



Short communication

All-solid secondary batteries with sulfide-based thin film electrolytes



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H I G H L I G H T S

- All-solid batteries with sulfide-based thin film electrolyte has been investigated.
- The battery has shown discharge of 10 C for 1 min at a room temperature.
- The battery has shown excellent cycle properties at a high temperature.

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We have been developing all-solid secondary batteries with sulfide-based thin film electrolyte and pellet-type electrodes. This battery has high performance – it has high-rate discharge properties and cycle properties at high temperature. The battery has shown discharge capability of 10 C for 1 min and cycle properties of 90% capacity-1500 cycle at 60 °C, 90% capacity-500 cycle at 80 °C, and 70% capacity-500 cycle at 150 °C. It has been found that thin film electrolyte gives good effect on both high-rate discharge and cycle performance at a high temperature.

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1. Introduction

Secondary batteries are widely used to power mobile electronic devices and other equipment, and extensive research has led to the development of lithium-ion batteries with a high energy density. As a larger number of vehicles use lithium-ion batteries, it has become increasingly important to improve their safety. However, lithium-ion batteries, which use combustible organic electrolyte solutions, have ignition and explosion risk. To address this problem, efforts are currently underway to significantly increase the safety of lithium-ion batteries by replacing the electrolyte solutions with flame-retardant electrolytes [1–3]. Among others, an all-solid lithium secondary battery, which has a high thermal stability from room temperature to 360 °C [3] and can operate using Li_2S – P_2S_5 sulfide solid electrolytes with a high lithium-ion conductivity of at least $1 \times 10^{-3} \text{ S cm}^{-1}$ at room temperature [4], is receiving

particular attention as a next-generation rechargeable battery. However, all-solid batteries using no organic electrolyte solutions have the following problems: it is difficult to ensure a wide contact area at the interface between the active material and electrolyte; a significantly low mobility of lithium ions at the contact interface between the cathode material and solid electrolyte increases the interface resistance, which affects the power density of the battery [5–7]. The first problem concerning the contact area is particularly serious with bulk-type, all-solid batteries; it is necessary to apply a strong press force to the electrode during its evaluation, which has been an obstacle to its practical use. Regarding the second problem, you can effectively reduce the interface resistance by coating the surface of the cathode material with a film of lithium-ion conductive oxide to create a buffer layer (interlayer) [8]. Thinning the solid electrolyte layer between the positive and negative-electrode to reduce the interface resistance also effectively improves the high-rate charge and discharge performance. We produced a prototype all-solid-state battery consisting of laminated layers of positive- and negative-electrode materials and a solid electrolyte, and the solid electrolyte thin film layer of the battery maintained its performance during charging and discharging with a cycle of 500 [9–

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11]. All-solid-state lithium cells using a sulfide thin film electrolyte as a separator to the powder composite electrodes also has been reported [12].

We produced a new structured prototype of the all-solid battery with a sulfide solid electrolyte film by the vapor-phase method, between the bulk electrodes consisting of a mixture of powders. Because of the preparation of thin film electrolytes on both of cathode and anode before attaching electrodes, the defects that penetrate through the electrolyte layer were reduced. Additionally, it is possible to use the “rocking chair” type active material on both electrodes. As a result, short circuiting was reduced, and we succeeded in achieving the high-rate discharge and cycle (at a high temperature). The present study reports the assessment results.

2. Experimental

2.1. Preparation of electrode materials

The commercial $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ (Toda Kogyo Corp.) and 2 wt% carbon-added $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (Ishikawa Sangyo Kaisha, Ltd.) were used for the cathode and anode materials, respectively, and Li_2S – P_2S_5 glass ceramic powder as a solid electrolyte. A mixture of active material and solid electrolyte powders was used as electrode materials: a $80\text{Li}_2\text{S}$ – $20\text{P}_2\text{S}_5$ solid electrolyte with an Li:P molar ratio of 8:2 or a $70\text{Li}_2\text{S}$ – $30\text{P}_2\text{S}_5$ solid electrolyte with an Li:P molar ratio of 7:3 for the positive-electrode, and a $70\text{Li}_2\text{S}$ – $30\text{P}_2\text{S}_5$ solid electrolyte for the negative-electrode. The synthetic condition of these electrolyte powders is shown in previous reports [13].

