

Preparation of Fast Lithium Ion Conducting Glasses in the System $\text{Li}_2\text{S}-\text{SiS}_2-\text{Li}_3\text{N}$

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$\text{Li}_2\text{S}-\text{SiS}_2-\text{Li}_3\text{N}$ fast lithium ion conducting glasses were prepared by a melt-quenching procedure for the compositions $(60 - 3x/2)\text{Li}_2\text{S} \cdot 40\text{SiS}_2 \cdot x\text{Li}_3\text{N}$ ($x = 0, 3, 5$). Both temperatures of glass transition and crystallization increased with an increase in the Li_3N content. The temperature dependence of conductivities followed an Arrhenius type equation. The incorporation of nitrogen into the glasses increased the conductivities at room temperature and decreased the activation energies for conduction. The lithium ion transport number of the thionitride glasses was more than 0.999. The glasses were electrochemically stable, exhibiting a very wide electrochemical window of about 10 V.

Introduction

Lithium ion secondary batteries have been popularized because of their high voltage and high capacity since several portable electronic instruments such as cellular phones and notebook-type personal computers have been developed. A safety problem, however, has been noted for such batteries because they include a flammable organic liquid as an electrolyte. Solid state lithium ion secondary batteries might improve their safety and reliability drastically if nonflammable solid electrolytes could be used. Sulfide glasses in the system $\text{Li}_2\text{S}-\text{SiS}_2$ are one of the best lithium ion conducting solid electrolytes, the conductivity of which is in the order of $10^{-4} \text{ S cm}^{-1}$ at room temperature.¹ We have prepared the oxysulfide glasses in the systems of $\text{Li}_2\text{S}-\text{SiS}_2-\text{Li}_x\text{MO}_y$ ($\text{Li}_x\text{MO}_y = \text{Li}_3\text{PO}_4, \text{Li}_4\text{SiO}_4, \text{Li}_4\text{GeO}_4$) by twin-roller rapid quenching.^{2–4} It was found that the addition of small amounts of the oxides to the sulfides improved both conductivity at room temperature and stability against crystallization.⁵

On the other hand, incorporation of nitrogen into oxide glasses has been known to increase the glass transition temperature and improve the hardness and chemical durability.^{6,7} In the field of solid state ionics, ionic conductivity was also reported to be improved by introducing nitrogen into oxide systems.^{8,9} However, incorporation of nitrogen into sulfide glasses has not been reported so far as we know.

Lithium nitride (Li_3N) crystals have attracted much attention as a solid electrolyte because of their extremely high ion conductivity ($1.2 \times 10^{-3} \text{ S cm}^{-1}$ at 25°C).^{10,11} However, since the decomposition voltage of Li_3N was found to be very low (0.445 V),¹⁰ it is impossible to use Li_3N itself as an electrolyte for lithium ion secondary batteries.

We tried to prepare $\text{Li}_2\text{S}-\text{SiS}_2$ -based thionitride glasses, where Li_3N was used as a nitrogen source. This paper reports the preparations and thermal, electrical, and electrochemical properties of $\text{Li}_2\text{S}-\text{SiS}_2-\text{Li}_3\text{N}$ glasses. The effects of incorporation of nitrogen on thermal stability and ionic conductivity of sulfide glasses are discussed.

Experimental Procedure

The composition of the glasses studied here is written as $(60 - 3x/2)\text{Li}_2\text{S} \cdot 40\text{SiS}_2 \cdot x\text{Li}_3\text{N}$ (molar ratio), where the Li/Si ratio

was kept constant. High-purity Li_2S (99.9%), SiS_2 (99.9%), and Li_3N (99.9%) were mixed and put into a silica ampule, the inside of which was carbon coated. The ampule was then flame-sealed under vacuum, and the mixture was melted at $1000-1200^\circ\text{C}$ for 1 h and quenched in ice water to obtain bulk glasses. The raw materials and the glasses obtained were handled in a dry N_2 filled glovebox.

