Discharge Performance of All-Solid-State Battery Using a Lithium Superionic Conductor Li$_{10}$GeP$_2$S$_{12}$

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Abstract

A solid electrolyte, Li$_{10}$GeP$_2$S$_{12}$, exhibits a high lithium ionic conductivity of 12 mS/cm at room temperature. Because of its high ionic conductivity, high charge-discharge performance would be expected for the all-solid-state batteries using the Li$_{10}$GeP$_2$S$_{12}$ electrolytes. In this study, all-solid-state batteries using Li$_{10}$GeP$_2$S$_{12}$, were constructed and their battery performances were examined. The batteries using the Li$_{10}$GeP$_2$S$_{12}$ electrolyte showed higher discharge capacities than those with glass electrolyte, 75Li$_2$S·25P$_2$S$_5$, particularly under the high-rate current discharge.

Keywords: All-Solid-State Battery, Super Lithium Ion Conductor, Solid Electrolyte

1. Introduction

Recently, depletion of oil and global warming due to CO$_2$ emission are serious issues in the world, and reduction of CO$_2$ emission and improvement of fuel efficiency are required for cars. One of solutions to those issues is to produce cars powered by batteries, such as hybrid electric vehicle and electric vehicle. For such an electric powered vehicle, high energy density of battery is required for long range electric drive. And high energy batteries are also required in smart grids to store solar and wind energy. An all-solid-state battery using solid electrolyte instead of organic liquid electrolyte is expected to be a higher energy density one than a lithium ion batteries using organic liquid electrolyte, because bipolar stack structure, shown in Fig. 1, could be taken with all-solid-state battery owing to no liquidity of solid electrolyte. However, none of solid electrolytes have their conductivities comparable to organic liquid electrolyte. In previous study, we found a lithium super ionic conductor Li$_{10}$GeP$_2$S$_{12}$ and that exhibits extremely high lithium ionic conductivity of 12 mS/cm at room temperature. Figure 2 shows thermal evolution of ionic conductivity of the new Li$_{10}$GeP$_2$S$_{12}$ phase, together with those of other lithium solid electrolytes, organic liquid, ionic liquid, Li$_{10}$GeP$_2$S$_{12}$ is comparable to or even higher than liquid organic electrolyte in lithium ion conductivity. Because of its high ionic conductivity, high charge-discharge performance would be expected for the all-solid-state batteries using the Li$_{10}$GeP$_2$S$_{12}$ electrolytes. In this study, all-solid-state batteries using Li$_{10}$GeP$_2$S$_{12}$, were constructed and their battery performances were examined. An all-solid-state battery using another electrolyte was also constructed to investigate the influence of lithium ion conductivity of solid electrolyte on the power of all-solid-state battery. To synthesize Li$_{10}$GeP$_2$S$_{12}$, starting materials were weighted, mixed in an appropriate molar ratio in an argon-filled glove box, put into a quartz glass tube and heated at 550°C. Another solid electrolyte, 75Li$_2$S·25P$_2$S$_5$ glass was synthesized by ball milling method. Starting materials were mixed in an appropriate ratio and the mixture was put into the ZrO$_2$ pot with 9X10 mm ZrO$_2$ balls and then the mixture was mechanically milled by planetary ball milling apparatus at the rotating speed of 370 rpm. Two type of all-solid-state batteries using Li$_{10}$GeP$_2$S$_{12}$ and 75Li$_2$S·25P$_2$S$_5$ glass as electrolyte respectively, were consisted. The ion conductivity of solid electrolytes were examined by the AC impedance method. The outline of an all-solid-state battery is shown in Fig. 3. The cathode...
results of the Nyquist plot of AC impedance measurement were measured in the state of compressed powder pellet. The ion conductivities of electrolytes synthesized in this study were expressed by the sum of the bulk and grain boundary conductivities because it is difficult to separate the bulk and grain boundary conductivities. The results suggest that there is no significant difference between the electrolytes at low discharge density of 1.15 mA/cm². However, the discharge capacities have a difference at higher discharge current density. The batteries of electrolyte with Li$_{10}$GeP$_2$S$_{12}$ have the discharge capacities of 73.7 mAh/g at the discharge current of 57.5 mA/cm², respectively. This result suggests that the resistance of the battery was reduced by using high ionic conductor then the discharge capacity of the battery was improved. The results obtained in this study show that Li$_{10}$GeP$_2$S$_{12}$, which have high ionic conductivity, extremely improved the discharge characteristics of the all-solid-state battery, especially at the high current density. These results suggest that the ion conductivity of solid electrolyte plays the important roles to improve the power of all-solid-state batteries.

Figure 2. (Color online) Thermal evolution of ionic conductivity of the new Li$_{10}$GeP$_2$S$_{12}$ phase, together with those of other lithium solid electrolytes, organic liquid, ionic liquids. The new Li$_{10}$GeP$_2$S$_{12}$ exhibits the highest lithium ionic conductivity (12 mS/cm at 27°C) of the solid lithium conducting membranes of inorganic systems. Because organic electrolytes usually have transport numbers below 0.5, inorganic lithium electrolytes have extremely high conductivities.

Figure 3. (Color online) Outline of all-solid-state battery consisted in this study. (Cathode layer is consisted by mixing LiCoO$_2$ powder and solid electrolyte powder. Anode layer is consisted by mixing Li$_4$Ti$_5$O$_{12}$ powder and solid electrolyte powder. Separator is consisted by solid electrolyte powder. Each layer is pressed in the ceramic cylinder. After the press, pellet is sandwiched by SUS current corrector.)

Figure 4. (a) Charge and discharge curves of the all-solid-state battery using Li$_{10}$GeP$_2$S$_{12}$. (b) Charge and discharge curves of the all-solid-state battery using 75Li$_2$S·25P$_2$S$_5$. (The discharge capacity of the battery using Li$_{10}$GeP$_2$S$_{12}$ is higher than that of using 75Li$_2$S·25P$_2$S$_5$ glass especially under the condition of high current density.)
4. Conclusion

A super ionic conductor Li$_{10}$GeP$_2$S$_{12}$ was practically used for an all-solid-state battery. The all-solid-state batteries with solid electrolyte of Li$_{10}$GeP$_2$S$_{12}$ and 75Li$_2$S·25P$_2$S$_5$ glass were examined. At lower discharge current density, there was no significant difference of discharge capacities between the battery using Li$_{10}$GeP$_2$S$_{12}$ and the one using 75Li$_2$S·25P$_2$S$_5$ glass. On the other hand, at higher current densities, difference can be seen on the discharge capacities. The battery performance was extremely improved by using Li$_{10}$GeP$_2$S$_{12}$ as solid electrolyte. These results suggest that the solid electrolyte, which exhibits high ionic conductivity, enables to make the high power all-solid-state batteries.

References