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Ion conducting composites from Li_2S–SiS_2–Li_4SiO_4 oxysulfide glass and poly(oxyethylene)s

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Abstract

Novel inorganic/organic composites were constructed from highly conductive Li_2S–SiS_2–Li_4SiO_4 oxysulfide glass and linear poly(oxyethylene)s (POEs) or high molecular weight branched POE without adding any lithium salts. The ionic conductivity of composites was lower than that of the oxysulfide glass, but the mixing of glass powder into the POEs allowed the preparation of thin films. The composites prepared from low molecular weight linear oligomeric POEs ($M_n = 600$ and 1000) showed higher ionic conductivities than those from the high molecular weight POEs ($M_n = 4000$ and 10000). Interestingly, the composite from the high molecular weight branched POE ($M_n = 1.3 \times 10^5$) showed ionic conductivity comparable with those from linear oligomeric POEs and afforded a flexible film form.

Keywords: Solid electrolyte; Oxysulfide glass; Poly(oxyethylene)

1. Introduction

The need for a completely solid-state rechargeable battery with high voltage and high energy density is increasing more and more from the viewpoint of saving energy and affording mobile devices. In order to realize this type of battery, the development of solid electrolyte with high ionic conductivity is most urgent. However, solid electrolytes with both practical high ionic conductivity at room temperature (r.t.) and preferable processability are yet to appear [1–4]. Thus, the objective of this study is a preparation of novel inorganic/organic composites with excellent performance as a solid electrolyte. Highly lithium ion conductive Li_2S–SiS_2–Li_4SiO_4 oxysulfide glasses [5–11] were chosen as the inorganic component of the composite. Ionic conductivity of the bulk glasses was reported to be $\sim 10^{-3}$ S/cm at r.t. [7,8,10,11]. Linear oligomeric poly(oxyethylene)s (POEs) and high molecular weight branched POE were used as matrices for the preparation of the composites in this study. High molecular weight linear POE is crystalline, which is not good as a matrix for ionic conduction in general, whereas the high molecular weight branched POE was found to be much less crystalline and hence better as an ion-conducting matrix [12–16].

Till now, several studies were published on the ionic conductivity of the composites prepared from POEs and ion conductive inorganic glasses [17] or crystalline materials [18]. However, characteristics of the composites prepared from Li_2S–SiS_2–Li_4SiO_4 oxysulfide glass and POE have not been investigated, although Li_2S–SiS_2–Li_4SiO_4 oxysulfide glass shows a high lithium conductivity at r.t., a high glass stability against crystallization and a wide electrochemical window [7,8]. In this communication, the preliminary results on $95(0.6Li_2S \cdot 0.4SiS_2) \cdot 5Li_4SiO_4$ oxysulfide glass/POE composites are reported.

2. Experimental

$95(0.6Li_2S \cdot 0.4SiS_2) \cdot 5Li_4SiO_4$ oxysulfide glass was prepared from crystalline Li_4SiO_4 and reagent-grade Li_2S and SiS_2 using a twin-roller quenching technique [7,8]. The obtained glass was ground for 1 h by a planetary ball mill. The preparation of the glass was carried out in a glove box under dry nitrogen atmosphere ($[H_2O] < 1$ ppm). The diameter of the powder glass was ca. 1–15 μm according to scanning electron micrography. The structural unit

