X-ray photoelectron spectroscopy for sulfide glass electrolytes in the systems Li$_2$S–P$_2$S$_5$ and Li$_2$S–P$_2$S$_5$–LiBr

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X-ray photoelectron spectra of S$_2$p and P$_2$p were obtained for the xLi$_2$S·(100−x)P$_2$S$_5$ (x = 70, 75 and 80 mol %) glasses prepared by mechanochemical treatment. A peak deconvolution technique was used to separate the S$_2$p spectra into three sulfur components of bridging sulfur (S°), non-bridging sulfur (S−) and sulfide ion (S²−) with different photoelectron binding energies. The fractions of sulfurs at different electronic states were obtained from the area ratio of each peak. No apparent difference in the fractions of S° and S− were almost the same in each glass regardless of the amount of added LiBr content. The addition of LiBr did not affect the electronic state of sulfur in the Li$_2$S–P$_2$S$_5$–LiBr glasses.

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1. Introduction

Nowadays, lithium secondary batteries are being used as power sources in various portable electronic devices because of their high-energy density.1) Furthermore, much attention has been paid to all-solid-state lithium secondary batteries using inorganic solid electrolytes. Compared to conventional lithium-ion batteries using flammable organic liquid electrolytes, all-solid-state lithium secondary batteries have their advantages in safety and reliability.2–5) By solving this issue, excellent cell performance such as long cycle life and high capacity could be obtained. In addition to favorable electrode–electrolyte interface, solid electrolytes with high ionic conductivities are also essential to ensure the effective transportation of lithium ions in the battery. Recently, Kanno et al. have reported that solid electrolytes such as Li$_4$GeP$_2$S$_5$ crystal showed extremely high lithium-ion conductivity of over 10$^{-2}$S cm$^{-1}$ at room temperature, which is as high as those of liquid electrolytes.6) In addition, we previously discovered the 70Li$_2$S·30P$_2$S$_5$ (mol %) glass-ceramics, which were prepared by the crystallization of mother glasses, showed high lithium-ion conductivity of 10$^{-2}$–10$^{-3}$ S cm$^{-1}$ at room temperature.7,8)

To achieve higher ion conductivity, adding halides to the mother glasses have been studied for many years. We previously found that by adding AgI into the Ag$_2$MoO$_4$ oxide glasses, the Ag$^+$ ion conductivity increased from 10$^{-2}$ to 10$^{-1}$ S cm$^{-1}$ at room temperature.9) The addition of different halides affected ion conductivity of glasses because of their distortion in ionic radii. In our laboratory, ion conductivities of Li$_2$S–P$_2$S$_5$–LiX (X = F, Cl, Br, I) glasses were discussed.10) The conductivity of the 70Li$_2$S·30P$_2$S$_5$ (mol %) glasses added with LiBr and LiI increased concomitantly with increasing lithium halides contents. However, the conductivity decreased when LiF and LiCl were added to the glasses. The influence of the added lithium halide on sulfide glass structures has not been discussed in detail.

Ion conductivities of solid electrolytes are closely related to their structures. Finding out the structures of electrolytes with high ion conductivities is thus significant. Structural analyses such as solid state NMR, Raman spectroscopy and X-ray diffraction have been used generally to investigate the structures of sulfide electrolytes. In this study, we have focused on X-ray photoelectron spectroscopy (XPS). However, because of the atmospheric instability of sulfide glass electrolytes, XPS analysis reports about sulfide solid electrolytes are limited. It is important to determine an appropriate process for measuring sulfide solid electrolytes without exposure to the air. We previously used XPS to analyze the structures of Li$_2$S–SiS$_2$ and Li$_2$S–SiS$_2$–Li$_2$SiO$_4$ glasses.11,12) By measuring S$_2$p photoelectron spectra, the fractions of bridging and non-bridging sulfurs were determined in the glasses. Bridging and non-bridging oxygen ions were also distinguished from O$_{1s}$ spectra and bridging oxygen ions were mainly observed in the glasses with small amounts of Li$_2$SiO$_4$. XPS is useful for analyzing the electronic states of each element in solid electrolytes. Especially, the XPS analysis for sulfur element which directly interacts with lithium ions is important to understand conductivity behavior. However, XPS analysis has not been done for the Li$_2$S–P$_2$S$_5$ solid electrolytes which are promising electrolytes for all-solid-state lithium secondary batteries.

