Paper

Preparation of Amorphous Solid Electrolytes in The System $\text{Li}_2\text{S}-\text{Al}_2\text{S}_3-\text{P}_2\text{S}_5$ by High-energy Ball-milling Methods

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SYNOPSIS

Lithium-ion conducting solid electrolytes in the composition $(100-x)\text{Li}_3\text{PS}_4 \cdot x\text{LiAlS}_2$ (mol %) were prepared by use of a high-energy ball-milling process at room temperature. Amorphous samples were obtained in the composition range of $x=0$ to $x=13.1$. In the samples with $x \geq 18.2$, a crystalline Al_2S_3 phase was remained after the ball-milling for 35 h. The lithium ion conductivity at 298 K of the obtained samples was increased with an increase in the compositional parameter x and attained the maximum ($\sigma_{298\text{K}} = 6.0 \times 10^{-4} \text{ Scm}^{-1}$ at 298 K) at $x = 13.1$. Measurement of DC polarization confirmed that the main carrier for the conduction of the samples was lithium ions. A laboratory-scale all-solid-state battery using the amorphous $86.9\text{Li}_3\text{PS}_4 \cdot 13.1\text{LiAlS}_2$ (mol %) as solid electrolytes, $\text{Li}_{4.4}\text{Si}$ as anode, and TiS_2 as cathode materials showed good discharge-charge cycle performance at room temperature.

KEY WORDS

solid electrolytes, lithium ion conductor, solid-state battery, mechanical milling, lithium battery

1 Introduction

All-solid-state lithium batteries using inorganic solid electrolytes are promising devices with high safety performance against to conventional lithium ion batteries with electrolyte solution. The advantage of the all-solid-state batteries is ascribed to non-flammable properties of the inorganic solid electrolytes. Thus, non-flammable lithium ion conducting solid electrolytes are indispensable materials for producing all-solid-state lithium batteries with high safety performance and with high energy density.

For those applications, the inorganic solid electrolytes are required to have high lithium ion conductivity and good electrochemical stability over wide potential range. Thus, many efforts have been devoted to develop the materials with high lithium ion conductivity such as lithium germanium thio-phosphate crystalline materials¹⁻³⁾, lithium silicon oxysulfide glasses^{4,5)} and sulfide-based glass ceramics⁶⁻⁸⁾. Those materials show high lithium ion conductivities more than 10^{-3} Scm^{-1} at room temperature.

On the other hand, $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$ amorphous materials have attracted much attention because of the low cost and easy availability of the raw materials P_2S_5 ⁶⁻¹⁰⁾. In addition to those advantages, the $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$ amorphous materials can be prepared at room temperature by use of a high-energy ball-milling process¹¹⁻¹³⁾. The amorphous solid electrolytes, however, have slightly lower conductivities in the range

of 10^{-3} to 10^{-4} Scm^{-1} at room temperature. Hence, the improvement of lithium-ion conductivity is required for the $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$ based amorphous materials.

In general, it is known that alkaline-silicate glasses have non-bridging oxygens which are generated by alkaline oxide components such as Li_2O , and that electrostatic interaction between non-bridging oxygens and mobile ions retards the movements of the mobile ions and reduces mobility of the ions. Alexander et al. have reported that addition of small amounts of Al_2O_3 into alkaline-silicate glasses eliminates non-bridging oxygens in the glasses and thus brings about an increase in ion conductivity¹⁴⁾. We suppose that electrostatic interaction between lithium ions and non-bridging sulfurs depresses the mobility of the lithium ions in the $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$ glasses, and also that the addition of Al_2S_3 component is expected to be effective to eliminate the non-bridging sulfurs. Thus, we have attempted to investigate amorphous solid electrolytes in the system $\text{Li}_2\text{S}-\text{Al}_2\text{S}_3-\text{P}_2\text{S}_5$.

In the present study, we have applied the high-energy ball-milling process to the preparation of amorphous $(100-x)\text{Li}_3\text{PS}_4 \cdot x\text{LiAlS}_2$ solid electrolytes, and have investigated the lithium ion conductivities of the obtained samples. Furthermore, a laboratory scale all-solid-state lithium battery with those samples has been assembled and the performance of the battery has been characterized.