The cathode materials contained in all samples were coated with LiNbO_3 , which serves as an intermediate layer. The intermediate layer was created using “Coating Equipment for Rolling Fluidized Beds MP-01” (Powrex Corp.) – the same method reported on in a study conducted by Takada et al. [8]. An alkoxide solution of metallic elements was used as the material for the intermediate layer; an ethanol solution containing 5 wt% of lithium ethoxide (structural formula: $\text{Li}(\text{OC}_2\text{H}_5)$) was used as the lithium source; pentaethoxyniobium (structural formula: $\text{Nb}(\text{OC}_2\text{H}_5)_5$, purity of 4N) was used as the niobium source. A mixture of an ethanol solution containing 5 wt% of lithium ethoxide and pentaethoxyniobium with a prescribed ratio was sprayed at 500 g of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ poured into the equipment at a temperature of 80°C at 1 g min^{-1} to create the coating, which then underwent heat treatment for 30 min at 300°C to create the intermediate layer of LiNbO_3 . Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES, iCAP6500DUO, Thermo Fisher Scientific) was performed to determine the ratio of elements contained in the intermediate layer and cathode material. Field Emission Auger Electron Spectroscopy (FE-AES, PHI700, ULVAC-PHI, INC.) was also performed to examine changes in the particle surface during coating, using an electron gun with an accelerating voltage of 10 keV. All of the batteries used for electrochemical measurements were made from the same processed $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$. No intermediate layer was formed in the anode material.

2.2. Process of forming bulk electrodes

Table 1 shows the mixture ratios of active materials/SE and pressurized conditions. No additive carbons were mixed. Mixed powders were put into a mold and pressed in a dry room with a dew point of -55°C . The electrodes were cut cross-sectionally using a focused ion beam system to observe the inside with scanning ion microscopy (FIB-SIM, FB2100, Hitachi, Ltd.). The electrodes for the batteries were prepared except for the electrodes for the analysis of FIB and SIM. When creating electrodes, aluminum plates were also pressed as power collectors.

Table 1
Materials and press condition of bulk-type electrodes.

	Electrode weight ratio (active material:electrode)	Active material weight	Press condition
Cathode	70 wt%:30 wt%	19.4 mg cm^{-2}	$540\text{ MPa} \times 10\text{ min}$
Anode	60 wt%:40 wt%	18.8 mg cm^{-2}	$540\text{ MPa} \times 10\text{ min}$

2.3. Preparation of electrolyte films

Solid electrolyte film was formed on both the positive and negative bulk electrodes. Using a vacuum deposition below 0.005 Pa, 5- μm solid electrolyte film was formed, with Li_2S and P_2S_5 as the starting materials. The sides of the sulfide solid electrolyte films of positive and negative bulk electrodes were put together and pressure of 16 MPa was applied to integrate the electrolytes. The bulk electrolytes were attached together over an area of $\phi 10\text{ mm}$, based on which the density of the battery capacity was calculated.

2.4. Evaluation of charge and discharge properties

Only constant-current, charge–discharge tests using a BLS battery test system (Keisokuki Center Co., Ltd.) were conducted to examine the high-rate discharge and cycle characteristics of the batteries. Prior to and following charging, an alternating-current impedance measurement using an analyzer (ALS model 6005C, BAS Inc.) was conducted under the following conditions: an alternating-current amplitude of 10 mV and a frequency range of 10 mHz–100 kHz.

3. Results and discussion

3.1. Evaluation of electrode

After coating the cathode powder $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ with LiNbO_3 , an intermediate layer, ICP analysis was conducted to determine the ratio of elements; the weight of Ni and Nb contained in 100 mg of coated powder was 48 and 0.85 mg, respectively. The mean thickness, calculated based on a specific surface area of the powder ($0.41\text{ m}^2\text{ g}^{-1}$) determined by the conventional gas absorption method and the theoretical density of the intermediate layer, was 7.2 nm. The results of the element mapping in Fig. 1, obtained using Auger spectroscopy, estimated the surface coverage of the intermediate layer LiNbO_3 to be approximately 80%. Previous studies reported that, regarding all-solid batteries, the thickness of the intermediate layer LiNbO_3 or $\text{Li}_4\text{Ti}_5\text{O}_{12}$ for the cathode material LiCoO_2 should be 5–7 nm [5,6], and the intermediate layer $\text{Li}_4\text{Ti}_5\text{O}_{12}$ for $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ should be approximately 5 nm [8]. The thickness of the intermediate layer LiNbO_3 for $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ reported in the present study is in line with the results of previous studies.

The FIB-SIM sectional image in Fig. 2 shows that the inside of the pressed electrodes in molds was dense, and that there was a close contact between the cathode and anode materials and solid electrolytes. Primary particles of 1 μm or smaller and secondary particles of approximately 6 μm were observed in both active materials. Even-grain boundaries were barely visible between the solid electrolyte particles, and the contact resistance was considered to be markedly low.

3.2. Charge and discharge performance

An examination was conducted on the charge and discharge characteristics of the battery that used an $80\text{Li}_2\text{S}$ – $20\text{P}_2\text{S}_5$ solid

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