In this study, the Li$_2$S–P$_2$S$_5$ glasses were analyzed by X-ray photoelectron spectroscopy (XPS). Electronic states of constituent elements (sulfur and phosphorus) in Li$_2$S–P$_2$S$_5$ electrolytes were examined by S$_2$p and P$_2$p XPS spectra. Electronic states of sulfur and phosphorus have an influence on the conductivity of the glasses. XPS measurement was also carried out for Li$_2$S–P$_2$S$_5$–LiBr glasses to examine the change in the electronic states.
of sulfur with the LiBr addition. Specific measurement conditions of XPS were also discussed to make sure that no damages were caused during the measurement.

2. Experimental

2.1 Sample preparation

Solid electrolytes $x\text{Li}_2\text{S}·(100-x)\text{P}_2\text{S}_5$ (x = 70, 75 and 80 mol %) glasses were prepared by a mechanochemical technique using a planetary ball mill apparatus. Reagent-grade Li$_2$S (Idemitsu Kosan Co., 99.9%) and P$_2$S$_5$ (Aldrich Chemical Co. Inc., 99.99%) were used as starting materials. They were mixed in an agate mortar and then put into a 45 ml ZrO$_2$ pot with 500 ZrO$_2$ balls (diameter: 4 mm). The pot was set in a planetary ball mill apparatus (Fritsch, Pulverisette 7) and mechanochemical treatment was performed to prepare glasses at the rotation speed of 510 rpm for 10–40 h. All the processes were carried out in a dry Ar glove box.

To prepare the ($100-y$)($0.7\text{Li}_2\text{S}·0.3\text{P}_2\text{S}_5$)$_y$LiBr ($y = 5, 10$ and 20 mol %) glasses, reagent-grade Li$_2$S, P$_2$S$_5$ and LiBr (Aldrich Chemical Co. Inc., 99.99%) were used. Mechanochemical treatment was done in a same manner mentioned above.

X-ray diffraction (XRD) measurements (Cu Kα) were performed using a diffractometer (Rigaku, UltimaIV) to identify the glasses. Local structures of these mechanically milled glasses were investigated by using the Raman spectrometer (Horiba, HR-800) with a green laser (wavelength: 532 nm). The pot was set in a planetary ball mill apparatus and then put into a 45 ml ZrO$_2$ pot with 500 ZrO$_2$ balls (diameter: 4 mm). The pot was set in a planetary ball mill apparatus (Fritsch, Pulverisette 7) and mechanochemical treatment was performed to prepare glasses at the rotation speed of 510 rpm for 10–40 h. All the processes were carried out in a dry Ar glove box.

