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Fabrication and Evaluation of All-solid-state Lithium Secondary Battery with Sulfide-based Solid Electrolytes

1. Introduction

Battery-Materials Analysis & Evaluation Center at the JFE Techno-Research Corporation performs battery prototype fabrication and evaluation services for clients who are developing lithium-ion secondary batteries and lithium-ion battery materials. Because the Center recently began fabrication and evaluation services for all-solid-state lithium-ion secondary batteries with sulfide-based solid electrolytes, which are expected to become one type of next-generation battery, this article introduces the fabrication and evaluation services which are possible at JFE Techno-Research.

2. Fabrication Technologies for All-solid-state Lithium-ion Secondary Batteries with Sulfide-based Solid Electrolytes

2.1 Features of All-solid-state Lithium-ion Secondary Batteries with Sulfide-based Solid Electrolytes

Conventional liquid-based lithium-ion secondary batteries (LIBs) are used in various fields from familiar smartphones to electric vehicles (EVs), but use a volatile, easily-inflammable organic solvent as an electrolyte to transport lithium ions. Because these liquid-based LIBs may emit smoke or burn as a result of heavy impact or damage or under high temperatures or other special environments, active research and development on all-solid-state batteries, in which the electrolytic solution is replaced with a sold-state electrolyte, have been underway in recent years. As representative solid-state electrolytes, sulfide-based solid electrolytes have been a focus of attention, as this type has flame retardance and stability under high voltages. Large expectations are also placed on all-solid-state batteries in EV applications, because this type also has a higher volumetric energy density than the existing batteries.

However, it has been pointed out that sulfide-based solid electrolytes mainly have the following three drawbacks: First, "Solid electrolytes generate hydrogen sulfide by reaction with water," second, "Higher surface boundary resistance and a consequent decrease in output due to the contact structure between particles is a concern" and third, "Lithium ion conduction is impeded by the formation of a heterogenous phase by the chemical reaction, etc. at the active material/solid electrolyte interface"[1]. In order to overcome these issues, government agencies and the private sector are making active efforts ranging from exploration of solid electrolyte materials to the development of production methods, and JFE Techno-Research has also created a fabrication environment for all-solid-state lithium-ion secondary batteries with sulfide-based solid electrolytes to respond to these needs.

2.2 Fabrication of All-solid-state Lithium-ion Secondary Batteries with Sulfide-based Solid Electrolytes by Pellet-type Method

This section introduces a fabrication method for all-solid-state lithium-ion secondary batteries with sulfide-based solid electrolytes using this company's pellet-type (powder compaction) method. **Figure 1** shows a schematic diagram of the half-cell structure of an all-solid-state lithium-ion secondary battery with sulfide-based solid electrolytes. The diameter of the battery is approximately 10 mm. The pellet-type method has the advantage that evaluation is possible with a comparatively small amount of powder, and it is particularly

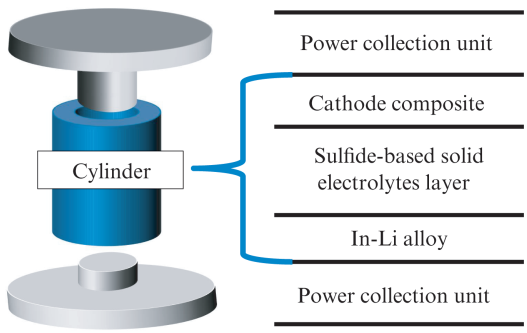

Fig. 1 Schematic diagram of structure of all-solid-state lithium secondary battery with sulfide-based solid electrolytes in half-cell

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suitable for material evaluation of active materials and solid electrolytes. Because solid electrolytes react easily with the small amount of moisture in the atmosphere and generate hydrogen sulfide, JFE Techno-Research introduced a glovebox which can maintain an ultra-low dew point (−80˚C or lower).

2.2.1 Sulfide-based solid electrolyte synthesis method

The sulfide-based solid electrolyte is synthesized by mechanical milling treatment of Li_2S and P_2S_5 with a ball mill. The size of the particle diameter is controlled by changing the mechanical milling conditions.

2.2.2 Assembly method for pellet-type batteries

All-solid-state lithium-ion secondary batteries with sulfide-based solid electrolytes are assembled as follows: First, the sulfide-based solid electrolyte is charged into the cylinder shown in Fig. 1 and pressed with a hand press. The cathode layer (cathode composite) is prepared by mixing the active material of the cathode, a conductive agent and the sulfide-based solid electrolyte by a dry method, and can be obtained further by injection in the sulfide-based solid electrolyte layer and pressing. An In-Li alloy is used as the counter electrode. The all-solid-state lithium-ion secondary battery with sulfide-based solid electrolytes is then restrained under a constant load and enclosed in a sealed container.

