

All-Solid-State Lithium Batteries with Wide Operating Temperature Range

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All-solid-state batteries do not use a flammable organic liquid electrolyte which has a risk of boiling, freezing or burning, and are therefore expected to operate in a wide temperature range. This paper reports on the development of a solid-state thin film lithium battery using a high conductive sulfide solid electrolyte and its charge-discharge characteristics at high and low temperatures. The high ionic conductivity of the sulfide solid electrolyte can reduce internal resistance, which greatly affects the charge-discharge characteristics of a battery. Test results show that, at room temperature, the capacity of this battery at a high discharge rate (24C) reaches 89% of the capacity at a low discharge rate (0.5 C). Cycle characteristics also confirmed that there was no degradation up to 100 cycles at both 170°C and -40°C.

Keywords: solid-state battery, lithium battery, solid electrolyte, operating temperature range

1. Introduction

Lithium ion secondary batteries have a high voltage and a high energy density, as shown in Fig. 1, and are widely used in mobile devices such as cell phones, notebook PCs and PDAs. However, since lithium ion secondary batteries use a flammable organic liquid electrolyte, there is a risk of explosion or fire. Fire accidents can also occur due to contamination during production or from overcharging. To reduce such risk, a protection circuit is added to the battery. However, since there is a trade-off between energy density and the risk of accidents, it is difficult to meet today's growing demand for high energy density. When the battery is larger, for automotive or industrial equipment for example, ensuring safety is increasingly important. On the other hand, in terms of performance, the battery capacity is significantly reduced or the battery becomes unusable when the electrolyte freezes in cold climates. This inconvenience is primarily due to the organic electrolyte. Moreover, high-capacity active materials, such as the sulfur cathode and lithium metal anode, cannot be used with liquid electrolytes due to dissolution or dendrite problems, respectively. This makes it difficult to increase

the battery's energy density.

Because of these issues, all-solid-state lithium batteries have been proposed as a fundamental solution (Fig. 2)⁽²⁾⁻⁽⁴⁾. All-solid-state batteries never use any liquid cell components. Instead of using organic electrolyte, a lithium ion conductive ceramic, known as a solid electrolyte, is used. This is expected to principally resolve various problems caused by the liquid electrolyte. Previously, all-solid-state batteries were significantly inferior to liquid batteries because of high internal resistance. However, active development has proceeded recently due to the discovery of a solid electrolyte with high lithium ion conductivity and reduction in the interfacial resistance by forming a buffer layer between the solid electrolyte and cathode material^{(5), (6)}.

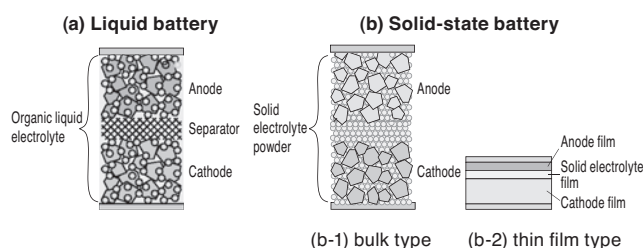


Fig. 2. Typical schematic cross-sectional view of a liquid battery and a solid-state battery

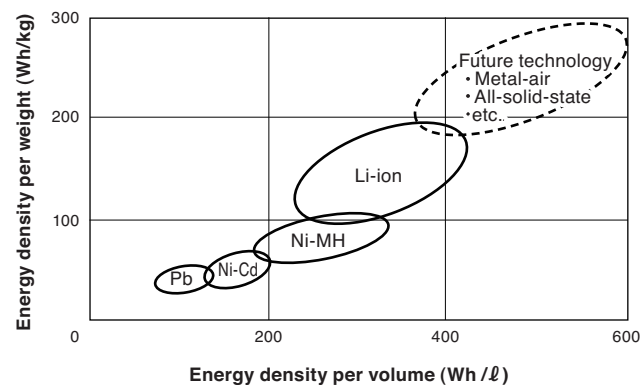


Fig. 1. Energy density of secondary batteries

The solid electrolyte is a key material for all-solid-state batteries, and there are two types: oxide and sulfide. The oxide solid electrolyte is easy to handle, but generally has a narrow potential window which lowers cell voltage, or has low ionic conductivity. On the other hand, the sulfide solid electrolyte has high ionic conductivity, but must be handled in a dry atmosphere because hydrogen sulfide is generated upon contact with moisture in the air. Our group has so far studied sulfide solid electrolyte thin film that has