2.2 XPS measurement

The XPS measurement was performed by using a spectrometer (K-Alpha, Thermo Fisher Scientific). Monochromatic Al-Kα radiation (1486.6 eV) was used as the X-ray source. To remove the influence of the charging effect on the spectra, neutralization of the glass surface was performed during the measurement by the combined use of a flood gun. Calibration of the spectra was performed by setting the measured binding energy (BE) of the C1s peak to 284.8 eV of adventitious carbon accumulated in the analysis chamber of the spectrometer. Samples were transferred to the XPS analysis chamber using a vessel where the samples were packed in a dry Ar gas to avoid structural changes of the sulfides by exposure to air. The Li$_2$S–P$_2$S$_5$ and Li$_2$S–P$_2$S$_5$–LiBr glass powders were pressed under 360 MPa for 5 min to obtain flat smooth surface and the Ar$^+$ ion-etching was done to remove the surface impurities. After elimination of the surface impurities, etching procedure was continued to obtain bulk information. S$_2p$ spectral changes with an increase in Ar$^+$ ion-etching time were monitored to examine structure deterioration by Ar$^+$ ion-etching. To suppress the damages of the samples caused by Ar$^+$ ion-etching, Ar clusters were emitted from Ar$^+$ ion gun during the etching process. To obtain the accurate spectra, the pass energy and scan number were set as 50 eV and 50 times, respectively. The electronic states of sulfur and phosphorus in the Li$_2$S–P$_2$S$_5$ and Li$_2$S–P$_2$S$_5$–LiBr glasses were analyzed by measuring S$_2p$ and P$_2p$ spectra. The separation of the S$_2p$ peaks is mainly due to spin–orbital splitting of S$^{2+}$-$1/2$ and S$^{2+}$-$3/2$ components. These two components are split by 1.2 eV, and the relative intensity ratio is 1:2. The full width at half maximum of both the peaks are set to be the same. These spectra are deconvoluted by using a best-fit program with a combination of Gaussian (70%) and Lorentzian (30%) distributions.

3. Results and discussion

3.1 Binary glasses in the system Li$_2$S–P$_2$S$_5$

The XRD patterns of the $x\text{Li}_2\text{S}·(100-x)\text{P}_2\text{S}_5$ (x = 70, 75 and 80 mol %) samples prepared are shown in Fig. 1. Halo patterns were basically observed in each sample, suggesting that Li$_2$S–P$_2$S$_5$ glasses were obtained by mechanochemical treatment. Crystalline Li$_2$S, one of the starting material, partially remained at the composition x = 80 after milling treatment.

Figure 2 shows the Raman spectra of the prepared glasses. One Raman band at 420 cm$^{-1}$ was observed for the x = 70, 75 and 80 glasses, while another band at 407 cm$^{-1}$ was observed for the x = 70 glass. These bands at 420 and 407 cm$^{-1}$ are respectively attributable to the P$_{2S_5}^{1-}$ and P$_{2S_7}^{2-}$ units. The x = 75 and 80 glasses are composed of P$_{2S_3}^{3-}$ units, while the x = 70 glass is composed of P$_{2S_3}^{3-}$ and P$_{2S_7}^{2-}$ units.

Figure 3 shows (a) C$_1$s and (b) S$_2p$ photoelectron spectra of the 75Li$_2$S·25P$_2$S$_5$ glass. Two peaks at around 284.3 and 288.7 eV were observed from C$_1$s spectra before etching. The peak around 288.7 eV is attributable to carbonates (O–C=O), while the other peak around 284.3 eV belongs to hydrocarbons. These indicate that impurities such as carbonates and hydrocarbons which existed on the surface of the glasses.

The decrease of the peak intensity for the C$_1$s spectra with etching time suggested that the amount of the impurities gradually decreased. After etching for 90 min., the peaks attributable to carbon impurities disappeared in the C$_1$s spectra. On the other
hand, no apparent difference was observed in the S_{2p} spectra after the etching process. Peak-broadening was not observed, suggesting that etching with Ar⁺ ions caused no structural changes of the glasses.