2 Experimental

The desired amounts of the raw materials, Li_2S (Aldrich, 98%), Al_2S_3 (Aldrich, 98%) and P_2S_5 (Aldrich, 99%) were weighed and mixed with an alumina mortar and a pestle. The mixture was placed into a stainless steel (SUS-316) vial with zirconia balls (7 balls of 10 mm diameter and 10 balls of 3 mm diameter) and the vial was sealed with an O-ring. High-energy ball milling was conducted by using a planetary ball-milling apparatus (Fritsch, P-7) and the ball-milling rotation rate was 380 rpm. Typical ball-milling time was 35 h. All the manipulations were carried out in a glove box (UNICO, UN1000F) filled with dry argon gas (dew point: -65°C).

The obtained samples were characterized by use of X-ray diffraction measurements with $\text{Cu-K}\alpha$ radiation. For the measurements, the samples were sealed in an airtight container with beryllium windows and the container was mounted on an X-ray diffractometer (Rigaku, Multi Flex).

For AC impedance measurements, the ball-milled sample was pressed into a pellet of 10 mm diameter under a pressure 380 MPa and indium foils were attached on both sides of the pellet to serve the electrodes. The AC impedance of the pellet was measured in a dry argon gas from 2 MHz to 20 Hz over the temperature range of 280 to 380 K with a precision LCR meter (Agilent, E4980A). The conductivity of the sample was determined by using complex impedance analysis.

DC polarization measurements were carried out to determine dominant carrier ion of the sample. Two types of cells were used for the measurements. One of them (cell 1) had two metallic lithium electrodes working as reversible electrodes for lithium ions. The other cell (cell 2) had two stainless steel (SUS-316) electrodes as blocking electrode for lithium ions. Time dependence of the electrical currents though the cells was measured during a constant voltage of 0.5 V was applied to the cells by use of a potentiostat (Hokuto, HSV-100).

Wagner's polarization measurements¹⁵⁾ were also carried out at 290 K in dry argon atmosphere to determine the electronic conductivities of the sample. In the cell for the measurements, the metallic lithium was used as a reversible electrode for lithium ions and the stainless steel (SUS-316) was used as a blocking electrode. The cell was polarized by applying a constant DC potential in the range of 1.75 to 3.5 V across the blocking electrode (positive) and the reversible electrode (negative).

We also attempted to assemble all-solid-state batteries employing the obtained samples. In the batteries, the positive electrode was a mixture of TiS_2 (60 mass %) and

the solid electrolytes (40 mass %). The negative electrode was $\text{Li}_{4.4}\text{Si}$ meta-stable alloy^{16,17)}, which was also prepared by the ball-milling process. The battery was prepared by successively pressing the positive electrode mixture, the solid electrolyte, and the $\text{Li}_{4.4}\text{Si}$ alloy powders into a pellet of 10 mm diameter at 380 MPa. Discharge-charge cycling tests were performed under a constant current density of $64\ \mu\text{Acm}^{-2}$ between 2.6 and 1.1 V at room temperature by use of a battery tester (Hokuto, HJR-110mSM6).

3 Results and Discussion

We attempted to prepare samples in the compositions of $(100-x)\ \text{Li}_3\text{PS}_4 \cdot x\text{LiAlS}_2$ (mol %) by the high-energy ball-milling process. In the notation for the chemical composition, x denotes the LiAlS_2 content in mole percent. Throughout the study, compositions will be given based on mole percent.

Fig. 1 shows the X-ray diffraction (XRD) spectra of the samples ball-milled 35 h. Halo patterns and no diffraction peaks due to any crystalline phase are observed for the samples with $x \leq 13.1$, which indicates that those samples become amorphous state after ball milling for 35 h. Halo patterns are basically observed in the samples with $x \geq 18.2$, whereas the diffraction peaks due to Al_2S_3 phase (JCPDS #47-1313) are still present after milling for 35 h. Thus, it

Fig. 1 X-ray diffraction patterns of the 35 h-ball-milled samples in the composition $(100-x)\ \text{Li}_3\text{PS}_4 \cdot x\text{LiAlS}_2$ (mol %).

is concluded that the amorphous $(100-x) \text{Li}_3\text{PS}_4 \cdot x\text{LiAlS}_2$ (mol %) samples are obtained in the composition range of 0 to 13.1 mol % LiAlS_2 content by the high-energy ball-milling process.

As an example of the AC conducting measurements, the complex impedance plots of the amorphous $86.9\text{Li}_3\text{PS}_4 \cdot 13.1\text{LiAlS}_2$ (mol %) sample are shown in Fig. 2. The complex impedance plots of the sample have a semicircle and a straight line. The bulk impedance is identified as the intersecting point of the semicircle with the real axis of the complex plane.