2.3 Results of Fabrication and Evaluation

Figure 2 shows the initial charging/discharging curves of all-solid-state lithium-ion secondary batteries with sulfide-based solid electrolytes in half-cell. As the N number, 2 samples were evaluated. Two types of the sample were used, one in which surface coating was performed on the cathode active material to suppress formation of a resistance layer, and the other using the same cathode active material but without surface coating, and the samples were compared. The current value during the first charge was 1/20 C. The charging capacity was increased from 120 mAh/g to 150 mAh/g by performing surface coating, and the discharge capacity was also increased from 140 mAh/g to 155 mAh/g.

Figure 3 shows the results of alternating current (A.C.) impedance measurements when the charged condition after the initial charge/discharge test was 50%. In these measurements, the resistance value of the reaction resistance component was substantially reduced by performing surface coating.

Figure 4 shows an example of the cycle performance of the all-solid-state lithium-ion secondary batteries with sulfide-based solid electrolytes in half-cell. The current value was 1/10 C. By performing surface coating, the discharge capacity at the 25th cycle was increased from approximately 90 mAh/g to approximately 140 mAh/g. These results show that the surface

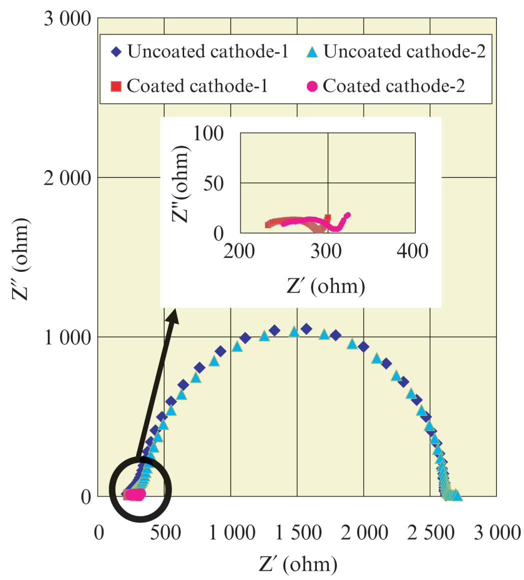

Fig. 3 Impedance of all-solid-state lithium secondary battery with sulfide-based solid electrolytes in half-cell at SOC50%

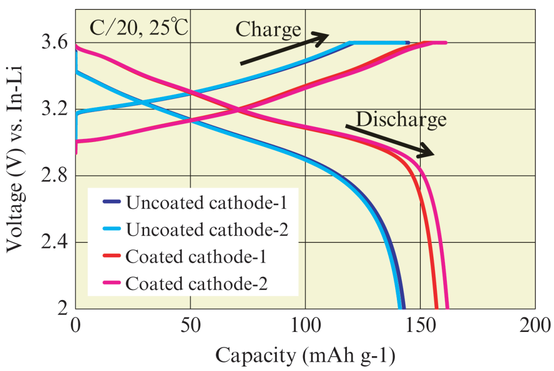

Fig. 2 Typical charge/discharge curves about all-solid-state lithium secondary battery with sulfide-based solid electrolytes in half-cell

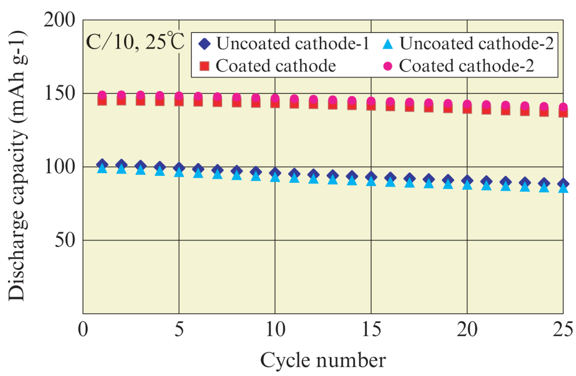

Fig. 4 Cycle performance of all-solid-state lithium secondary battery with sulfide-based solid electrolytes in half-cell

coating of the cathode active material contributes to lower resistance and improved cycle performance. Fabrication of all-solid-state batteries by the pellet-type method at JFE Techno-Research is also considered to be an effective technique for evaluation of coatings of coated cathodes.

3. Conclusion

This article presented an outline of fabrication technology for all-solid-state lithium-ion secondary batteries with sulfide-based solid electrolytes by the pellet-type (powder compaction) method. Battery-Materials Analysis & Evaluation Center of the JFE Techno-Research is promoting study of battery fabrication by a coating method and the development of laminated cells in order to respond even more effectively to the battery prototype fabrication needs of all-solid-state batteries. In the future, we will continue to improve our fabrication technologies for various types of batteries and promote research and development to ensure customer satisfaction.

Reference

1) For example, Reduction of Surface Boundary Resistance and Fabrication Processes and Evaluation Technology for All-solid-state Batteries, Technical Information Institute Co., Ltd.. 2020, 490 p.

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