Preparation and Characterization of Amorphous Based Solid Electrolytes

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Amorphous based solid electrolytes are promising for application to solid-state batteries and other electrochemical devices. We have prepared a number of the electrolytes by rapid quenching of melts using a twin-roller and by mechanical milling of starting materials using a planetary ball mill. Three topics of silver or lithium ion conducting amorphous electrolytes prepared by these techniques are reported. The first one is the formation and characterization of $\alpha$-AgI microcrystal-dispersed composite electrolytes, in which high temperature superionic phase of $\alpha$-AgI is stabilized at room temperature in a superionic glass matrix. The second one is the structural investigation of lithium ion conducting oxysulfide glasses prepared by rapid quenching of melts. The last one is the mechanochemical preparation of high lithium ion conducting oxysulfide glasses and their application to solid-state secondary batteries.

Key-words: Solid electrolyte, Glass, Rapid quenching, Mechanical milling, Amorphous, Ion conduction, Solid-state secondary battery

1. Introduction

Much attention has been denoted to fast ion-conducting solids, i.e. “solid electrolytes,” for application to solid-state batteries and other electrochemical devices. Amorphous or glassy materials have several advantages from a viewpoint of ion conduction in comparison with the crystal line ones: a wide range selection of compositions, isotropic properties, no grain boundaries, easy film formation, and so on. Because of the so-called open structure, the ionic conductivity of glassy materials is generally higher than that of crystalline ones. In addition, single ion conduction can be realized because glassy materials belong to the so-called decoupled systems in which the mode of ion conduction relaxation is decoupled from the mode of structural relaxation. Amorphous or glassy materials are thus the most promising candidates of solid electrolytes with single ion conduction and high ionic conductivities.

We have developed a number of amorphous based solid electrolytes from the idea that they are especially favorable for ion conductors, using two unique preparation techniques of glassy materials. One is rapid quenching of melts using a twin-roller, in which the cooling rate is larger than $10^5$ K/s. Using the rapid quenching of melts, it has become feasible to extend the glass formation range with large concentration of carrier ions. The other one is mechanical milling of starting materials using a planetary ball mill. This procedure is basically a room temperature process and useful to obtain fine powders directly used for solid-state secondary batteries.

The present paper reports three topics of silver or lithium ion conducting amorphous based materials, which we prepared using rapid quenching or mechanical milling. The first topic is the formation and characterization of $\alpha$-AgI dispersed composite electrolytes, in which high temperature superionic phase of $\alpha$-AgI is stabilized at room temperature in a superionic glass matrix. The second one is the structural investigation of lithium ion conducting oxysulfide glasses prepared by rapid quenching of melts. The last one is the mechanochemical preparation of high lithium ion conducting oxysulfide glasses and their application to solid-state secondary batteries.

2. Formation and characterization of $\alpha$-AgI stabilized composite electrolytes

Superionic conductor $\alpha$-AgI has high ionic conductivity of $1 \ S \cdot cm^{-1}$ and is thermodynamically stable only above 147°C. $\alpha$-AgI transforms to the low temperature phase, $\beta$-AgI, at 147°C; the conductivity reduces as low as about $10^{-5} \ S \cdot cm^{-1}$ at room temperature. We have succeeded in stabilizing $\alpha$-AgI in AgI–Ag2O–B2O3 glasses at room temperature by a rapid quenching technique. The rapid quenching of melt was performed using a twin-roller quenching apparatus for the starting materials of a mixture of AgI, Ag2O, and B2O3. The X-ray diffraction peaks due to $\alpha$-AgI were only observed in the twin-roller quenched 82AgI–18(0.75Ag2O–0.25B2O3) sample at room temperature. Figure 1 shows the cross-section of field-emission-type scanning electron microscope (FE-SEM) photograph for the $\alpha$-AgI stabilized 82AgI–18(0.75Ag2O–0.25B2O3) sample. The FE-SEM reveals that fine $\alpha$-AgI particles of 20–30 nm in size are dispersed in the glass matrix.
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Fig. 2 shows the temperature dependence of the ionic conductivity for the twin-roller quenched $82\text{AgI} \cdot 18(0.75\text{Ag}_2\text{O} \cdot 0.25\text{B}_2\text{O}_3)$ composite. The conductivity of a pure AgI crystal is also shown for comparison. The conductivity at room temperature for the composite is about $10^{-1} \text{S} \cdot \text{cm}^{-1}$ and the activation energy in the temperature range 25-140°C is 15 kJ/mol. These values are reasonable if the stabilized $\alpha$-AgI phase is present as highly dispersed, discrete particles as shown in Fig. 1. With decreasing temperature after heating up to above 147°C, the conductivity starts to decrease considerably at 110°C. The conductivity decrease is due to the transformation of the stabilized $\alpha$-AgI crystals in the glass matrices into $\beta$-phase.

