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Amorphous solid electrolytes in the system Li_2S-Al_2S_3-SiS_2 prepared by mechanical milling

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Amorphous solid electrolytes in the ternary system Li_2S-Al_2S_3-SiS_2 were successfully prepared by mechanical milling. The ambient temperature conductivity of the $60Li_2S{\cdot}10AlS_{1.5}{\cdot}30SiS_2$ (mol%) sample reached over 10^{-4} S cm^{-1} with amorphization by mechanical milling for 40 h. The binary Li_2S-Al_2S_3 amorphous electrolytes, which have not been synthesized by a conventional melt-quenching technique, were also obtained by mechanical milling. The $60Li_2S{\cdot}40AlS_{1.5}$ (mol%) amorphous electrolyte exhibited lower conductivity and higher activation energy for conduction than the $60Li_2S{\cdot}40SiS_2$ (mol%) amorphous electrolyte. The addition of SiS_2 to Li_2S-Al_2S_3 system monotonically increased electrical conductivity and decreased activation energy for conduction. The amorphous $60Li_2S{\cdot}10AlS_{1.5}{\cdot}30SiS_2$ material showed favorable features as a solid electrolyte such as unity of lithium ion transport number and wide electrochemical window.

1. Introduction

Li_2S-based lithium ion conducting glasses are one of the most promising solid electrolytes for all-solid-state rechargeable lithium batteries because of their favorable features such as high ambient temperature conductivity, wide electrochemical window, and unity of lithium ion transport number [1–3]. These glasses are conventionally prepared by a melt-quenching technique using a vacuum-sealed quartz tube. Recently, we have succeeded in preparation of Li_2S-SiS_2 and Li_2S-P_2S_5 sulfide glassy electrolytes by a mechanical milling technique using a high-energy ball-mill apparatus [4–6]. The mechanical milling method has the advantage of direct formation of amorphous fine powders, which are useful to achieve close contact between electrolyte and electrode in solid-state batteries, under room temperature and normal pressure. Electrical conductivities of pelletized samples of these powders were about 10^{-4} S cm^{-1} at room temperature. Solid-state NMR and X-ray photoelectron spectroscopy revealed that local structure of the Li_2S-SiS_2 powders obtained by mechanical milling was almost the same as that of the corresponding melt-quenched glasses [5]. We reported that all-solid-state cells with those sulfide powders worked as rechargeable lithium batteries and showed excellent cycling performances at room temperature [7, 8].

In the present study, amorphous powders in the ternary system Li_2S-Al_2S_3-SiS_2 were prepared by mechanical milling. The binary Li_2S-Al_2S_3 amorphous powders, which have not been prepared by a conventional melt-quenching technique, were also successfully obtained by milling. Electrical and electrochemical properties as a solid electrolyte were investigated for the obtained amorphous materials.

2. Experimental

Reagent-grade chemicals of Li_2S (Furuuchi Chem., 99.9%), Al_2S_3 (Koujundo Chem., 98%), and SiS_2 (Furuuchi Chem., 99.9%) crystalline powders were used as starting materials for sample preparation. The mechanical milling treatment was carried out for the batches (1 g) of the mixed materials at the composition of $60Li_2S{\cdot}(40-x)AlS_{1.5}\cdot xSiS_2$ (mol%) ($0 \leqq x \leqq 40$) in a stainless steel (SUS) pot (volume of 45 ml) with ten ZrO_2 balls (10 mm in diameter) using a high-energy planetary ball mill apparatus (Fritsch Pulverisette 7). The concentration of Li_2S was fixed to 60 mol% because the lithium concentration showed the maximum conductivity in the Li_2S-SiS_2 binary system [9]. The rotation speed was 230 rpm and all the processes were carried out at room temperature in a dry N_2-filled glove box.

XRD measurements (Cu K_α) were carried out for the milled powders, which were stuck on a glass plate in a N_2 atmosphere and then covered with polyimide thin film to avoid the attack of water and oxygen in air. Electrical conductivities were measured for the pelletized samples by ac impedance measurements in dry Ar atmosphere. Dc conductivity was also measured using

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lithium plates as nonblocking electrodes and platinum plates as blocking electrodes to determine a lithium ion transport number of the milled samples. Cyclic voltammetry was carried out for the simple two-probe cell with a platinum plate as a working electrode and a lithium plate as a counter electrode at the scanning rate of 5 mV s^{-1}.

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of powder samples of $60Li_2S{\cdot}10AlS_{1.5}{\cdot}30SiS_2$ (mol%) with different milling periods. Diffraction peaks due to the crystals of Li_2S, Al_2S_3, and SiS_2 are observed in the as-mixed sample (0 h). As the milling period increases, the intensity of those crystalline peaks decreases and the halo pattern becomes dominant. The peaks due to Al_2S_3 and SiS_2 disappear after milling for 10 h, and the peaks due to Li_2S disappear after milling for 100 h. Amorphization gradually proceeds during milling, and the amorphous material is obtained by continuous mechanical milling for 100 h.

