研究

Mechano-chemical Synthesis of Lithium Ion Conducting Materials in the System $\text{Li}_2\text{O}-\text{Li}_2\text{S}-\text{P}_2\text{S}_5$

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SYNOPSIS

Amorphous solid electrolytes were prepared in the compositions $75\{(1-x)\text{Li}_2\text{O} \cdot x\text{Li}_2\text{S}\} \cdot 25\text{P}_2\text{S}_5$ (mol%) by using a high-energy ball-milling process. The amorphous materials showed lithium ion conductivities higher than 10^{-3} Sm^{-1} at room temperature. The amorphous $7.5\text{Li}_2\text{O} \cdot 67.5\text{Li}_2\text{S} \cdot 25\text{P}_2\text{S}_5$ (mol%) sample showed the highest lithium ion conductivity $\sigma_{298\text{K}} = 2.7 \times 10^{-2} \text{ Sm}^{-1}$ at room temperature among the obtained samples. An all-solid-state battery was assembled by using the amorphous $7.5\text{Li}_2\text{O} \cdot 67.5\text{Li}_2\text{S} \cdot 25\text{P}_2\text{S}_5$ sample as solid electrolytes. In the battery, TiS_2 and $\text{Li}_4.4\text{Si}$ were employed as positive and negative electrode materials, respectively. The discharge-charge cycling test of the battery was carried out at room temperature under a constant current density of $64 \mu\text{Acm}^{-2}$ with the discharge-charge criteria of voltages 1.1 and 2.6 V. The battery showed successive reversibility with a large specific capacity; the specific capacity calculated on the base of the weight of the TiS_2 positive electrode materials was about 170 mAhg^{-1} .

KEY WORDS

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

1 Introduction

Lithium-ion conducting solid electrolytes¹⁻¹²⁾ have been extensively investigated because of their promising application for all-solid-state lithium batteries¹³⁻¹⁶⁾. The all-solid-state batteries have some advantages, no leakage of electrolyte solutions, easy miniaturization such as thin film batteries¹⁷⁻¹⁹⁾, and high safety performance for an accident such as thermal shock during utilization as against conventional lithium ion batteries with liquid electrolytes containing lithium salts and organic solvents. The organic solvents comprise oxygen atoms in their molecular structures, and accordingly, the organic solvents are flammable. In contrast to these organic liquid electrolytes, inorganic solid electrolytes are flameproof materials. Then, the all-solid-state batteries with the inorganic electrolytes are expected to show high safety performance. Consequently, much effort has been devoted to developing the inorganic solid electrolytes with high lithium ion conductivity for the all-solid-state lithium batteries.

Some papers^{20,21)} have reported the "mixed anion effect" and/or "mixed former effect", i.e. a positive deviation from additivity in the ionic conductivity, which is observed in the glasses containing two kinds of anion species. This phenomenon is an interest subject to obtain glasses with

high ion conductivities. Sulfide based glasses³⁻¹²⁾ are promising candidates for inorganic solid electrolytes of the all-solid-state battery because of their high lithium ion conductivities of more than 10^{-4} Sm^{-1} at room temperature. From the viewpoint of the mixed anion effect, we suppose that the glasses containing both sulfide and oxide anions probably show lithium ion conductivities higher than the glasses which contain only sulfide anions. However, the glasses containing both sulfide and oxide anions are difficult to be prepared by usual melt-quenching methods. The difficulty of the preparation relates to the instability and the immiscibility of their melts at high temperature.

High-energy ball-milling process is one of the most powerful methods for obtaining amorphous materials, inter-metallic compounds, and meta-stable phases^{22,23)}. The high-energy ball-milling process is interesting as a new process for obtaining thermally unstable compounds at high temperature, because the process works at room temperature²⁴⁻²⁸⁾. In addition, the ball-milling process produces samples as fine powders. This point is also advantageous for obtaining ionic conductors, because solid electrolytes are usually employed as powders in the assembling process of electrochemical devices such as all-solid-state batteries, capacitors, and so on^{5,13,14,28,29)}.

Recently, Hayashi et al.²⁸⁾ reported that amorphous substances were obtained in the system $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$ by the high-energy ball-milling process and they showed high lithium ion conductivities larger than 10^{-2} S m^{-1} at room temperature. We also reported that amorphous materials in the systems $\text{Li}_2\text{S}-\text{SiS}_2$ ¹³⁾ and $\text{Li}_2\text{S}-\text{P}_2\text{S}_3$ ⁵⁾ were obtained by the ball-milling process and that the obtained materials were capable to be utilized as solid electrolytes for all-solid-state lithium batteries.

