Evaluation of young’s modulus of Li$_2$S–P$_2$S$_5$–P$_2$O$_5$ oxysulfide glass solid electrolytes

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Mechanical properties such as elastic modulus of solid electrolytes are important for all-solid-state batteries. To investigate the effects of a partial substitution of oxide for sulfide on Young’s modulus, 70Li$_2$S·(30–x)P$_2$S$_5$xP$_2$O$_5$ (mol %) (x = 0, 3 and 10) oxysulfide glasses were prepared and characterized. Young’s moduli were measured by ultrasonic pulse echo method for the dense pellets prepared by hot pressing at around glass transition temperature. The Young’s moduli of 70Li$_2$S·(30–x)P$_2$S$_5$xP$_2$O$_5$ glasses were 22–27 GPa and increased with an increase in the P$_2$O$_5$ content. The highest Young’s modulus in this report was 27 GPa for the glass with 10 mol % P$_2$O$_5$.

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1. Introduction

Much attention has been paid to all-solid-state lithium secondary batteries using inorganic solid electrolytes because of their safety and reliability compared to conventional lithium-ion batteries using flammable organic liquid electrolytes.1,2 There are two approaches for developing all-solid-state batteries; one is a thin-film battery prepared by RF sputtering or laser ablation, and the other is a bulk-type battery constructed of electrolyte and electrode powders. The bulk-type battery is expected to have large energy density by the addition of large amounts of active materials to the cell.

Many studies have been done to progress the bulk-type battery. Solid electrolytes with high ionic conductivity are required for effective transportation of lithium ions in the bulk-type battery. Recent researches show that solid electrolytes such as Li$_2$P$_2$S$_{11}$ and Li$_3$GeP$_2$S$_{12}$ have conductivities as high as those of liquid electrolytes.3–5

In addition to high ionic conductivity, achieving intimate solid-solid contacts between electrode active materials and solid electrolytes is also essential to enhance the electrochemical performance of bulk-type batteries.6–8 This issue is characteristic for all-solid-state batteries since both electrode active materials and solid electrolytes are “solid”. To solve the issue is important to obtain excellent cell performance such as high capacity, long cycle life, and high rate capability. Moreover, in all-solid-state batteries, the volume of electrode active materials changes during charging and discharging processes. Solid electrolytes are thus required to maintain intimate electrode/electrolyte contacts against the volume change of electrode active materials. When solid electrolytes are difficult to suppress the volume change, electrode active materials would be broken to fragments or the area of contacts would decrease during their contraction, which lead to the degradation of cell capacity. The mechanical properties of electrode active materials and solid electrolytes, which are closely related, are important to retain the electrode/electrolyte contacts during charging and discharging.

Elastic modulus is an important mechanical property and would affect the electrode/electrolyte contacts during charging and discharging processes. Some elastic moduli of oxide solid electrolytes with high conductivities have been reported.9–11 For instance, for cubic Li$_2$La$_3$Zr$_2$O$_12$ solid electrolytes at a relative density of ~97%, the Young’s modulus was reported as 149.8 ± 0.4 GPa.11 In contrast, Young’s moduli of sulfide solid electrolytes have never been reported; it is difficult to evaluate their mechanical properties because they are generally unstable in air. Recently, our group has succeeded in evaluating the elastic modulus of Li$_2$S–P$_2$S$_5$ sulfide glass electrolytes in a previous report.12 Li$_2$S–P$_2$S$_5$ sulfide electrolytes show a high ionic conductivity13–16 and are applied to bulk-type all-solid-state lithium secondary batteries.17–19 The Young’s moduli of them are about 18–25 GPa and these moduli are lower than those of oxide solid electrolytes.

Various properties of Li$_2$S–P$_2$S$_5$ glass are controlled by adding a third component. We reported that the addition of oxides as a third component to Li$_2$S–P$_2$S$_5$ sulfide glass improved the electrochemical stability and chemical stability in air.20,21 These oxysulfide glasses are thus attractive electrolytes to apply for all-solid-state batteries. However, their mechanical properties have not been investigated.

In this study, the effects of partial substitution of network former P$_2$O$_5$ for P$_2$S$_5$ on the Young’s modulus were investigated. Dense Li$_2$S–P$_2$S$_5$–P$_2$O$_5$ oxysulfide glasses were prepared by hot pressing and the Young’s moduli were evaluated by ultrasonic pulse echo method.