We have investigated the formation process of $\alpha$-AgI stabilized composites in the system AgI-Ag$_2$O-B$_2$O$_3$ on the basis of the relationship between the cooling conditions in twin-roller quenching of melts and the microstructure of the products by means of X-ray diffraction and field emission type scanning electron microscopy. A microstructure in which $\alpha$-AgI microcrystals were dispersed in glass matrices was obtained during twin-roller quenching of the 80AgI-20(0.75Ag$_2$O-0.25B$_2$O$_3$) melts with the process: (1) a phase separation of liquid occurred to form dispersed particles of the AgI-rich amorphous phase, (2) the particles of the amorphous phase aggregated to form island regions, and (3) $\alpha$-AgI microcrystals were formed from the island regions. We have also shown that the similar process of phase separation—aggregation—crystallization was also observed during the heating process up to around 110°C of the 74AgI-26(0.33Ag$_2$O-0.67MoO$_3$) glass. When the heat treatment temperature was higher than 120°C, weak diffraction peaks due to $\beta$-AgI were observed in addition to the peaks due to $\alpha$-AgI. In the case of rapid quenching of melt the single phase of $\beta$-AgI in the system AgI-Ag$_2$O-MoO$_3$ could not be obtained. On the other hand, it is noteworthy that the single phase of $\alpha$-AgI is obtained at room temperature by the heat treatment of the glass at 110°C.

3. Structure of lithium ion conducting oxysulfide glasses prepared by rapid quenching of melts

Lithium sulfo based glasses are one of the most promising candidates of solid electrolytes utilized for solid-state lithium secondary batteries. We have prepared a variety of rapidly quenched glasses in the systems Li$_2$S-Si$_2$O$_5$-Li$_x$MoO$_y$ ($x+y$ lithium ortho-oxosalt) and showed that such oxysulfide glasses with small amounts of Li$_x$MO$_y$ exhibited high lithium ion conductivities and high stability against crystallization. Here, reported are the structure of the Li$_x$S-Si$_2$O$_5$-Li$_x$SiO$_3$ glasses, one of the typical oxysulfide systems, by means of MAS-NMR and X-ray photoelectron spectroscopy (XPS) measurements and the relation between the structure and properties of the glasses.
Glasses were prepared by rapid quenching of melt using a twin-roller. The starting materials were crystalline chemicals of Li$_2$CO$_3$, SiO$_2$, Li$_2$S, and SiS$_2$. Figure 4 shows the composition dependence of conductivities at room temperature and $T_c-T_g$ for the $(100-x)\,(0.6\text{Li}_2\text{S} \cdot 0.4\text{SiS}_2) \cdot x\text{Li}_4\text{SiO}_4$ oxysulfide glasses prepared by twin-roller quenching of melt. $T_g$ and $T_c$ are the glass transition and crystallization temperatures, respectively, and the difference between $T_g$ and $T_c$, $T_c-T_g$, is one of the measures of glass stability against crystallization.

The conductivity at the composition with $x=5$ is around $10^{-3}$ S cm$^{-1}$, which is a little higher than that of 60Li$_2$S• 40SiS$_2$ binary sulfide glass ($x=0$). Such a value of conductivity at room temperature is one of the highest conductivities in all the lithium ion conducting solid electrolytes developed so far. The conductivity monotonically decreases with an increase of $x$ when $x>5$. $T_c-T_g$ has a maximum at the composition with $x=5$. The addition of 5 mol% Li$_4$SiO$_4$ increases $T_c-T_g$ and, hence, improves the glass stability against crystallization and also enhances the electrical conductivity of about $10^{-3}$ S cm$^{-1}$. Further addition of Li$_4$SiO$_4$ decreases both conductivity and glass stability against crystallization.