Fig. 2 shows the temperature dependence of electrical conductivity of the pelletized $60Li_2S{\cdot}10AlS_{1.5}{\cdot}30SiS_2$ (mol%) samples prepared with different milling periods. In all the cases, conductivities follow the Arrhenius equation. The conductivity of the as-mixed sample is lower than 10^{-8} S cm^{-1} even at around 100°C. The conductivities of the mechanically milled samples increase with an increase in the milling periods. The conductivities of the samples milled for 40 h or more are higher than 10^{-4} S cm^{-1}at room temperature. Activation energies for conduction decrease from 63 kJ mol^{-1} (0 h) to 27 kJ mol^{-1}(100 h) with an increase in the milling periods. As shown in Fig. 1, amorphous materials were gradually formed during mechanical milling, suggesting that amorphization of the starting materials increases the conductivity and decreases the activation energy for conduction. The improvement on conductivity with amorphization by mechanical milling was also observed in the systems Li_2S-SiS_2 [4, 5] and Li_2S-P_2S_5 [6].

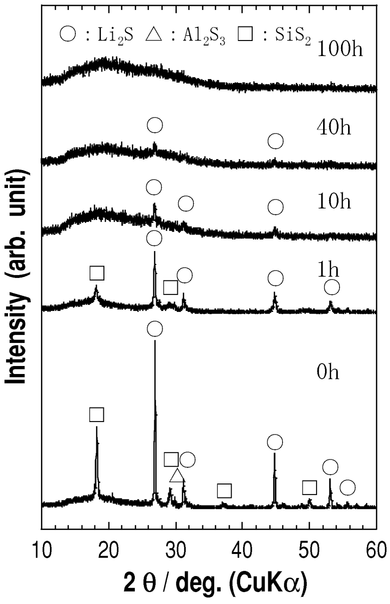

Figure 1 XRD patterns of powder samples of $60Li_2S{\cdot}10AlS_{1.5}{\cdot}30SiS_2$ (mol%) with different milling periods.

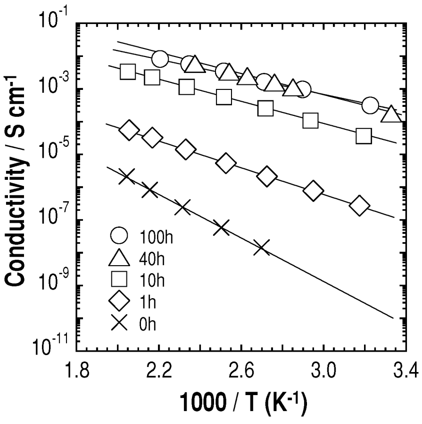

Figure 2 Temperature dependence of electrical conductivity of the pelletized $60Li_2S{\cdot}10AlS_{1.5}{\cdot}30SiS_2$ (mol%) samples prepared with different milling periods.

The $60Li_2S{\cdot}(40-x)AlS_{1.5}{\cdot}xSiS_2$ (mol%) ($x = 0$, 10, 20, 30, and 40) samples were mechanically milled for 100 h at the rotation speed of 230 rpm. All the samples showed halo patterns on XRD measurements, suggesting that the obtained materials were amorphous. Glasses in the binary system Li_2S-Al_2S_3 have never been synthesized by the conventional melt-quenching method. The amorphous $60Li_2S{\cdot}40AlS_{1.5}$ (mol%) ($x = 0$) powder proved to be prepared by mechanical milling for the first time. Fig. 3 shows the composition dependence of conductivity at 25°C (σ_{25}) and the activation energy (Ea) for conduction of the $60Li_2S{\cdot}(40-x)AlS_{1.5}{\cdot}xSiS_2$ (mol%) amorphous powders. The σ_{25} values monotonically increase while the Ea values decrease with an increase in x. The $60Li_2S{\cdot}40SiS_2$ powder shows the highest σ_{25} of 3.4×10^{-4} S cm^{-1} and the lowest Ea of 22 kJ mol^{-1} while the $60Li_2S{\cdot}40AlS_{1.5}$ powder exhibits the lowest σ_{25} of 6.7×10^{-5} S cm^{-1} and the highest Ea of 35 kJ mol^{-1}. The addition of SiS_2 to Li_2S-Al_2S_3 system proves to increase electrical conductivity and decrease activation energy for conduction.