In the present study, we have applied the high-energy ball-milling process to the preparation of amorphous materials in the system $\text{Li}_2\text{O}-\text{Li}_2\text{S}-\text{P}_2\text{S}_5$, and have investigated the lithium ion conducting properties of the obtained amorphous materials. Furthermore, an all-solid-state battery with those amorphous materials is assembled and the performance of the battery is characterized.

2 Experimental

High-energy ball-milling process was applied to the preparation of amorphous samples in the system $\text{Li}_2\text{O}-\text{Li}_2\text{S}-\text{P}_2\text{S}_5$. Reagent-grade Li_2O (Aldrich, 99.9%), Li_2S (Fulukawa, 99.99%) and P_2S_5 (Aldrich, 98%) were used as raw materials. The desired amounts of the raw materials were weighed and mixed in an alumina mortar about 10 minutes. The mixture was placed in a stainless steel container with tetragonal zirconia balls (7 balls of 10 mm diameter and 10 balls of 5 mm diameter) and then the container was sealed with an O-ring. The total mass of the raw materials was 2 g. The container was mounted on a planetary ball-milling apparatus (Fritsch, P-7) and the ball-milling rotation rate was 380 rpm. All the manipulations were carried out in a glove box (UNICO, UN-800S) filled with dry argon gas (dew point, -65°C) and thus the milling was performed in argon atmosphere.

The obtained samples were characterized by using X-ray diffraction measurements. For the measurements, the sample was sealed in an airtight container with the beryllium windows and the container was mounted on an X-ray diffractometer (Rigaku, RINT2000) with $\text{Cu-K}\alpha$ radiation.

The electrical conductivity of the samples was measured by using ac impedance methods. The ball-milled sample was pressed into a pellet (10 mm in diameter and 1–2 mm in thickness) and indium plates (0.2 mm in thickness) were affixed on both sides of the pellet to serve the electrodes. The total electrical conductivity of the pellet was measured in a dry argon atmosphere from 42 Hz to 5 MHz with a precision LCR meter (HIOKI, 3532). The conductivity was determined by employing complex admittance analysis.

Dc polarization measurements were carried out to

determine dominant mobile ions in the samples. Two types of cells were used for the dc measurements. One of them (cell A) had two lithium electrodes working as reversible electrodes for lithium ions, and the other cell (cell B) had two stainless steel (sus-316) electrodes working as blocking electrodes for lithium ions. A constant dc voltage of 0.5 V was applied to the cells at room temperature employing a potentiostat (Hokuto, HA-501).

Wagner's polarization measurements were carried out at 273 K in a dry argon atmosphere to determine the electronic conductivities of the ball-milled samples. In the cell for this measurement, 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 1.8 to 3.4 V across the blocking electrode (positive) and the reversible electrode (negative).

We also assembled all-solid-state batteries employing the ball-milled samples. Fig. 1 shows the schematic diagram of the all-solid-state cell. In the cell, the $a\text{-}7.5\text{Li}_2\text{O} \cdot 67.5\text{Li}_2\text{S} \cdot 75\text{P}_2\text{S}_5$ (mol%) powder prepared by the high-energy ball-milling process was used as a solid electrolyte. The positive electrode was a mixture of TiS_2 (60 wt%) and the solid electrolyte (40 wt%). The negative electrode was a metastable phase $\text{Li}_{4.4}\text{Si}$ alloy, which was also prepared by the ball-milling process²⁷⁾. The cell was prepared by successively pressing the positive electrode mixture, solid electrolyte, and the $\text{Li}_{4.4}\text{Si}$ alloy powders at 300 MPa into a pellet of 10 mm diameter. The assembling process was carried out in a glove box (UNICO, UN-800S) filled with dry argon gas (dew point -65°C). The galvanostatic discharge-charge cycling test was performed between 2.6 and 1.1 V at room

Fig.1 Schematic diagram of a laboratory-scale all-solid-state battery with the amorphous $7.5\text{Li}_2\text{O} \cdot 67.5\text{Li}_2\text{S} \cdot 25\text{P}_2\text{S}_5$ (mol%) solid electrolyte prepared by the ball-milling process. The positive electrode was a mixture of TiS_2 (60 wt%) and the solid electrolyte (40 wt%) powders. The negative electrode was $\text{Li}_{4.4}\text{Si}$ alloy powders.

temperature by use of a battery tester (Hokuto, HJR-110mSM6).