Figure 5 shows the $^{29}$Si MAS-NMR spectra of the $(100-x)\,(0.6\text{Li}_2\text{S} \cdot 0.4\text{SiS}_2) \cdot x\text{Li}_4\text{SiO}_4$ oxysulfide glasses. Three peaks are observed at chemical shifts, $\delta$, around 5, -3, and -25 ppm in the 60Li$_2$S• 40SiS$_2$ glass ($x=0$). Such a value of conductivity at room temperature is one of the highest conductivities in all the lithium ion conducting solid electrolytes developed so far. The conductivity monotonically decreases with an increase of $x$ when $x>5$. $T_c-T_g$ has a maximum at the composition with $x=5$. The addition of 5 mol% Li$_4$SiO$_4$ increases $T_c-T_g$ and, hence, improves the glass stability against crystallization and also enhances the electrical conductivity of about $10^{-3}$ S cm$^{-1}$. Further addition of Li$_4$SiO$_4$ decreases both conductivity and glass stability against crystallization.

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The $S_2p$ and $O_1s$ photoelectron spectra of the $(100-x)\,(0.6\text{Li}_2\text{S} \cdot 0.4\text{SiS}_2) \cdot x\text{Li}_4\text{SiO}_4$ oxysulfide glasses were measured. A four peak deconvolution technique was used to separate the $S_2p$ peak of the glass in the components of bridging and nonbridging sulfur atoms ($S_B$ and $S_{NB}$). From the $S_2p$ photoelectron spectra the relative amount of $S_{NB}$ was more than 90% at the composition with 5 mol% Li$_4$SiO$_4$, indicating that most sulfur atoms are present as non-bridging sulfurs in the oxysulfide glass with $x=5$. Figure 6 shows the $O_1s$ photoelectron spectrum of the 95(0.6Li$_2$S• 0.4SiS$_2$)• 5Li$_4$SiO$_4$ oxysulfide glass. This spectrum is separated into two components of bridging ($O_B$) and non-bridging oxygen atoms ($O_{NB}$) by using the best-fit deconvolution program. The peak at the higher binding energy side is attributed to $O_B$ and the other to $O_{NB}$. The relative amount of $O_B$ calculated from the area attributed to $O_B$ divided by the total area of $O_1s$ peak is approximately 85%. These results show that most oxygen atoms, approximately 85% of the total oxygen atoms, are present as bridging oxygens in the oxysulfide glass with small amounts of Li$_4$SiO$_4$.

Figure 7 shows a structural unit expected to be present in the 95(0.6Li$_2$S• 0.4SiS$_2$)• 5Li$_4$SiO$_4$ glass based on the results of $^{29}$Si NMR and XPS. The addition of 5 mol% Li$_4$SiO$_4$ to
the Li$_2$S-SiS$_2$ system was shown to increase $T_c-T_g$ and improve the stability against crystallization and to keep the conductivity of about $10^{-3}$ S·cm$^{-1}$ at room temperature as shown in Fig. 4. The structure unit in which silicon atoms are coordinated with both sulfur and oxygen atoms have never been observed in any crystalline compounds. The glasses containing this structure unit are thus expected to be difficult to crystallize, and consequently the glass stability against crystallization must be improved in the glass with small amounts of lithium ortho-oxosalts. We confirmed that the precipitated crystals from the oxysulfide glasses with small amounts of ortho-oxosalts exhibited no such a structural unit shown in Fig. 7. From a viewpoint of lithium ion conduction, bridging oxygen atoms work as a weak trap of lithium ions compared to non-bridging ones because the electron density of bridging oxygen atoms is smaller than that of non-bridging ones. Therefore, the conductivities of the oxysulfide glass with 5 mol% Li$_4$SiO$_4$ are as high as those of 60Li$_2$S·40SiS$_2$ glass as shown in Fig. 4.

4. Mechanochemical synthesis of high lithium ion conducting oxysulfide glasses and their application to solid-state secondary batteries

We have prepared a variety of oxysulfide glasses with high performance as solid electrolytes by using melt quenching procedures. However, when these glasses are used as solid electrolytes for lithium secondary batteries, the glasses should be ground to fine powders in order to have a good contact with electrode materials. We have demonstrated that the lithium ion conductive glassy materials in the sulfide and oxysulfide systems can be synthesized by use of a new procedure of mechanical milling. This procedure is basically a room-temperature process and useful to obtain fine powders directly for solid-state lithium secondary batteries.

Here, reported are the formation, electrical properties, and local structure of the glassy materials in the system Li$_2$S–SiS$_2$–Li$_4$SiO$_4$ obtained by use of a high energy ball milling technique. The charge–discharge behaviors and cycling performance of solid-state cells using the glassy materials as electrolytes are also reported.

[Fig. 8 shows the X-ray diffraction patterns of the mechanically milled 95(0.6Li$_2$S·0.4SiS$_2$)·5Li$_4$SiO$_4$ powders with different milling periods.]