Fig. 4 shows the time dependence of the dc conductivity for the $60Li_2S{\cdot}10AlS_{1.5}{\cdot}30SiS_2$ (mol%) amorphous powder. A constant dc voltage of 1 V is applied to the sample. In the case of using lithium

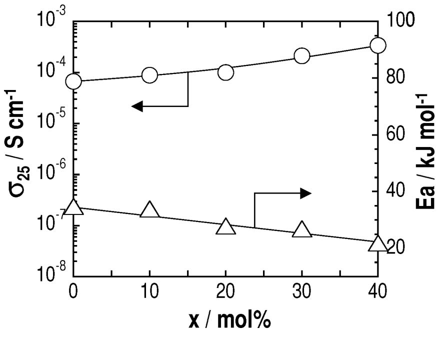

Figure 3 Composition dependence of conductivity at 25°C (σ_{25}) and the activation energy (Ea) for conduction of the $60Li_2S{\cdot}(40-x)AlS_{1.5}{\cdot}xSiS_2$ (mol%) amorphous powders.

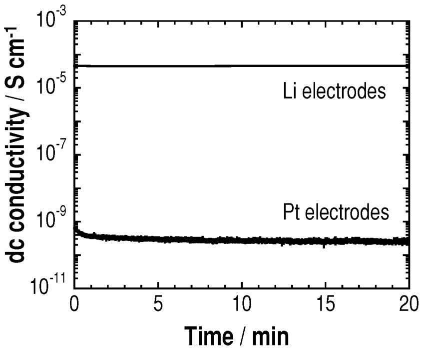

Figure 4 Time dependence of dc conductivity obtained from currents after applying a constant dc voltage of 1 V to the $60Li_2S\cdot10AlS_{1.5}\cdot30SiS_2$ (mol%) amorphous powders.

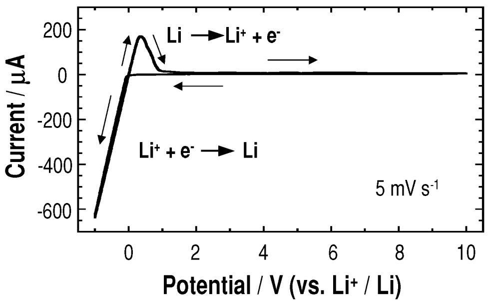

Figure 5 Cyclic voltammogram of the $60Li_2S\cdot10AlS_{1.5}\cdot30SiS_2$ (mol%) amorphous powder.

electrodes (nonblocking electrodes), the dc conductivity is almost constant with time; the conductivity is around 5×10^{-5} S cm^{-1}, which almost agrees with the value obtained from the ac impedance measurement using platinum electrodes (blocking electrodes). In the case of using platinum electrodes, a decrease of dc conductivity is initially observed and then the conductivity becomes almost constant. The conductivity is about 5 orders of magnitude lower than that obtained by using the lithium electrodes, suggesting that the electronic conduction in a total conductivity is almost negligible. Lithium ion transport number of the amorphous electrolyte proves to be almost unity.

Fig. 5 shows the cyclic voltammogram of the $60Li_2S\cdot10AlS_{1.5}\cdot30SiS_2$ (mol%) amorphous powder. A cathodic current due to a deposition of metallic lithium ($Li^+ + e^- \rightarrow Li$) is observed on a cathodic sweep up to -0.5 V (vs. Li^+/Li), and then an anodic current peak due to a dissolution of metallic lithium ($Li \rightarrow Li^+ + e^-$) is observed around $+0.3$ V on an anodic sweep. No anodic current peaks except for the peak due to lithium dissolution are observed up to $+10$ V, suggesting that the amorphous powder has wide electrochemical window. The amorphous powder is a promising solid electrolyte for all-solid-state batteries with a high voltage operation.

4. Conclusions

Amorphous powders in the system Li_2S-Al_2S_3-SiS_2 were prepared by mechanical milling for 100 h at the rotation speed of 230 rpm. The ambient temperature conductivity of the $60Li_2S\cdot10AlS_{1.5}\cdot30SiS_2$ sample reached over 10^{-4} S cm^{-1} with amorphization by mechanical milling. The binary Li_2S-Al_2S_3 amorphous powders were also obtained for the first time by mechanical milling, and the $60Li_2S\cdot40AlS_{1.5}$ amorphous powder exhibited lower conductivity and higher activation energy for conduction than the $60Li_2S\cdot40SiS_2$ amorphous powder. The addition of SiS_2 to Li_2S-Al_2S_3 system monotonically increased electrical conductivity and decreased activation energy for conduction. The amorphous $60Li_2S\cdot10AlS_{1.5}\cdot30SiS_2$ material showed favorable features as a solid electrolyte such as unity of lithium ion transport number and wide electrochemical window.

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