3 Results and Discussion

We applied the high-energy ball-milling process to prepare amorphous samples in the compositions of $75\{(1-x)\text{Li}_2\text{O} \cdot x\text{Li}_2\text{S}\} \cdot 25\text{P}_2\text{S}_5$ ($0 \leq x \leq 1$) (mol%). In this notation for the chemical composition, x denotes the fraction of Li_2S against total amounts of lithium salts, Li_2O and Li_2S . Throughout the paper, compositions will be given base on mole percent.

Fig. 2 shows the X-ray diffraction (XRD) spectra of the ball-milled samples. In this figure, ball-milling time is denoted by MM. Those XRD spectra show only halo patterns and no diffraction peaks due to any crystalline phase for all samples prepared by the ball milling. These results indicate that the high-energy ball-milling process longer than 34 h makes the samples over the whole composition range of $x = 0$ to $x = 1.0$ into the amorphous states.

The electrical conductivities of the ball-milled samples were analyzed by the ac admittance method. The complex admittance plots of the samples showed only a semicircle. The bulk admittance was identified as the intersecting point

of the semicircle with the real axis. Fig. 3 shows the temperature dependence of conductivities of the ball-milled samples with various compositional parameter, x . The conductivities, σ , fit the Arrhenius equation (1);

$$\sigma \cdot T = A \cdot \exp(-E_a / R \cdot T) \quad (1)$$

where T is the absolute temperature, A the pre-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 , are shown in Fig. 4 as a function of the compositional parameter x in $75\{(1-x)\text{Li}_2\text{O} \cdot x\text{Li}_2\text{S}\} \cdot 25\text{P}_2\text{S}_5$. In the figure, open circles and open squares denote the $\sigma_{298\text{K}}$ and E_a , respectively. The conductivity of the $a\text{-}75\text{Li}_2\text{S} \cdot 25\text{P}_2\text{S}_5$ sample at 298 K reported by Hayashi et al.³⁰⁾ is also shown as a star in the figure for comparison. The conductivity reported by Hayashi shows good agreement with that of the present study.

The $\sigma_{298\text{K}}$ shows the maximum at around the compositional parameter $x = 0.9$. The enhancement of conductivity is probably caused by the mixed anion effect of oxide and sulfide anions. The E_a is also shows the minimum at around $x = 0.9$. The position of the minimum in E_a is the same as that of the maximum in $\sigma_{298\text{K}}$ of those samples. This result suggests that the enhancement of conductivity is dominantly governed by the decrease in E_a by mixing of two kinds of lithium salts, Li_2O and Li_2S .

Fig. 5 shows the results of the dc polarization measurements, which have been carried out to determine dominant mobile

Fig. 2 X-ray diffraction patterns of the ball-milled samples in the compositions $75\{(1-x)\text{Li}_2\text{O} \cdot x\text{Li}_2\text{S}\} \cdot 25\text{P}_2\text{S}_5$ (mol%); (a) $x = 0.0$, (b) $x = 0.3$, (c) $x = 0.5$, (d) $x = 0.6$, (e) $x = 0.7$, (f) $x = 0.8$, (g) $x = 0.9$, and (h) $x = 1.0$. In the figure, MM denoted the milling times for obtaining samples.

Fig. 3 Temperature dependence of the ac conductivities of the amorphous $75\{(1-x)\text{Li}_2\text{O} \cdot x\text{Li}_2\text{S}\} \cdot 25\text{P}_2\text{S}_5$ (mol%) samples prepared by the ball-milling process.

Fig.4 Composition dependence of the conductivity at 298 K, σ_{298K} , and the activation energy for conduction, E_a , of the amorphous $75\{(1-x)\text{Li}_2\text{O} \cdot x\text{Li}_2\text{S}\} \cdot 25\text{P}_2\text{S}_5$ (mol%) samples prepared by the ball-milling process. Open circles and open squares denote σ_{298K} and E_a , respectively.

ions of the ball-milled $7.5\text{Li}_2\text{O} \cdot 67.5\text{Li}_2\text{S} \cdot 25\text{P}_2\text{S}_5$ sample ($x=0.9$) at 292 K. In the measurements, we have utilized the two types of cells, cells A and B. The cell A has two lithium electrodes working as reversible electrodes and the cell B has two stainless steel (sus-316) electrodes working as blocking electrodes. The schematic diagrams of those cells are illustrated as insets of Fig. 5. The constant voltage of 0.5 V is applied to the cells A and B. For the cell A, a current more than 0.43 mA is observed and the current is almost constant with time. The dc conductivity is calculated to be $2.06 \times 10^{-2} \text{ Sm}^{-1}$ from the observed current and the applied voltage. This dc conductivity is almost same as the ac conductivity of $2.1 \times 10^{-2} \text{ Sm}^{-1}$ at 292 K, which is calculated from the temperature dependence of the ac conductivity by using the equation (1) mentioned above.