Fig. 3 shows the temperature dependence of conductivity of the 35 h-ball-milled $(100-x) \text{Li}_3\text{PS}_4 \cdot x\text{LiAlS}_2$ (mol %) samples. The conductivity of the samples follows the Arrhenius equation $\sigma T = A \exp(-E_a/RT)$, where σ is the conductivity, T the absolute temperature, A the pre-

Fig. 2 Complex impedance plots of the $86.9\text{Li}_3\text{PS}_4 \cdot 13.1\text{LiAlS}_2$ (mol %) sample at various temperatures.

Fig. 3 Temperature dependences of AC conductivities of the 35 h-ball-milled samples in the composition $(100-x) \text{Li}_3\text{PS}_4 \cdot x\text{LiAlS}_2$ (mol %).

exponential factor, E_a the activation energy for conduction, and R the gas constant. The conductivities at 298 K, $\sigma_{298\text{K}}$, and the activation energy for conduction, E_a , of the ball-milled samples are determined from Fig. 3.

The composition dependences of the $\sigma_{298\text{K}}$ and E_a are shown in Fig. 4(a) and (b), respectively. In the figure, open circles, open triangle and closed circles denote amorphous, partially crystalline and crystalline samples, respectively. The value of $\sigma_{298\text{K}}$ increases with an increase in the compositional parameter x and attains the maximum value at a compositional parameter $x = 13.1$. Further increase in x results in a decrease in $\sigma_{298\text{K}}$. The decrease in conductivity with further addition of LiAlS_2 is mainly due to the presence of low-conductive Al_2S_3 crystalline phase included in the samples. The $\sigma_{298\text{K}}$ of the amorphous $86.9\text{Li}_3\text{PS}_4 \cdot 13.1\text{LiAlS}_2$ sample ($x = 13.1$) is $6.0 \times 10^{-4} \text{ Scm}^{-1}$ and is about two to three times higher than that of the amorphous Li_3PS_4 sample ($x = 0$). On the other hand, activation energy for conduction, E_a , is shown in Fig. 4(b) as a function of the

Fig. 4 Composition dependences of (a) AC conductivities at 298 K, $\sigma_{298\text{K}}$, and (b) activation energy for conduction, E_a , of the $(100-x) \text{Li}_3\text{PS}_4 \cdot x\text{LiAlS}_2$ (mol %) samples.

compositional parameter x . The E_a gradually decreases with x value in the range of $x=0$ to $x=18.2$. In the range of $x=30$ to 46 , the E_a became almost constant. The E_a shows a minimum at around $x=13.1$. The position of the minimum in E_a is the same as that of the maximum in σ_{298K} of those samples. This result suggests that the enhancement of conductivity is dominantly governed by the decrease in E_a .

In order to determine the carriers for the electrical conductivities, DC polarization measurements were carried out for the amorphous $86.9\text{Li}_3\text{PS}_4 \cdot 13.1\text{LiAlS}_2$ sample. Two types of cells, cell 1 and cell 2, were used for the measurements. The cell 1 had two lithium electrodes working as reversible electrodes for lithium ions. On the other hand, the cell 2 had two SUS-316 electrodes working as blocking electrodes for lithium ions. A constant voltage of 0.5 V was applied to the two cells 1 and 2.

Fig. 5 shows the polarization curves of the cells 1 and 2 at 298 K . The current through the cell 1 is almost constant with time. The current of 0.18 mA is observed 600 s after the voltage has been applied to the cell. On the other hand, the cell 2 shows a large polarization phenomenon and the current through the cell 2 is close to zero after the constant voltage has been applied to the cell. The residual current after 600 s is about 7.2 nA . The residual current is about 4 to 5 order of magnitude smaller than that of the cell 1.

Fig. 5 DC polarization curves of the $86.9\text{Li}_3\text{PS}_4 \cdot 13.1\text{LiAlS}_2$ (mol%) sample. The cell (1) has two lithium electrodes working as reversible electrodes. The cell (2) has two stainless steel (SUS-316) electrodes working as blocking electrodes. The constant voltage of 0.5 V is applied to the cells.

Those results suggest that the main carrier of the amorphous $86.9\text{Li}_3\text{PS}_4 \cdot 13.1\text{LiAlS}_2$ sample is lithium ions.