**Figure 4** shows the S_{2p} photoelectron spectra of the xLi_2S·(100−x)P_2S_5 (x = 70, 75 and 80 mol %) glasses after Ar⁺ ion-etching for 90 min. One main peak at 161.5 eV was observed in each sample. Although all the glasses showed similar spectra, some differences were observed in the spectra. One small peak was observed at the lower energy side in the compositions of x = 75 and 80. On the other hand, the shape of the spectrum of x = 70 glass became broader at the high energy side. These phenomena indicate that sulfurs at diverse electronic states existed in the glasses. As the results of peak deconvolution, doublet peaks attributable to S_{2p1/2} and S_{2p3/2} of non-bridging sulfur (S⁻) were observed in all the glasses. Because the x = 80 glass contained residual Li_2S crystal, the doublet peaks attributable to sulfide ions (S^{2−}) were found at the lower energy side of the spectrum. The observed binding energy of Li_2S (S_{2p1/2}: 159.9 eV) almost corresponds to the binding energy for S^{2−} reported in the literature (S_{2p1/2}: 160.5 eV). The same phenomenon was observed for the spectrum of the x = 75 glass. Besides the peak at 161.2 eV (S_{2p3/2}) of non-bridging sulfur (S⁻), the S_{2p3/2} peak positioned at 159.8 eV was attributable to S^{2−}. In respect of the spectrum of the x = 70 glass, other doublet peaks existed at the higher energy side in addition to the peaks of S⁻. The peak at 162.7 eV (S_{2p3/2}) was characteristic of the bridging sulfur (S³⁺) in the P₂S₇⁴⁻ unit. Components of S⁰, S⁻ and S^{2−} were separated on the basis of the difference in their photoelectron energies for S_{2p} spectra.

Furthermore, the fractions of sulfurs at different electronic states were calculated from the area ratio of each spectrum. The specific information about S_{2p3/2} binding energy (BE) and the relative area of S_{2p} peaks in the xLi_2S·(100−x)P_2S_5 (x = 70, 75 and 80 mol %) glasses after Ar⁺ ion-etching for 90 min. is summarized in Table 1. With the increase of Li_2S in the glass composition, the fraction of bridging sulfur S³⁺ decreased, while that of S^{2−} increased. Non-bridging sulfur S⁻ was the main component in each glass.

**Figure 5** shows the P_{2p} photoelectron spectra of the xLi_2S·(100−x)P_2S_5 (x = 70, 75 and 80 mol %) glasses after Ar⁺ ion-etching. In terms of phosphorus, no apparent difference in the spectra was observed with an increase in the Li₂S content. Because the surrounding electronic environment of phosphorus in the PS₄³⁻ unit is similar to that in the P₂S₇⁴⁻ unit, these two types of phosphorus did not show a large difference in binding energy.

The correlation between the electronic state of sulfurs and the ion conductivity is also discussed. Based on our previous report, ionic conductivity of the xLi_2S·(100−x)P_2S_5 glasses increased from 5.0 × 10⁻⁴ to 2.0 × 10⁻⁴ S/cm with an increase in x from 70 to 75 mol %. At the same time, the amount of bridging sulfur S³⁺ decreased and the amount of non-bridging sulfur S⁻, which is the counter anion of Li⁺ ions, increased from 89 to 93%. This indicates that the increase of S⁻ relates to the conductivity enhancement. On the other hand, ionic conductivity slightly decreased when the Li₂S content increased to 80 mol %. The amount of S^{2−} increased to 13% in the x = 80 glass, indicating that ionic conductivity decreased with an increase in the fraction of S^{2−} as Li₂S crystal.
3.2 Ternary glasses in the system Li$_2$S–P$_2$S$_5$–LiBr

The XRD patterns of the (100–$y$)(0.7Li$_2$S·0.3P$_2$S$_5$)$y$LiBr ($y = 0, 5, 10$ and $20$ mol %) glasses after mechanochemical treatment for $20$ h are shown in Fig. 6. Halo patterns were observed in each sample and thus Li$_2$S–P$_2$S$_5$–LiBr glasses were obtained by mechanochemical treatment. The DTA curves of the glasses are shown in Fig. 7. An endothermic change attributable to glass transition (T$_g$) was observed, indicating that these amorphous samples were in glassy state. An exothermic peak attributable to crystallization was observed between 220 and 270°C for all the samples. The glass transition temperatures (T$_g$) and the crystallization temperatures (T$_c$) of glasses added with lithium halide shifted to lower temperature side with an increase of the LiBr content.