On the other hand, a large polarization phenomenon is observed for the cell B and the current comes close to zero. The residual current after 600 s is $0.026 \mu\text{A}$. The residual current is about 3 orders of magnitude smaller than that of the cell A. Those results suggest that the main carrier of the $7.5\text{Li}_2\text{O} \cdot 67.5\text{Li}_2\text{S} \cdot 25\text{P}_2\text{S}_5$ sample is Li^+ ions.

Fig. 6 shows the current-voltage characteristics for the determination of electronic conductivities by use of the cell (-) Li | sample | sus-316 (+). According to the Wagner polarization analysis³⁰⁾, the total electronic current, I , is

Fig.5 Dc polarization curves of the amorphous $7.5\text{Li}_2\text{O} \cdot 67.5\text{Li}_2\text{S} \cdot 25\text{P}_2\text{S}_5$ (mol%) sample; the cell (A) had two lithium electrodes working as reversible electrodes and the cell (B) had two stainless steel (sus-316) electrodes working as a blocking electrodes. The applied voltage was 0.5 V.

given by the equation (2),

$$I = I_e + I_h$$

$$= \frac{R \cdot T \cdot A}{F \cdot L} \left\{ \sigma_e \left[1 - \exp\left(-\frac{E \cdot F}{R \cdot T}\right) \right] + \sigma_h \left[\exp\left(\frac{E \cdot F}{R \cdot T}\right) - 1 \right] \right\} \quad (2)$$

where I_e and I_h are the currents due to electrons and holes, respectively, R is the gas constant, T is the absolute temperature, A is the electrode area, L is the sample thickness, F is the Faraday constant, E is the 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 $\sigma_h [\exp(E \cdot F / R \cdot T) - 1]$ is negligible and I becomes independent of E . If $\sigma_e \ll \sigma_h$, the term $\sigma_e [1 - \exp(-E \cdot F / R \cdot T)]$ is negligible and I increases exponentially with E . The current-voltage characteristics shown in Fig. 6 indicate that the relation $\sigma_e \gg \sigma_h$ holds for

Fig. 6 Current vs. voltage characteristics of the amorphous $75\text{Li}_2\text{S} \cdot 25\text{P}_2\text{S}_5$ (mol%), $7.5\text{Li}_2\text{O} \cdot 67.5\text{Li}_2\text{S} \cdot 25\text{P}_2\text{S}_5$ (mol%), and $30\text{Li}_2\text{O} \cdot 45\text{Li}_2\text{S} \cdot 25\text{P}_2\text{S}_5$ (mol%) samples at 273 K for the determination of electronic conductivities by means of the Wagner polarization technique.

those samples. The electronic conductivities σ_e at 273 K, determined from the equation (2), are summarized in Table 1, with the ac conductivities at 273 K that are estimated from the temperature dependence of the ac conductivities. The electronic conductivities σ_e are lower by 3 to 4 orders of magnitude than the total ac conductivities. The ion transport numbers, t_{ion} , calculated from the total and electronic conductivities are also summarized in Table 1. It is evident that the transport numbers of the lithium ions are practically unity.

The $a\text{-}7.5\text{Li}_2\text{O} \cdot 67.5\text{Li}_2\text{S} \cdot 25\text{P}_2\text{S}_5$ sample shows the best electrochemical properties as the solid electrolytes of all-solid-state lithium batteries among the obtained samples.

Fig. 7 Charge-discharge cycle curves of the all-solid-state cell, $\text{Li}_{4.4}\text{Si} | a\text{-}7.5\text{Li}_2\text{O} \cdot 67.5\text{Li}_2\text{S} \cdot 25\text{P}_2\text{S}_5 | \text{TiS}_2$. The current density of the charge-discharge measurements was $64 \mu\text{Acm}^{-2}$.