Fig. 6 shows the current-voltage characteristics for the determination of electronic conductivities by use of cell $(-)\text{Li} | 86.9\text{Li}_3\text{PS}_4 \cdot 13.1\text{LiAlS}_2 \text{ sample} | \text{SUS-316}(+)$. According to Wagner's polarization analysis¹⁵⁾, the total electronic current, I_{total} , is given by Eq. (1)

$$I_{\text{total}} = I_e + I_h = \frac{R \cdot T \cdot A}{F \cdot L} \left[\sigma_e \cdot \left\{ 1 - \exp\left(-\frac{E \cdot F}{R \cdot T}\right) \right\} + \sigma_h \cdot \left\{ \exp\frac{E \cdot F}{R \cdot T} - 1 \right\} \right] \quad (1)$$

where I_e and I_h are the currents due to electrons and holes, respectively, R is the gas constant, T absolute temperature, A electrode area, L sample thickness, F the Faraday constant, E applied voltage, and σ_e and σ_h are the conductivities due to electrons and holes, respectively.

If $\sigma_e \gg \sigma_h$, the term $\sigma_h \left\{ \exp\frac{E \cdot F}{R \cdot T} - 1 \right\}$ is negligible and I_{total} becomes independent of E . If $\sigma_e \ll \sigma_h$, the term $\sigma_e \left\{ 1 - \exp\left(-\frac{E \cdot F}{R \cdot T}\right) \right\}$ is negligible and I_{total} increases exponentially with an increase in E .

The current-voltage curve shown in Fig. 6 indicates that the relation $\sigma_e \gg \sigma_h$ holds for the $86.9\text{Li}_3\text{PS}_4 \cdot 13.1\text{LiAlS}_2$ sample. The electronic conductivity σ_e , which is determined from Eq. (1), is $3.5 \times 10^{-7}\text{ Scm}^{-1}$ at 290 K . The AC conductivity σ_{AC} at 290 K is $3.8 \times 10^{-4}\text{ cm}^{-1}$, which is estimated from the temperature dependence of AC conductivity. The electronic conductivity σ_e are lower by 3 orders of magnitude than the total AC conductivity. The ion transport number of the $86.9\text{Li}_3\text{PS}_4 \cdot 13.1\text{LiAlS}_2$ sample, t_{ion} , is 0.999 which is calculated from the σ_e and σ_{AC} according to Eq. (2).

Fig. 6 Current vs. voltage characteristic of the amorphous $86.9\text{Li}_3\text{PS}_4 \cdot 13.1\text{LiAlS}_2$ sample at 290 K for the determination of electronic conductivities by means of the Wagner's polarization technique.

$$t_{\text{ion}} = (\sigma_{\text{AC}} - \sigma_{\text{e}}) / \sigma_{\text{AC}} \quad (2)$$

This result suggests that the transport number of the lithium ions is practically unity.

We have attempted to assemble all-solid-state batteries with the obtained amorphous $86.9\text{Li}_3\text{PS}_4 \cdot 13.1\text{LiAlS}_2$ sample. In the battery, TiS_2 and $\text{Li}_{4.4}\text{Si}$ powders have been used as positive and negative electrode materials, respectively. Fig. 7 shows the discharge-charge curves of the all-solid-state battery. The abscissa of the figure is the specific capacity that has been calculated on the base of the weight of the TiS_2 positive electrode material. At the first discharge, the capacity is 208 mAhg^{-1} , which corresponds to about 87% of the theoretical capacity of TiS_2 . While the capacity of the second discharge is smaller than that of the first discharge, the discharge-charge curves after second cycle are almost same. The discharge-charge efficiency is almost unity after second cycle.

Those results suggest that the amorphous $86.9\text{Li}_3\text{PS}_4 \cdot 13.1\text{LiAlS}_2$ sample prepared by the high-energy ball-milling process has the superior electrochemical performance as solid electrolytes for all-solid-state lithium batteries.

4 Conclusions

We attempted to prepare the lithium ion conducting solid electrolytes in the composition $(100-x)\text{Li}_3\text{PS}_4 \cdot x\text{LiAlS}_2$ (mol %) by use of the high-energy ball-milling process at room temperature. The amorphous samples were obtained in the composition range of $x=0$ to $x=13.1$. The maximum ion conductivity at 298 K, $\sigma_{298\text{K}} = 6.0 \times 10^{-4} \text{ Scm}^{-1}$, and the minimum activation energy for conduction, $E_a = 39 \text{ kJmol}^{-1}$, were obtained for the amorphous sample with $x = 13.1$. The measurement of DC polarization was performed to determine dominant mobile ions in the samples and confirmed that the main carrier was lithium ions. The amorphous sample with $x = 13.1$ showed the best electrochemical properties as solid electrolytes among the obtained samples. The laboratory-scale all-solid-state battery was also assembled by using of the sample with $x = 13.1$ and the battery showed good discharge-charge cycle performance at room temperature.

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