Figure 8 shows the Raman spectra of the prepared glasses. The spectra did not change with an increase in the LiBr content. Two bands attributable to PS$_4^{3-}$ and P$_2$S$_7^{4-}$ units were observed in all the glasses. This indicates that the addition of LiBr had no influence on structural units of PS$_4^{3-}$ and P$_2$S$_7^{4-}$ in the glasses.

The composition dependence of electrical conductivities at 25°C for (100–$y$)(0.7Li$_2$S·0.3P$_2$S$_5$)$y$LiBr ($y = 0, 5, 10$ and $20$ mol %) glasses is shown in Fig. 9. The conductivities of the glasses concomitantly increased from $8.5 \times 10^{-5}$ to $3.4 \times 10^{-4}$ S cm$^{-1}$ with increasing the LiBr content.

Fig. 5. P$_2$p spectra in the $x$Li$_2$S(100–$x$)P$_2$S$_5$ ($x = 70, 75$ and $80$ mol %) glasses after Ar$^+$ ion-etching for $90$ min.

Fig. 6. XRD patterns of the (100–$y$)(0.7Li$_2$S·0.3P$_2$S$_5$)$y$LiBr ($y = 0, 5, 10$ and $20$ mol %) glasses prepared by mechanochemical treatment.

Fig. 7. DTA curves of the (100–$y$)(0.7Li$_2$S·0.3P$_2$S$_5$)$y$LiBr ($y = 0, 5, 10$ and $20$ mol %) glasses.

Fig. 8. Raman spectra of the (100–$y$)(0.7Li$_2$S·0.3P$_2$S$_5$)$y$LiBr ($y = 0, 5, 10$ and $20$ mol %) glasses.

Fig. 9. Composition dependence of the lithium-ion conductivities at 25°C for the (100–$y$)(0.7Li$_2$S·0.3P$_2$S$_5$)$y$LiBr ($y = 0, 5, 10$ and $20$ mol %) glasses.
The conductivity enhancement by the addition of LiBr is discussed. Li$^+$ ions gathered around PS$_4^{3-}$ and P$_2$S$_7^{4-}$ units to have an electrostatic interaction with non-bridging sulfur (S$^-$). The addition of LiBr makes little impact on the electronic state of sulfur in the glasses. Therefore, the other factors except for electronic state changes in sulfur will increase the conductivity. Two plausible reasons are as follows: firstly, the introduction of Br$^-$ anions with larger polarizability promotes the movement of Li$^+$ ions. Secondly, the addition of LiBr increases the carrier concentration of Li$^+$ ions in the glasses. Based on these two reasons, Li$_2$S–P$_2$S$_5$–LiBr glasses showed higher ionic conductivities than the pristine 70Li$_2$S·30P$_2$S$_5$ glasses. The conductivity enhancement by the addition of LiBr is attributed to the two reasons: firstly, the introduction of Br$^-$ anions with larger polarizability promotes the movement of Li$^+$ ions. Secondly, the addition of LiBr increases the carrier concentration of Li$^+$ ions in the glasses. Based on these two reasons, Li$_2$S–P$_2$S$_5$–LiBr glasses showed higher ionic conductivities than the pristine 70Li$_2$S·30P$_2$S$_5$ glasses.

4. Conclusions

S$_{2p}$ and P$_{2p}$ photoelectron spectra were measured for the xLi$_2$S·(100−x)P$_2$S$_5$ (x = 70, 75 and 80 mol%) glasses. Etching with Ar$^+$ ions caused no structural changes of the glass, and etching was sufficient to eliminate the impurities on the surface of the glasses.

A peak deconvolution technique was used to separate the S$_{2p}$ spectra in xLi$_2$S·(100−x)P$_2$S$_5$ glasses. Because of the difference in photoelectron binding energies, bridging sulfur S$^0$, non-bridging sulfur S$^-$ and S$^2$ were distinguished respectively. No apparent difference in the P$_{2p}$ spectra was observed in all the glasses. The addition of LiBr had no influence on the electronic state of sulfur in the Li$_2$S–P$_2$S$_5$–LiBr glasses.

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