Hence, we have attempted to assemble a laboratory-scale all-solid-state battery with the $a\text{-}7.5\text{Li}_2\text{O} \cdot 67.5\text{Li}_2\text{S} \cdot 25\text{P}_2\text{S}_5$ sample. In the laboratory-scale battery, TiS_2 and $\text{Li}_{4.4}\text{Si}$ powders have been employed as positive and negative electrode materials, respectively. The discharge-charge cycling test of the battery has been carried out under a constant current density of $64 \mu\text{Acm}^{-2}$ ($C/20$ in C -rate). The discharge-charge criteria of voltages are set 1.1 and 2.6 V, respectively.

Fig. 7 shows the discharge-charge curves of the 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. For reader's information, the specific capacity of the $\text{Li}_{4.4}\text{Si}$ negative electrode material is additionally plotted in the top abscissa of the figure. While the capacity of the second discharge is smaller than that of the first discharge, the discharge and charge curves after the second cycle are almost same. The all-solid-state lithium battery shows good discharge-charge

Table 1 Ion and electronic conductivities at 273 K and ion transport number of the ball-milled samples, $75\text{Li}_2\text{S} \cdot 25\text{P}_2\text{S}_5$, $7.5\text{Li}_2\text{O} \cdot 67.5\text{Li}_2\text{S} \cdot 25\text{P}_2\text{S}_5$, and $30\text{Li}_2\text{O} \cdot 45\text{Li}_2\text{S} \cdot 25\text{P}_2\text{S}_5$.

Samples	$\sigma_{\text{ac } 273\text{K}}/\text{Sm}^{-1}$	$\sigma_{\text{e } 273\text{K}}/\text{Sm}^{-1}$	t_{ion}
$75\text{Li}_2\text{S} \cdot 25\text{P}_2\text{S}_5$	4.30×10^{-3}	7.0×10^{-7}	99.98
$7.5\text{Li}_2\text{O} \cdot 67.5\text{Li}_2\text{S} \cdot 25\text{P}_2\text{S}_5$	8.37×10^{-3}	2.0×10^{-6}	99.98
$30\text{Li}_2\text{O} \cdot 45\text{Li}_2\text{S} \cdot 25\text{P}_2\text{S}_5$	1.11×10^{-3}	3.0×10^{-6}	99.73

cycle properties. The discharge-charge efficiency is almost unity after the second cycle. Those results suggest that the $a\text{-}7.5\text{Li}_2\text{O} \cdot 67.5\text{Li}_2\text{S} \cdot 25\text{P}_2\text{S}_5$ (mol%) sample prepared by the ball-milling process is capable to be used as solid electrolytes for all-solid-state lithium batteries.

4 Conclusions

We attempted to prepare the lithium-ion conducting solid electrolytes in the system $\text{Li}_2\text{O}-\text{Li}_2\text{S}-\text{P}_2\text{S}_5$ by using a high-energy ball-milling process at room temperature. The amorphous samples were obtained over the whole composition range of $x=0$ to $x=1.0$ in the $75\{(1-x)\text{Li}_2\text{O} \cdot x\text{Li}_2\text{S}\} \cdot 25\text{P}_2\text{S}_5$ (mol%). The obtained amorphous samples showed lithium ion conductivities higher than 10^{-3} S m^{-1} at room temperature. The maximum ion conductivity, $\sigma_{298\text{K}} = 2.7 \times 10^{-2} \text{ S m}^{-1}$, and the minimum activation energy for conduction, $E_a = 34.5 \text{ kJ mol}^{-1}$, were obtained for the amorphous sample with the compositional parameter $x=0.9$. The ion transport number of the sample with $x=0.9$ was estimated to be almost unity by the dc polarization and the Wagner polarization experiments.

This amorphous sample with $x=0.9$ showed the best electrochemical properties as solid electrolytes among the obtained samples. Hence, the laboratory-scale all-solid-state lithium battery was also assembled by using the sample with $x=0.9$. In the battery, TiS_2 and $\text{Li}_{4.4}\text{Si}$ were used as positive and negative electrode materials, respectively. The all-solid-state battery showed good discharge-charge properties at room temperature. Those results suggested that the $a\text{-}7.5\text{Li}_2\text{O} \cdot 67.5\text{Li}_2\text{S} \cdot 25\text{P}_2\text{S}_5$ (mol%) sample prepared by the ball-milling process was capable to be employed as solid electrolytes for all-solid-state lithium batteries.

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