A New Amorphous Lithium-ion Conductor in the System Li_2S–P_2S_3

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Amorphous solid electrolytes in the system Li_2S–P_2S_3 were obtained in a narrow composition range at around 66.7 mol % Li_2S content by a high-energy ball-milling process. The $66.7Li_2S \cdot 33.3P_2S_3$ (mol %) sample showed the highest ion conductivity of 1.1×10^{-4} S·cm^{-1} at room temperature among the obtained samples. Cyclic voltammetry revealed that the sample had a wide electrochemical window of about 5 V.

Nonflammable lithium ion conducting solid electrolytes are indispensable materials for producing all-solid-state lithium batteries with high safety performance and with high energy density.[1–3] The solid electrolytes are required to have high lithium ion conductivity and good electrochemical stability over a wide potential range. Sulfide glasses such as Li_2S–B_2S_3, Li_2S–SiS_2, Li_2S–GeS_2, and Li_2S–P_2S_5 systems were investigated as solid electrolytes exhibiting lithium ion conductivities higher than 10^{-5} S·cm^{-1} at room temperature.[4–6]

Among them, P_2S_5-based glasses have attracted much attention because of their lithium-ion conductivities larger than 10^{-4} S·cm^{-1} at room temperature. Recently, mechanochemical synthesis of the amorphous Li_2S–P_2S_5 powders has been reported.[7] The obtained powders have exhibited high conductivities of approximately 10^{-4} S·cm^{-1} at room temperature.

The P_2S_5-based amorphous solid electrolytes probably contain small amounts of free S^{2-} ion. It is feared that the free S^{2-} ions will degrade the electrochemical stability of the solid electrolytes, because the oxidation potential of the free S^{2-} ions is thermodynamically estimated to be 2.2 V vs the Li/Li$^+$ electrode.[8] Then, we are interested in the P_2S_3-based amorphous solid electrolytes, because the sulfur content of the P_2S_3-based solid electrolytes is lower than that of the P_2S_5-based solid electrolytes and the amounts of the free S^{2-} ion are accordingly expected to be negligible for the P_2S_3-based solid electrolytes. However, the glass formation and also the electrical properties have never been reported so far for the system Li_2S–P_2S_3.

The present paper reports the formation of the amorphous solid electrolytes in the system Li_2S–P_2S_3 via mechanochemical synthesis and their electrochemical properties.

The desired amounts of the raw materials Li_2S (Furukawa, 99.9%) and P_2S_3 (Aldrich Chem., 98%) were weighed and placed in a stainless steel (SUS-316) vial with zirconia balls 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. All the manipulations were carried out in a glove box filled with dry argon gas. The obtained samples were characterized by using X-ray diffraction (XRD) measurements (Rigaku, RINT2000). For the measurements, the samples were sealed in an air-tight container.

The ball-milled sample was cold-pressed into a pellet of 10-mm diameter and indium plates were attached on the both sides

of the pellet to serve the electrodes. The electrical conductivity of the pellet was measured in a dry argon atmosphere from 42 Hz to 5 MHz over the temperature range of 280 to 400 K with a precision LCR meter (Hioki, 3532). The conductivity was determined by using complex impedance analysis.

The electrochemical stability of the obtained samples was investigated by using cyclic voltammetry. Lithium thin plate was attached on one face of the cold-pressed pellet and used as the counter and reference electrodes. A stainless steel (sus-316) plate was also attached on the other face of the pellet and used as a working electrode for the measurement. The potential sweep was performed in the range of -0.5 to 5.0 V vs the lithium reference electrode with a scanning rate of 1 mV·min^{-1} using a potentiostat (Hokuto, HSV-100).

Figure 1 shows the XRD spectra of the $xLi_2S \cdot (100 - x)P_2S_3$ powders that have been subjected to ball-milling for 50 h. Throughout this paper, compositions will be given based on mole percent. The $66.7Li_2S \cdot 33.3P_2S_3$ sample shows only a halo pattern and no diffraction peaks due to crystalline phases. This result indicates that the $66.7Li_2S \cdot 33.3P_2S_3$ sample becomes amorphous after milling for 50 h. Halo patterns are also basically observed in the samples with $x > 70$, whereas the diffraction peaks due to Li_2S phase (JCPDS #26-1188) are still present after milling for 50 h.
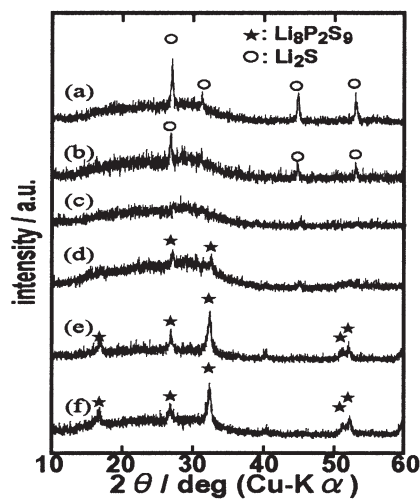

Figure 1. X-ray diffraction spectra of the 50 h ball-milled $xLi_2S \cdot (100 - x)P_2S_3$ (mol%) samples; (a) $x = 75$, (b) $x = 70$, (c) $x = 66.7$, (d) $x = 63$, (e) $x = 60$, and (f) $x = 50$.

The other samples with the Li_2S content smaller than 63 mol % show diffraction peaks due to the $Li_8P_2S_9$ crystalline phase (JCPDS #34-699). Thus it is concluded that the amorphous $xLi_2S \cdot (100 - x)P_2S_3$ sample is obtained in a very narrow composition range at around $x = 66.7$ by the high-energy ball-milling process. The SEM observation suggested that the amor-

phous sample was 1–2 μm in diameter as the average particle size.