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expected to be mainly present in $95(0.6Li_2S{\cdot}0.4SiS_2){\cdot}5Li_4SiO_4$ oxysulfide glass is illustrated in Fig. 1 [11]. Linear POEs, whose molecular weights were 600, 1000, 4000 and 10000, were Aldrich commercial products and are abbreviated as POE-600, POE-1000, POE-4000 and POE-10000, respectively. A high molecular weight branched POE with 19 mol% copolymer units of branching, abbreviated as TEC-19 (see Fig. 1), was synthesized by coordination polymerization of ethylene oxide with 1,2-epoxy-4,7,10,13-tetraoxatetradecane using a catalyst of condensation product of dibutyltin oxide and tributylphosphate (1/2) at r.t. [19]. The weight-average molecular weight (M_w), the number-average molecular weight (M_n) and the index of polydispersity (M_w/M_n) of TEC-19 were evaluated to be 8.0×10^5, 1.3×10^5 and 6.3 by size exclusion chromatography (SEC) using polystyrene standards, respectively. The SEC measurement was carried out using *N*,*N*-dimethylformamide with 0.1 mmol/lLiBr at 60°C. The polymers were dried at 80°C under high vacuum over a week before mixing. At 80°C for 2 h, the glass powder and polymer were mixed for the composites, the ratio of which was glass/polymer = ca. 1 (v/v). The composite was put into the Teflon® ring spacer (10 mm in outer diameter, 6 mm in inner diameter and 1 mm in thickness) for an electrochemical measurement. The operations were conducted in a glove box under dry nitrogen atmosphere ($[H_2O] < 1$ ppm). Ionic conductivity was determined by complex impedance measurement with blocking electrodes using a Solartron SI 1260 impedance analyzer at a controlled temperature. An alternating current over the frequency range 1–10 MHz was used, and the applied voltage was 0.1 V. The measurement was carried out under dry nitrogen atmosphere ($[H_2O] < 1$ ppm) from r.t. to 100°C. Differential scanning calorimetry (DSC) at −100 to 80°C and differential thermal analysis (DTA) at r.t.–200°C were cyclically conducted by Rigaku DSC 8230B and Rigaku thermal analyzer thermo-plus 8110 under nitrogen at heating and cooling rates of ca. 10°C/min.

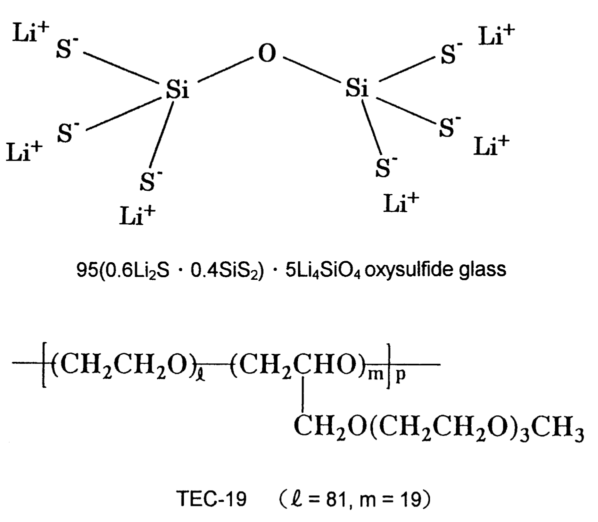

Fig. 1. Main structural unit expected to be present in the oxysulfide glass and chemical structure of TEC-19.

3. Results and discussion

Fig. 2 shows the observed ionic conductivities as a function of temperature for the composites composed of $95(0.6Li_2S{\cdot}0.4SiS_2){\cdot}5Li_4SiO_4$ oxysulfide glass and linear and branched POEs. Ionic conductivity of the powder pellet from $95(0.6Li_2S{\cdot}0.4SiS_2){\cdot}5Li_4SiO_4$ oxysulfide glass [11] is included in this figure. The ionic conductivities of the composites were lower than that of the glass. However, it is to be noted that the concentration of lithium in the composites was lower compared with that in the glass. It is also noteworthy that no ionic salts such as lithium perchlorate were mixed in the composites. It means that a lithium cation in the glass illustrated in Fig. 1 may be the only carrier in these systems.

It was observed that the composites prepared from POE-600 and POE-1000 showed similar ionic conductivities, which were higher than those of the composites from POE-4000 and POE-10000. The composites from POE-4000 and POE-10000 did not give fully reproducible results below ca. 70°C due to the presence of many crystalline regions and probably unstable state of interfaces between the electrodes and the composite. On the other hand, the ionic conductivity of oxysulfide glass/TEC-19 composite, which was prepared from the high molecular weight branched POE as a matrix, was higher than those of the oxysulfide glass/POE-4000 and oxysulfide glass/POE-10000 composites, and comparable with those of the composites prepared from POE-600 and POE-1000. The ionic conductivities of the oxysulfide glass/TEC-19 composite were 3.3×10^{-6} S/cm at 31°C and 2.5×10^{-5} S/cm at 75°C