high lithium ion conductivity, and we have already successfully fabricated solid-state thin film batteries using the solid electrolyte thin film⁽⁷⁾. In this paper, we report on the charge/discharge characteristics at high and low temperatures that are expected with solid-state thin film lithium batteries, and also report about the output characteristics at room temperature.

2. Preparation of the Thin Film Lithium Battery

The thin film lithium battery is prepared by laminating a cathode thin film, solid electrolyte thin film, and anode thin film onto a substrate. **Figure 3** shows a schematic sectional view of the battery. The cathode is LiCoO_2 and the anode is lithium metal. To reduce interfacial resistance, the oxide buffer layer is inserted at the cathode interface. A silicon layer is also inserted at the anode interface in order to prevent electrochemical reduction of the solid electrolyte. All films were deposited under a vacuum. Specifically, the cathode film was deposited by sputtering; the buffer layer, solid electrolyte, and Si layer were deposited by pulsed laser deposition (PLD); and the anode film by vapor deposition. All steps after the solid electrolyte film is deposited must be carried out under a dry atmosphere.

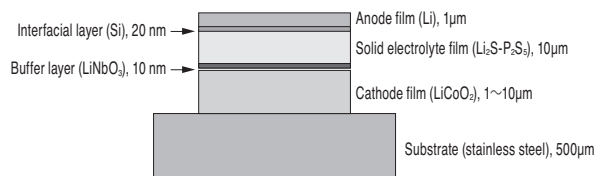


Fig. 3. Schematic cross-sectional view of the thin film battery

The cell element, as noted above, was evaluated in a 2032-type coin cell. A coin cell is usually sealed by caulking using a polypropylene packing. In high temperature testing, however, normal packing has insufficient heat resistance, and therefore polytetrafluoroethylene (PTFE) packing was used. To adjust the thickness to the battery case, a 0.5 mm-thick lithium foil was stacked on the thin film battery in contact with the lithium film anode.

Battery performance tests at high and low temperatures were carried out by placing the coin cell into a thermostat that was set to the test temperature. All testing was performed with constant current (CC) charge-discharge measurements.

3. Battery Performance at Room Temperature

Although in principle solid-state batteries are expected to operate at high and low temperatures, the output char-

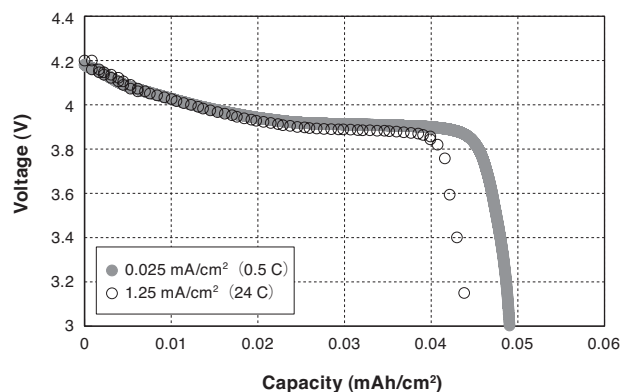


Fig. 4. Rate performance of the thin film battery

acteristics at room temperature (25°C) were investigated in advance. As shown in **Fig. 4**, at as high as 24C rate, the discharge capacity was 89% of the capacity at a low rate, which indicates that this battery has excellent power characteristics. 1C rate is the current value that can charge (or discharge) the designed capacity in one hour. Thus, 24C is the current value that can completely charge/discharge in 2 minutes 30 seconds. This indicates that the thin film battery is capable of completing 90% charge/discharge in less than 3 minutes. Nevertheless, the capacity itself is not very large because the battery is made of “thin” films.

