuda

Abstract Sheet-type all-solid-state batteries, which consist of a solid electrolyte separator layer and positive and negative electrodes coated on current collectors, have a more practical configuration than pellet-type batteries. In this section, the slurry coating process, which is the most commonly used method for sheet-type all-solid-state batteries, is discussed. The developments of solid electrolyte fine particles, electrode and solid electrolyte sheets, pressing, and confining pressure are outlined.

Keywords All-solid-state batteries · Slurry · Solid electrolyte particles · Electrode sheets

1 Introduction

Sheet-type all-solid-state batteries, which consist of a solid electrolyte separator layer and positive and negative electrodes coated on current collectors, have a more practical configuration than pellet-type batteries. However, reports on sheet-type all-solid-state batteries remain scarce [1–7]. In this chapter, the slurry coating process, which is the most commonly used method for sheet-type all-solid-state batteries, is discussed.

2 Basic Requirements

Cell design is basically the same as with lithium-ion batteries except for the differences derived from using solid electrolytes. Positive and negative electrodes are separated by the solid electrolyte layer. The electrode layers require active materials and sufficient ionic and electronic conductivity. Both ionic and electronic conductivity must be implemented based on the desired current density. Because all materials are

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solid, good contact between the solids, which include active materials, solid electrolytes, conducting additives, and current collectors, must be ensured. In particular, ionic conduction must be ensured by means of homogeneous solid electrolyte distribution. Thus, composite electrodes in which solid electrolytes are mixed into the positive and electrode layer are standard design. Because the solid electrolyte plays a role in maintaining the structure, a binder is not essential in all-solid-state batteries [8]. By contrast, bulk-type all-solid-state cells are constructed using a powder process. Therefore, the use of a binder facilitates cell fabrication [4].

The most important requirement in this process is determining a good combination of solid electrolyte, binder, and solvent to enable slurry coating [4]. The binder should have a low resistance, and appropriate-sized solid electrolyte particles should be used to obtain homogeneous solid electrolyte and electrode sheets.

All-solid-state cells that use inorganic solid electrolytes are less flexible than conventional lithium-ion batteries. Thus, round/flat jelly roll-type cells, which are common for conventional lithium-ion batteries with liquid electrolytes, are difficult to construct, and stacking-type cells are considered to be the most promising configuration for all-solid-state batteries.

3 Solid Electrolyte Fine Particles

To obtain a homogeneous solid electrolyte separator layer, the largest solid electrolyte particles should be at least less than half the target thickness of the solid electrolyte layer. Typical target thickness is 10–30 μm for bulk-type all-solid-state batteries. Thus, the maximum size of the solid electrolyte must be less than at least ten micrometers. To form an effective lithium-ion conducting pathway, using fine solid electrolyte particles that are smaller than active material particles is essential [9]. However, excessive miniaturization makes handling difficult, increases side reactions, and reduces the density of the solid electrolyte. Therefore, examining an appropriate size according to the purpose is necessary.

It is known that sulfide-based solid electrolytes densify easily simply by cold pressing [10]. This is the greatest advantage of sulfide-based solid electrolytes. However, their mechanical property also makes it difficult to obtain small solid electrolyte particles, as their size increases during the pulverization process [11]. Thus, preparing solid electrolytes without secondary particles of several tens of micrometers is relatively difficult. It has been reported that wet ball milling in the presence of dispersants is an effective means of obtaining small particles [12]. Figure 1 shows fine Li_3PS_4 glass powder synthesized from Li_2S and P_2S_5 using dibutyl ether as a dispersant [4, 12]. Solid electrolyte small particles were obtained by using dibutyl ether.

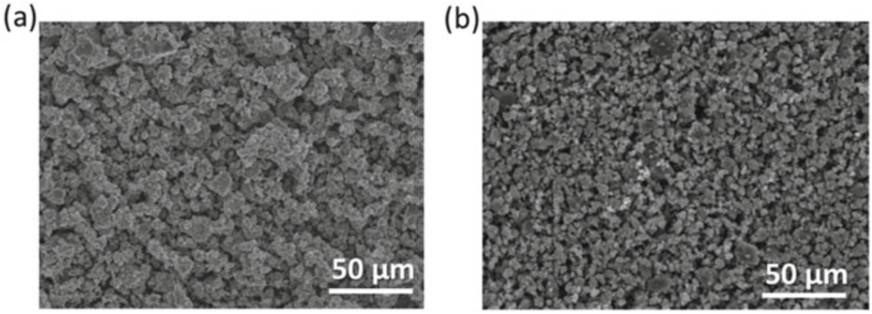

Fig. 1 SEM images of Li_3PS_4 glass powder mechanochemically prepared by wet ball milling using a heptane solvent **a** without and **b** with dibutyl ether as a dispersant

4 Electrode and Solid Electrolyte Sheets

Preparation of electrode and electrolyte slurries is essential to achieve high performance. Figure 2 shows simplified preparation procedures of electrode and electrolyte sheets. The first requirement is to identify the right combination of solid electrolyte, binder, and solvent that does not exhibit an unfavourable side reaction and enables slurry coating. Note that the binder can interfere with the contact between the particles and become a large resistance component [4]. Reducing the binder amount affects the binding force between the current collector foil and electrode layer. Therefore, a device that prevents the peeling of the electrode layer is critical for the current collector foil. Roughening the current collector surface or introducing an additional layer is also effective. For the solvent, using one that has low polarity and that does not easily react with the sulfide-based solid electrolyte is preferable. Viscosity, wettability with particles, and volatility of solvents are also important parameters for preparing a good slurry. Figure 3 is a photograph of a solid electrolyte slurry. That the particles are well dispersed in the solvent is necessary, and this often requires a suitable disperser.