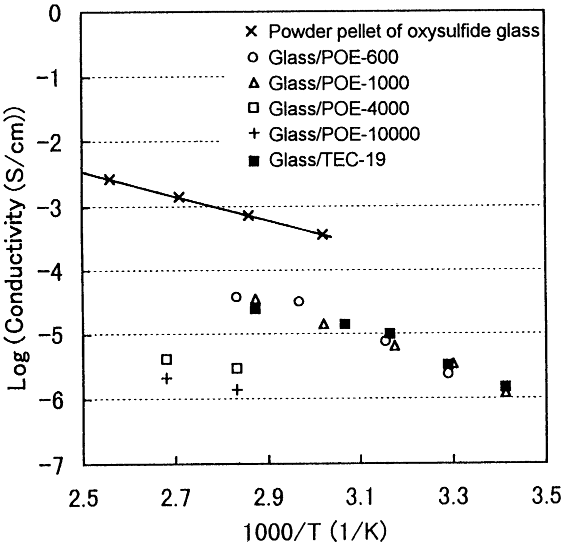

Fig. 2. Arrhenius plots of ionic conductivities for powder pellet of oxysulfide glass, oxysulfide glass/linear POE composites and oxysulfide glass/TEC-19 composite.

without adding any inorganic salts. The tri(oxyethylene) side chains prevented the oxyethylene segments of TEC-19 from crystallization, although the molecular weight of TEC-19 was very high ($M_w = 8.0 \times 10^5$, $M_n = 1.3 \times 10^5$). Additionally, the tri(oxyethylene) side chains were effective for plasticizing matrix to result in decreasing its glass transition temperature. DSC results showed that the glass transition temperature of TEC-19 was −68.3°C and the melting temperature and its heat of fusion were 45.2°C and 0.25 cal/g, respectively, whereas those of linear POE, whose molecular weight was 9×10^5, were −58.5, 65.4°C and 39 cal/g, respectively [13]. The effect of branched oxyethylene chains on the ionic conductivity was also reported in POE networks [20,21]. However, no-crosslinked high molecular weight POE was more preferred for processing of the inorganic/organic composite, because the mechanical mixing was available in this case. Therefore, the characteristics of TEC-19 are concluded to be very attractive as a matrix for high conductive composites with glasses. High molecular weight branched POEs with mono(-oxyethylene) or di(oxyethylene) side chains [13,14] are also expected to be good matrices.

In the Arrhenius plots shown in Fig. 2, the temperature dependence of ionic conductivity for the powder pellet of glass gave a linear plot, whereas the experimental points of ionic conductivity for the inorganic/organic composites seem to be convexly curved profiles rather than straight lines. They may be expressed by the Williams–Landel–Ferry (WLF) equation [22] or Vogel–Tamman–Fulcher (VTF) [23–25] equation at least semiquantitatively. This observation suggests that the segmental motion of oxyethylene units influences the diffusion of lithium cation in the glass/POE composites. The details about the ion transportation in the glass/POE composites will be discussed elsewhere.

Moreover, the composites were mechanically flexible and tough and should be easily fabricated. Accordingly, the high molecular weight polymer is preferable from the viewpoint of mechanical properties and processing of solid materials. The oxysulfide glass/TEC-19 composite also showed a good stability to lithium metal as illustrated in Fig. 3, where the melting and solidification of lithium metal were reversibly observed when the mixture of composite electrolyte and several pieces of lithium metal was subjected to the cycle of heating and cooling three times. This suggests that the oxysulfide glass/TEC-19 composite was stable against metallic lithium in a wide temperature range up to 200°C.

In conclusion, inorganic/organic composites were prepared from powder pellet of $95(0.6Li_2S{\cdot}0.4SiS_2){\cdot}5Li_4SiO_4$ oxysulfide glass and linear and branched POEs. The composites composed of the oxysulfide glass and POE-600 and POE-1000 displayed the ionic conductivity in order of 10^{-6} S/cm at r.t., but were not completely solid-like. The composite from the oxysulfide glass and TEC-19 showed the ionic conductivity comparable with those from POE-600 and POE-1000, and afforded a flexible solid film form at r.t.