4. Battery Performance at High Temperature

As mentioned above, the lithium ion secondary battery has a concern of boiling and evaporation of the organic liquid electrolyte, which is present at temperatures below about 60°C. Moreover, since electrolyte deterioration and the side reactions are accelerated at high temperature, battery life generally tends to become shorter than that at room temperature.

Figure 5 shows the results of charge/discharge tests of the thin film battery at a high temperature of 170°C. This

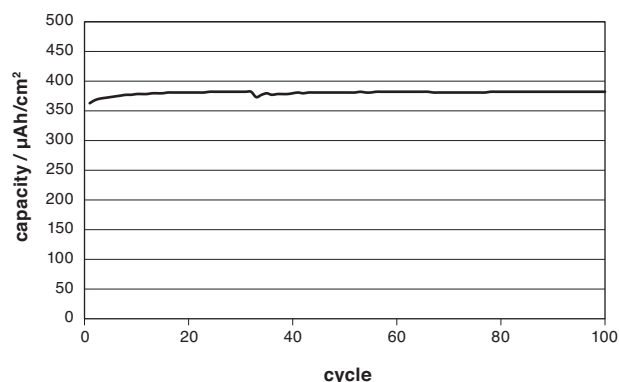


Fig. 5. Cycle performance of the thin film battery at high temperature (170°C)

temperature is close to the melting point of the lithium metal anode (180°C). The test conditions were a constant current of 0.3 mA charge/discharge, charged to 0.3 mAh, and discharged to 3.0 V.

From Fig. 5, it was confirmed that this battery can operate at high temperatures. Moreover, capacity degradation was not observed during 100 cycles, confirming that there is no remarkable increase in side reactions. Being able to operate at high temperatures enables the battery to be used in hot areas, and thus battery applications are expected to become wider.

5. Battery Performance at Low Temperature

Since battery reaction is essentially a chemical reaction, the reaction barely proceeds at low temperatures. That is, the output characteristics are reduced due to the battery's higher internal resistance. In addition, with liquid batteries, the characteristics may deteriorate rapidly due to increased viscosity or freezing of the liquid electrolyte. With all-solid-state batteries, performance degradation is considered to be dependent on the temperature. Figure 6 shows the results of charge/discharge tests in a chamber temperature of -40°C. The test conditions were a constant current of 0.02 mA, charged to 0.02 mAh, and discharged to 3.0 V. Although battery performance unavoidably degrades such as at low capacity, it was confirmed that battery operation is basically possible. Cycle characteristics also confirmed that there was no degradation up to 100 cycles. Although performance is still low, the results showed that this battery can be used at low temperature, in principle.

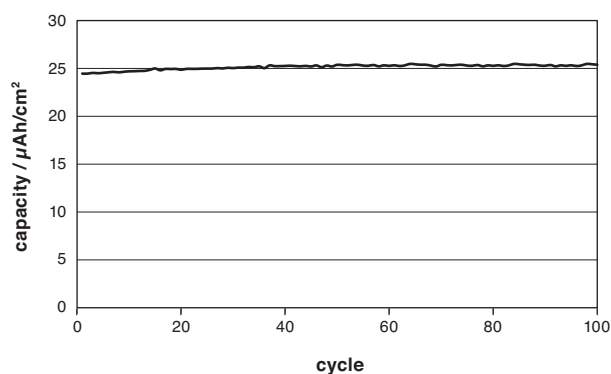


Fig. 6. Cycle performance of the thin film battery at low temperature (-40°C)

6. Conclusion

Battery performance of the solid-state battery at high and low temperatures was investigated, and it was confirmed that the battery can operate stably at high and low

temperatures. In the future, a wide operating temperature range is considered to be a big advantage in expanding the applications of lithium batteries.

Output characteristics at room temperature were also investigated, where the solid-state battery showed that it has power characteristics comparable to those of current liquid batteries. These results indicate the high potential of solid-state batteries. With continued development of materials and processes, the realization of a secondary battery with both excellent safety and battery performance is increasingly expected.

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