2. Experimental

Oxysulfide glasses of 70Li$_2$S·(30–x)P$_2$S$_5$xP$_2$O$_5$ (mol %) (x = 0, 3 and 10) were prepared by mechanical milling. The
oxysulfide glasses at the composition with $x \leq 10$ prepared by melt quenching were glassy state.\textsuperscript{22} In addition, the glass-ceramics at $x = 3$ showed the highest lithium-ion conductivity in the composition region because of the precipitation of Li$_7$P$_3$S$_{11}$ crystal in which sulfur was partially replaced by oxygen.\textsuperscript{20} Thus, we selected two compositions ($x = 3$ and 10 mol\% for the investigation of the effect of partial substitution of P$_2$O$_5$ for P$_2$S$_5$ on the Young’s modulus.

Reagent-grade Li$_2$S (Idemitsu Kosan >99.9\%), P$_2$S$_5$ (Aldrich 99\%) and P$_2$O$_5$ (Aldrich 99\%) crystalline powders were used as starting materials. The mixture of these materials was mechanically milled by a planetary ball milling apparatus (Fritsch Pulverisette 7) using zirconia balls (4 mm in diameter). The milling time was 8–15 h and the rotating speed was 510 rpm.

Conductivities were determined for the pellets prepared by powder compaction of the milled glass powders at 360 MPa. The pellets were sandwiched between stainless-steel rods as an ion-blocking electrode. Electrical conductivities of the pellets were measured using an AC impedance analyzer (VMP3, Bio-logic) at a frequency range from 10 Hz to 1 MHz at room temperature in Ar atmosphere. X-ray diffraction measurements were done for the milled powders by using an X-ray diffractometer (Ultima IV, Rigaku). DTA was performed by using a thermal analyser (Thermo Plus TG8110, Rigaku) at a heating rate of 10°C min$^{-1}$.

The Young’s modulus were evaluated for hot pressed pellets by ultrasonic pulse echo method.\textsuperscript{23} The milled powders were pelletized by hot pressing at 360 MPa in the range of 210–230°C for 4 h in Ar atmosphere to form dense glass pellets. The thickness and diameter of the prepared pellets were 2–3 mm and 10 mm, respectively. Their apparent densities were determined by the mass and dimensions of the pellets. The hot pressed pellets were packed in a polymer bag (thickness of 0.04 mm) in an Ar filled glove box and evaluated using a ultrasonic pulse/receiver (model 5900PR, Panametrics Co.). The contact transducers for longitudinal and shear waves were used. The frequency was 5 MHz. A coaxial cable (ULTRA PHONIC, elk Co.) was used as the media between the pellet packed in a polymer bag and the contact transducer.

3. Results and discussion

The XRD patterns of 70Li$_2$S·(30 – $x$)P$_2$S$_5$·$x$P$_2$O$_5$ samples after mechanical milling are shown in Fig. 1. Halo patterns were observed for all the samples. It was suggested that these samples were amorphous at the compositions with $x \leq 10$.

The DTA curves of the milled samples are shown in Fig. 2. 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 250 and 280°C for all the samples.

Electrical conductivities at ambient temperature for 70Li$_2$S·(30 – $x$)P$_2$S$_5$·$x$P$_2$O$_5$ ($x = 0$, 3 and 10) oxysulfide glasses were investigated. The conductivities of the glass pellets at $x = 0$, 3, and 10 were $1.2 \times 10^{-4}$, $6.4 \times 10^{-5}$, $2.0 \times 10^{-3}$ S cm$^{-1}$, respectively. The conductivities of the glasses decreased with increasing the P$_2$O$_5$ content. It is reported that the substitution of oxide for sulfide produces not only bridging oxygens but also non-bridging oxygens.\textsuperscript{24} Non-bridging oxygens act as trapping sites for lithium ions and thus the conductivity of glasses tends to decrease. Although electronic state of oxygen has not been analyzed by XPS in this study, the formation of non-bridging oxygens in the glasses would decrease the conductivity.