Figure 2 shows the temperature dependence of the electrical conductivities of the 50 h ball-milled $x\mathrm{Li_2S\cdot(100-x)P_2S_3}$ samples. The conductivities of the samples follows the Arrhenius equation; $\sigma \cdot T = A \cdot \exp(-E_a/R \cdot T)$, where σ is the conductivity, T the thermodynamical temperature, A the pre-exponential factor, E_a the activation energy for conduction, and R the gas constant.
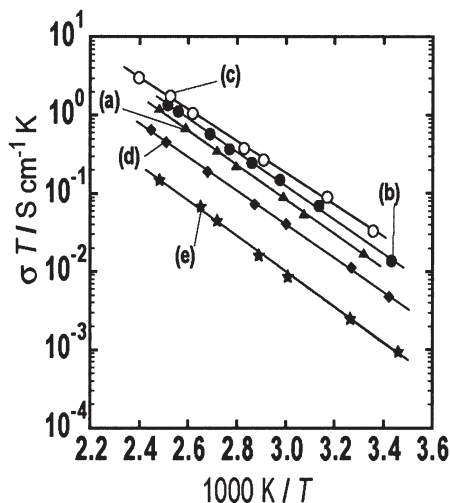

Figure 2. Temperature dependence of the ion conductivity of the 50 h ball-milled samples $x\mathrm{Li_2S\cdot(100-x)P_2S_3}$; (a) $x = 75$, (b) $x = 70$, (c) $x = 66.7$, (d) $x = 63$, and (e) $x = 60$.

The 66.7$\mathrm{Li_2S\cdot33.3P_2S_3}$ sample, which is in amorphous state, shows the maximum conductivity of $1.1 \times 10^{-4}\,\mathrm{S\cdot cm^{-1}}$ at 298 K and the smallest E_a of 39 kJ·mol^{-1} among the ball-milled samples. The conductivity value is very high as pelletized sample that is obtained by the cold-press of solid electrolyte powders.[9] The samples containing any crystalline phases $\mathrm{Li_2S}$ and/or $\mathrm{Li_8P_2S_9}$ show lower conductivities than the amorphous 66.7$\mathrm{Li_2S\cdot33.3P_2S_3}$ sample.

Figure 3a shows the cyclic voltammogram of the amorphous 66.7$\mathrm{Li_2S\cdot33.3P_2S_3}$ sample prepared by the ball-milling for 50 h. In the figure the voltammogram of the amorphous 66.7$\mathrm{Li_2S\cdot}$ 33.3$\mathrm{P_2S_5}$ sample is also shown as Figure 3b for comparison. The measurements are examined from the rest potential to the cathodic direction and then to the anodic direction up to $+5\,\mathrm{V}$ vs Li/Li$^+$ electrode. The rest potentials are indicated by the small arrows in the figures.

The lithium deposition (Li$^+$ + e$^-$ → Li) and dissolution (Li → Li$^+$ + e$^-$) reactions are observed in the potential range of $-0.5\,\mathrm{V}$ to 0.8 V in the voltammograms. The coulombic efficiency due to the lithium deposition/dissolution reactions is calculated from the voltammograms in the potential range. The coulombic efficiencies of the 66.7$\mathrm{Li_2S\cdot33.3P_2S_3}$ and the 66.7$\mathrm{Li_2S\cdot}$ 33.3$\mathrm{P_2S_5}$ samples are 98 and 63%, respectively. The P$_2$S$_3$-based sample shows the superior coulombic efficiency to the P$_2$S$_5$-based sample.
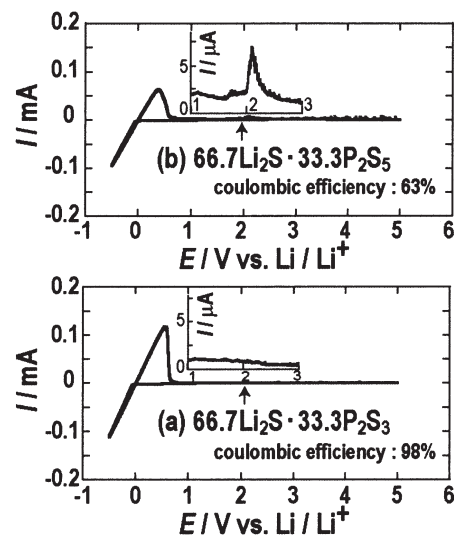

Figure 3. Cyclic voltammograms of (a) the amorphous 66.7$\mathrm{Li_2S\cdot33.3P_2S_3}$ sample and (b) the amorphous 66.7$\mathrm{Li_2S\cdot}$ 33.3$\mathrm{P_2S_5}$ sample. The voltammetry was performed at a room temperature with a scanning rate of 1 mV·min^{-1}.

In addition, the P$_2$S$_3$-based sample shows no reactions in the potential range of 1 to 5 V. On the other hand, the P$_2$S$_5$-based sample shows a small anodic peak at about 2.1 V in its voltammogram. The enlarged voltammograms are shown as the insets of the figures. The small anodic peak is probably due to the oxidation of free S^{2-} ions, because the oxidation potential of the free S^{2-} ions is calculated to be 2.2 V vs Li/Li$^+$ electrode from the thermodynamic data.[8] These results suggest that the amorphous 66.7$\mathrm{Li_2S\cdot33.3P_2S_3}$ sample has prominent electrochemical stabilities as the solid electrolytes for all-solid-state lithium batteries.

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