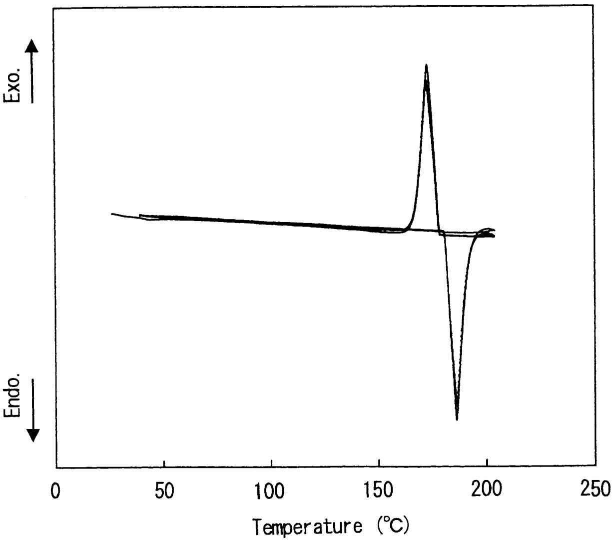

Fig. 3. DTA curves of oxysulfide glass/TEC-19 composite mixed with lithium metal: 1st (—), 2nd (– – – –) and 3rd (- - -).

Therefore, the high molecular weight branched POE with oxyethylene units as side segments is expected to be a good matrix of solid electrolyte for high ionic conduction. The variations in particle size of the glass and in composition of the composite may increase the ionic conductivity of this new inorganic/organic solid electrolyte. The results will be reported in the near future.

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References

[1] Kohjiya S, Ikeda Y. Mater Sci Res Int 1998;4:73–8.

[2] Scrosati B, Vincent CA. MRS Bull 2000;25(3):28–30.

[3] Ikeda Y. J Appl Polym Sci 2000;78:1530–40.

[4] Ikeda Y. Kobunshi Ronbunshu 2000;57(12):761–9.

[5] Kondo S, Takada K, Yamamura Y. Solid State Ionics 1992;53–56:1183–6.

[6] Tatsumisago M, Hirai K, Minami T, Takada K, Kondo S. J Ceram Soc Jpn 1993;101(11):1315–7.

[7] Hirai K, Tatsumisago M, Minami T. Solid State Ionics 1995;78:269–73.

[8] Tatsumisago M, Hirai K, Hirata T, Takahashi M, Minami T. Solid State Ionics 1996;86–88:487–90.

[9] Hayashi A, Tatsumisago M, Minami T, Miura Y. J Am Ceram Soc 1998;81(5):1305.

[10] Hayashi A, Tatsumisago M, Ninami T. J Electrochem Soc 1999;146:3472–5.

[11] Tatsumisago M, Yamashita H, Hayashi A, Morimoto H, Minami T. J Non-Cryst Solids 2000;274:30–8.

[12] Ballard DGH, Cheshire P, Mann TS, Przeworski JE. Macromolecules 1990;23:1256–68.
[13] Ikeda Y, Masui H, Shoji S, Sakashita T, Matoba Y, Kohjiya S. Polym Int 1997;43:269–73.
[14] Nishimoto A, Watanabe M, Ikeda Y, Kohjiya S. Electrochim Acta 1998;43:1177–84.
[15] Ikeda Y, Matoba Y, Murakami S, Kohjiya S. Electrochim Acta 2000;45:1167–74.
[16] Ikeda Y, Wada Y, Matoba Y, Murakami S, Kohjiya S. Rubber Chem Technol 2000;73:720–30.
[17] Cho J, Liu M. Electrochim Acta 1997;42:1481–8.
[18] Skaarup S, West K, Zachau-Christiansen B. Solid State Ionics 1990;28–30:975–8.
[19] Nakata T, Kawamata K. US Patent 1997;3:773694.
[20] Motogami K, Kono M, Mori S, Watanabe M, Ogata N. Electrochim Acta 1992;37:1725–7.
[21] Nishimoto A, Agehara K, Furuya N, Watanabe T, Watanabe M. Macromolecules 1999;32:1541–8.
[22] Williams ML, Landel RF, Ferry JD. J Am Chem Soc 1955;77:3701–7.
[23] Vogel H. Phys Z 1921;22:645–6.
[24] Tammann G, Hesse W. Z anorg allg Chem 1926;156:245–57.
[25] Fulcher GS. J Am Ceram 1925;8:339–56.