The glass powders were pressed at around glass transition temperature ($T_g$) for the measurement of Young’s moduli of the glasses. Heating at temperatures higher than glass transition temperatures makes glasses soften via a supercooled liquid state, which gives highly dense glass pellets. Figure 3 shows the XRD patterns of the 70Li$_2$S·(30 – $x$)P$_2$S$_5$·$x$P$_2$O$_5$ oxysulfide glasses after hot pressing. Sharp peaks attributed to precipitation of crystals were not observed, although broad peaks at around 2$\theta$ = 18 and 30° were observed. The angles of broad peaks were consistent with that of Li$_7$P$_3$S$_{11}$ crystal firstly precipitated by heat treatment above the crystallization temperatures. Therefore, the glass structure after hot pressing would be similar to the crystal structure of Li$_7$P$_3$S$_{11}$.

Figure 4 shows the SEM image of the cross section of 70Li$_2$S·20P$_2$S$_5$·10P$_2$O$_5$ oxysulfide glass after hot pressing at 230°C and the inset shows the photograph of a pelletized sample. An
obvious grain boundary or any voids were not observed in the hot-pressed glass, and the pellet looked transparent. Densification phenomenon of Li$_2$S–P$_2$S$_5$ sulfide glasses by hot pressing was also observed in our previous work. Such dense pellets are appropriate for ultrasonic wave velocity measurements because Young’s moduli, which are not affected by grain boundaries or voids, are determined.

Figure 5 shows the composition dependence of Young’s moduli of 70Li$_2$S·(30 – x)P$_2$S$_5$·xP$_2$O$_5$ oxysulfide glasses prepared by hot pressing. Their Young’s moduli were calculated using the following equations:

$$G = \rho V_s^2$$
$$v = (V_L^2 - 2V_s^2)/(2(V_L^2 - V_s^2))$$
$$E = 2G(1 + v)$$

where $V_s$ is velocity of shear wave, $V_L$ is velocity of longitudinal wave, $G$ is shear modulus, $\rho$ is density of the pellet, $v$ is the Poisson’s ratio, and $E$ is Young’s modulus.

The Young’s modulus was measured for the glass pellet packed in a plastic bag to avoid exposure to air. The influence of a plastic polymer bag on Young’s modulus was concerned. The influence was checked using Si$_3$N$_4$ which is stable in air; the Young’s modulus of Si$_3$N$_4$ measured in the plastic bag was the same as that measured without the bag. The contribution of a polymer bag was thus negligible because the thickness of the bag was thin enough to conduct ultrasonic waves between the pellet and the contact transducer when the bag was pressed by a hand. The Young’s moduli of 70Li$_2$S·(30 – x)P$_2$S$_5$·xP$_2$O$_5$ (mol %) ($x = 0$, 3 and 10) glasses were 22, 24, 27 GPa, respectively, and increased with increasing the amount of substitution of P$_2$O$_5$ for P$_2$S$_5$. The highest Young’s modulus in this report was 27 GPa in the case of the substitution of 10 mol % P$_2$O$_5$ for P$_2$S$_5$. This was slightly higher than those of Li$_2$S–P$_2$S$_5$ glassy solid electrolytes, which are 18–25 GPa. The effects of the increase of Young’s modulus of solid electrolytes on cell performance are now under study.

The Young’s modulus of a glass can be discussed from the bond dissociation energy per unit volume and the ion packing density. The bond dissociation energy will increase by the substitution of P$_2$O$_5$ for P$_2$S$_5$ since the P–O bonds are stronger than the P–S bonds. Furthermore, the ion packing density will also increase. Figure 5 also shows the molar volumes of 70Li$_2$S·(30 – x)P$_2$S$_5$·xP$_2$O$_5$ glasses. The molar volume is calculated from density and molecular weight, and decreased with an increase in the P$_2$O$_5$ content, suggesting that ions in the glass containing oxygens are more closely packed. On the basis of the increase of bond dissociation energy and ion packing density, Young’s modulus of 70Li$_2$S·(30 – x)P$_2$S$_5$·xP$_2$O$_5$ glasses increased with an increase in the P$_2$O$_5$ content.

4. Conclusion

The Young’s moduli of 70Li$_2$S·(30 – x)P$_2$S$_5$·xP$_2$O$_5$ ($x = 0$, 3 and 10) sulfide glasses were measured by ultrasonic pulse echo method. The Young’s moduli increased with an increase in the P$_2$O$_5$ content; the Young’s modulus of the $x = 10$ glass was about 27 GPa. The increase of Young’s modulus was understood by the increase of both bond dissociation energy and ion packing density.

References

20) K. Minami, A. Hayashi and M. Tatsumisago, Solid State