Thermal analyses of the glasses were performed (Rigaku, TG8100) for the powdered samples sealed in an Al pan. Conductivity measurements were carried out for bulk samples using carbon paste and lithium metal as electrode materials under a dry Ar atmosphere. The impedance was measured from 100 Hz to 15 MHz using an impedance/gain-phase analyzer (Solartron, SI 1260) in the temperature range $70-200^\circ\text{C}$; conductivities were determined by employing complex impedance analysis. The dc conductivity was also measured using lithium metal as nonblocking electrodes and carbon paste as blocking electrodes to determine the lithium ion transport number. The measurements were carried out at room temperature using a digital microammeter (Advantest R8340A). Cyclic voltammetry was carried out for the powdered and pelletized sample using Pt metal as a working electrode and a Li-In alloy as counter and reference electrodes in dry Ar atmosphere. The potential scan was performed using a potentiostat (Hokuto Denko, HA-501) and a function generator (Hokuto Denko, HB-104).

Results and Discussion

We tried to prepare glasses of the compositions $(60 - 3x/2)\text{Li}_2\text{S} \cdot 40\text{SiS}_2 \cdot x\text{Li}_3\text{N}$ under a variety of melting conditions. All the samples obtained were basically colorless, and any carbon contamination was not observed in them. At the composition of $x = 3$, the samples melted at 1000°C were partly opaque and those melted at 1100°C were transparent. At the composition of $x = 5$, a temperature of 1200°C was necessary for obtaining transparent glasses. The higher the Li_3N contents, the higher were the melting temperatures needed to obtain transparent glasses. The samples of $x = 3$ and $x = 5$, including the opaque ones, were amorphous because no X-ray diffraction peaks were observed. The opaqueness was caused not by the crystallization of the sample but by the formation of small bubbles. At lower temperatures or higher Li_3N contents, the

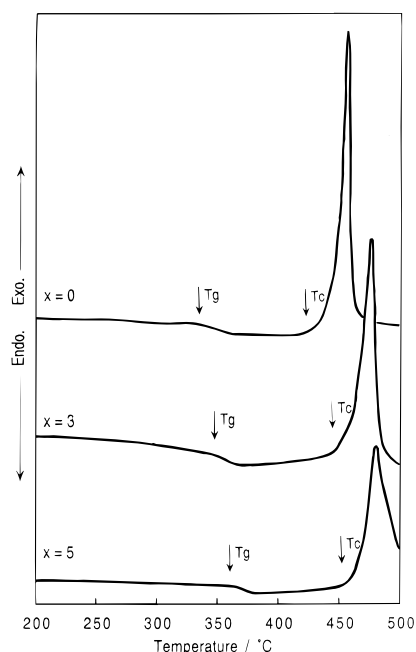


Figure 1. DTA curves of $(60 - 3x/2)\text{Li}_2\text{S} \cdot 40\text{SiS}_2 \cdot x\text{Li}_3\text{N}$ glasses (ordinate: heat flow).

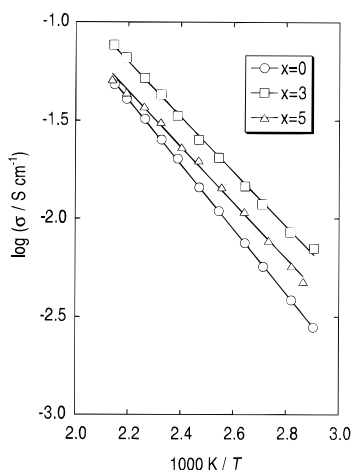


Figure 2. Temperature dependence of conductivities of $(60 - 3x/2)\text{Li}_2\text{S} \cdot 40\text{SiS}_2 \cdot x\text{Li}_3\text{N}$ ($x = 0, 3, 5$) glasses.

bubbles remained in the glasses since the viscosity of the molten samples was higher. Characterizations of the glasses in the present study were carried out only for the transparent glasses. The Li_3N -doped glasses were as hygroscopic as the Li_2S – SiS_2 base glasses so that they had to be handled in a glovebox under a dry atmosphere.