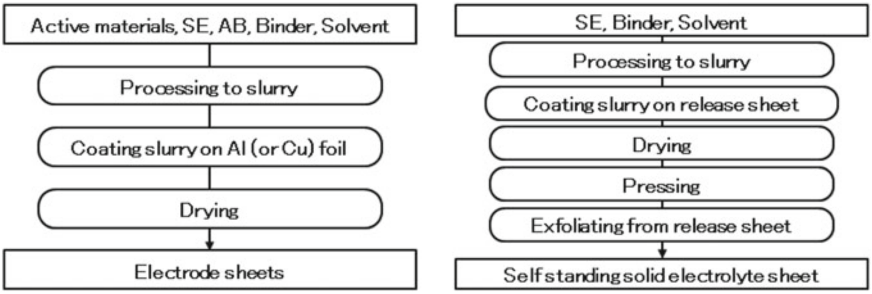

Fig. 2 Procedure for preparing electrode sheets and self-standing solid electrolyte sheets

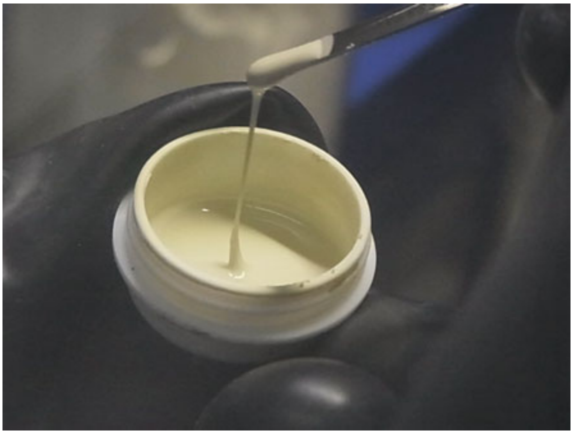

Fig. 3 Photo of a sulfide solid electrolyte slurry

5 Pressing

Pressing is one of the most important processes in constructing all-solid-state batteries. Figure 4 is an SEM image of the cross-section of a sheet-type all-solid-state test cell constructed by stacking the electrode and electrolyte sheets by applying uniaxial pressing of 370 MPa at room temperature. A relatively dense all-solid-state cell was constructed simply by pressing at room temperature. For mass production, a roll-to-roll process is favourable, and roll pressing is used to press the electrode layer for conventional lithium-ion batteries using liquid electrolytes. However, all-solid-state cells require higher pressure than conventional cells to enable good contact between solid particles. This means using roll pressing is not easy. Development of advanced technology that enables roll pressing for fabrication of all-solid-state cells is anticipated. Furthermore, not only pressing of the electrode sheet but also pressing of the whole cell is required to ensure the positive electrode, solid electrolyte, and negative electrode layers all contact one another. As an alternative, the processes using high-pressure uniaxial pressing and cold (or hot) isostatic pressing have been

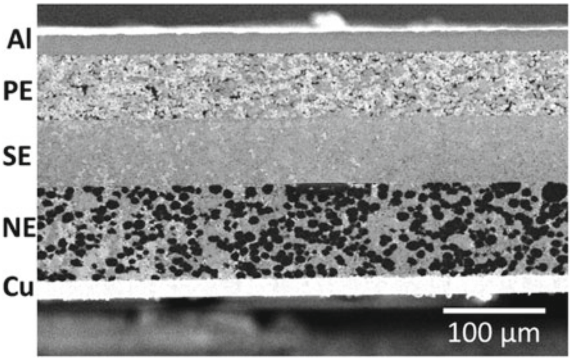

Fig. 4 SEM image of the cross-section of a sheet-type all-solid-state test cell

developed. Development of new materials and processes that decrease the required pressure is desired. The test cell shown in Fig. 4 has a thick solid electrolyte layer and inhomogeneous electrolyte distribution in the electrode layers. Recent progress in the manufacturing of cells has enabled to construct a homogeneous electrode layer that has a thinner electrolyte layer and a less-solid electrolyte.

6 Confining Pressure

All-solid-state cells usually perform well when applied with high confining pressure because the pressure assists the contact between solids. To apply such a high pressure for large-scale all-solid-state batteries, a heavy and large jig is required. The development of external packaging for all-solid-state batteries is critical. In addition, the development of high-temperature-resistant exteriors that take advantage of the high-temperature stability of all-solid-state batteries is expected.

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