Figure 8 shows the X-ray diffraction patterns of the 95(0.6Li$_2$S·0.4SiS$_2$)·5Li$_4$SiO$_4$ powders with different milling periods of time. Here, the mechanical milling was carried out using a planetary ball mill for the powder mixture of starting materials of Li$_2$S, SiS$_2$ and Li$_4$SiO$_4$ crystals. Alumina pots and balls were mainly used for milling and the rotation speed was about 370 rpm. Diffraction peaks due to Li$_2$S, SiS$_2$ and Li$_4$SiO$_4$ are observed in the powder mixture without mechanical milling (0 h). After milling for 1 h the peaks due to SiS$_2$ and Li$_4$SiO$_4$ almost disappear and the halo pattern overlaps to the peaks due to Li$_2$S. As the milling period increased, the intensity of the Li$_2$S peaks decreases and the halo pattern becomes dominant, indicating that the amorphous part in the mixture increases with an increase in the milling periods.

[Fig. 9 shows the temperature dependence of electrical conductivity of the 95(0.6Li$_2$S·0.4SiS$_2$)·5Li$_4$SiO$_4$ powders...]

Fig. 6. O1s photoelectron spectrum of the 95(0.6Li$_2$S·0.4SiS$_2$)·5Li$_4$SiO$_4$ oxysulfide glass prepared by twin-roller rapid quenching.

Fig. 7. A structural unit expected to be present in the 95(0.6Li$_2$S·0.4SiS$_2$)·5Li$_4$SiO$_4$ glass based on the results of $^{29}$Si NMR and XPS.

Fig. 8. X-ray diffraction patterns of the mechanically milled 95(0.6Li$_2$S·0.4SiS$_2$)·5Li$_4$SiO$_4$ powders with different milling periods.
prepared with different milling periods. These conductivity data were obtained on the compressed pellets. Figure 9 also shows the conductivity data of the 95(0.6Li₂S–0.4SiS₂)–5Li₄SiO₄ rapidly quenched glass in the powder-compressed pellet for comparison. In all milling periods of time, conductivities can be fit with an Arrhenius type equation. The conductivity at room temperature of the as-mixed sample (0 h) is much lower than the order of 10⁻⁹ S·cm⁻¹. In contrast, the conductivities of the mechanically milled powders increase with an increase in the milling periods. The conductivities of the powders milled for more than 5 h are higher than 10⁻⁴ S·cm⁻¹, which is comparable to the conductivity of the corresponding quenched glass in the powder-compressed pellet samples. It is interesting to notice that the mechanical milling for only 1 h increases the conductivity of the oxysulfide powders by more than three orders of magnitude although the intense diffraction peaks due to Li₂S crystals remain in the X-ray diffraction patterns as shown in Fig. 8.

29Si MAS NMR spectra of the 95(0.6Li₂S–0.4SiS₂)–5Li₄SiO₄ powders prepared with different milling periods revealed that, after mechanical milling for only 1 h, the peak due to the SiS₂ crystal almost disappeared and two peaks due to the SiS₄ tetrahedral units with one edge sharing (E(1)) and no edge sharing (E(0)) appeared. The spectra of the powders mechanically milled for more than 5 h had three new peaks attributable to SiO₂S₂, SiO₃S, and SiO₄ tetrahedral units. The NMR pattern for the powder milled for 20 h was similar to that of the corresponding rapidly quenched glass shown in Fig. 5, indicating that the local structure of the 95(0.6Li₂S–0.4SiS₂)–5Li₄SiO₄ glassy powder prepared by mechanical milling is close to that of the rapidly quenched glass. Solid-state lithium secondary batteries have been constructed using the mechanochemically prepared solid electrolytes. Figure 10 shows the first charge–discharge curves of the electrochemical cell, In/solid electrolyte/LiCoO₂, in which the 95(0.6Li₂S–0.4SiS₂)–5Li₄SiO₄ solid electrolytes were synthesized with different milling periods. The current density was 64 μA/cm². The first charge–discharge curves of the cell with the corresponding oxysulfide glass by melt-quenching are also shown in Fig. 10 for comparison (denoted as “glass”). The cell using the oxysulfide sample milled for 3 h can be charged, but not discharged. The charge–discharge curves of the cell with the samples milled for 10 h, are similar to those of the cell using the melt-quenched glass sample. The average cell voltages on charge and discharge are 3.6 and 3.1 V, respectively. This result indicates that the milling period of 10 h, under the present experimental conditions, is enough to construct an electrochemical cell which shows similar properties to that using the melt-quenched glass.

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