Figure 1 shows the DTA curves of the $(60 - 3x/2)\text{Li}_2\text{S} \cdot 40\text{SiS}_2 \cdot x\text{Li}_3\text{N}$ ($x = 0, 3, 5$) glasses. The endothermic peak due to the glass transition and the exothermic one due to the crystallization are observed in all the curves. Both temperatures of glass transition, T_g , and crystallization, T_c , increase with an increase in the Li_3N content. When oxides were added to Li_2S – SiS_2 glasses, T_c increased but T_g changed very slightly.^{2–4} The increase of T_g for the Li_3N -doped glasses suggests that nitrogen was incorporated into the glass network probably as three-coordinated nitrogen to make the glass network tighter.

Figure 2 shows the temperature dependence of the conductivity of the $(60 - 3x/2)\text{Li}_2\text{S} \cdot 40\text{SiS}_2 \cdot x\text{Li}_3\text{N}$ glasses. For all the

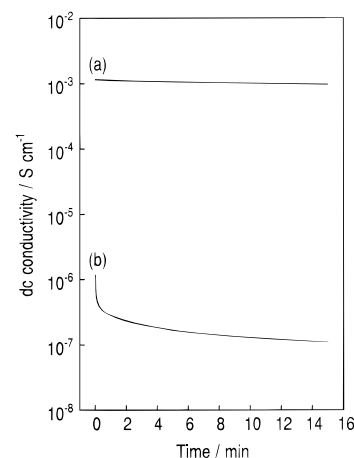


Figure 3. Conductivities at 25 °C as a function of time, derived from the dc current–time curves for the glass with $x = 3$ using a pair of lithium metal electrodes (a) and carbon paste electrodes (b).

TABLE 1: Conductivities at 25 °C, σ_{25} , Preexponential Factors, σ_0 , and Activation Energies for Conduction, E_a , of $(60 - 3x/2)\text{Li}_2\text{S} \cdot 40\text{SiS}_2 \cdot x\text{Li}_3\text{N}$ ($x = 0, 3, 5$) Glasses

	$\sigma_{25}/\text{S cm}^{-1}$	$\sigma_0/\text{S cm}^{-1}$	$E_a/\text{kJ mol}^{-1}$
$x = 0$	5.1×10^{-4}	170	32
$x = 3$	1.5×10^{-3}	75	27
$x = 5$	9.6×10^{-4}	70	28

samples the conductivities follow the Arrhenius type equation

$$\sigma = \sigma_0 \exp(-E_a/RT)$$

where E_a is the activation energy for conduction, σ_0 the preexponential factor, and R the gas constant. The conductivities at 25 °C, σ_{25} , and the activation energies of the glasses are listed in Table 1. At the composition of $x = 0$, σ_{25} is on the order of 10^{-4} S/cm, which agrees with the reported value.¹ At $x = 3$, a higher σ_{25} , 1.5×10^{-3} S/cm, and a smaller E_a , 27 kJ/mol, are obtained. At $x = 5$, σ_{25} is 9.6×10^{-4} S/cm. It is noteworthy that the addition of small amounts of Li_3N apparently enhanced the conductivity at room temperature. A maximum of conductivity may be observed in the composition of $x = 3$. However, we cannot say that the glass with $x = 3$ is apparently more conductive than that with $x = 5$ because the melting temperatures of these glasses are different by 100 °C. Moreover, Figure 2 shows a slight curvature of Arrhenius plot only in the case of $x = 5$, the origin of which is not clear at the present stage.

In order to determine the lithium ion transport number of the thionitride glasses, the dc conductivity was measured using blocking and nonblocking electrodes. A constant dc voltage of 1 V was applied to the glassy samples to obtain dc current–time curves. Figure 3 shows the conductivity at 25 °C as a function of time which was derived from the dc current–time curves for the glass with $x = 3$ using a pair of lithium metal electrodes (a) and carbon paste electrodes (b). The dc conductivity measured using lithium metal electrodes is almost constant with time, and the value is around 1×10^{-3} S cm^{-1} , which basically agrees with the conductivity obtained from ac impedance measurements as shown in Table 1, indicating that lithium ions and electrons only contribute to the total conductivity. The dc conductivity measured using carbon paste electrodes, however, decreases with time, which is apparently due to strong polarization. After polarization, the conductivity value is smaller by 4 orders of magnitude than the value obtained using lithium metal electrodes, which means the electronic conductivity is smaller by 4 orders of magnitude than the total conductivity.

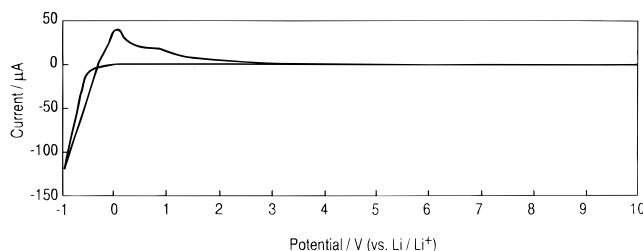


Figure 4. Cyclic voltammogram of the glass with $x = 3$ measured using Pt as a working electrode and a Li–In alloy as counter and reference electrodes.

The main charge carrier of the thionitride glasses is thus lithium ions, and the transport number of the lithium ion is more than 0.999. Therefore, the enhancement of conductivity with the addition of small amounts of Li_3N must result from the increase of Li^+ mobility due to the nitrogen incorporation as well as the increase of carrier concentration.

The presence of three-coordinated nitrogen atoms in the glass structure has already been mentioned. The mobility increase probably relates to the presence of two-coordinated nitrogen ions $-\text{Si}-\text{N}^--\text{Si}-$. Such two-coordinated nitrogen ions can work as weak lithium ion traps like nonbridging sulfur ions and bridging oxygen ions, shown in the previous study.⁵ The mixed-anion effect resulting from a mixture of nitride ions and sulfide ions in the glass structure could be a factor to increase the lithium ion mobility in the thionitride glasses.¹²

Determining the electrochemical window of the glasses is very important in order to judge whether the glasses can be used as electrolytes for lithium ion secondary batteries. Figure 4 shows the cyclic voltammogram of the glass with $x = 3$. Upon a cathodic sweep to -1 V (vs Li/Li^+), the cathodic current due to the deposition of lithium metal is observed. Then the anodic current due to dissolved lithium metal is observed around $+1$ V. After this peak, no anodic current peaks are observed up to $+10$ V, indicating that the thionitride glass has a very wide electrochemical window of about 10 V and high electrochemical stability in the potential range as observed for the oxysulfide glasses.¹³ Considering that the decomposition voltage of Li_3N is as low as 0.445 V, the electrochemical window of more than

10 V observed here is a remarkably large value. The thionitride glasses obtained in this study are thus promising solid electrolytes for use in new solid lithium ion secondary batteries with high voltages over 5 V.

Conclusions

$(60 - 3x/2)\text{Li}_2\text{S} \cdot 40\text{SiS}_2 \cdot x\text{Li}_3\text{N}$ ($x \leq 5$) glasses were obtained by melt-quenching under vacuum. Both temperatures of glass transition and crystallization increased with an increase in the nitrogen content. The incorporation of nitrogen atoms into the glasses increased the conductivities at room temperature and decreased the activation energies for conduction. The highest conductivity at room temperature was 1.5×10^{-3} S/cm at $x = 3$, and its activation energy for conduction was 27 kJ/mol. The main charge carrier of the glasses was the lithium ion, and the glasses exhibited high electrochemical stability in a wide potential range of 10 V.

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