Preparation and Characterization of Lithium Ion Conducting Glass–Polymer Composites

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Glass–polymer composite electrolytes of high lithium ion conducting oxysulfide glass and the comb-shaped poly(oxyethylene) polymer (TEC-19) were prepared. The conductivity of the composite with 2 vol% TEC-19 doped with $LiClO_4$ was 1×10^{-3} at 100 °C and 3×10^{-5} S cm^{-1} at 30 °C. The composite exhibited a 4 V stable potential window versus Li^+/Li.

The development of all-solid-state lithium secondary batteries using solid electrolytes is strongly desired to improve safety and reliability of the widely popularized lithium ion secondary batteries using liquid electrolytes. The Li_2S–SiS_2 based oxysulfide glasses prepared by melt-quenching[1–3] have considerably high conductivity over 10^{-3} S cm^{-1} at room temperature and a wide electrochemical window of > 10V, suggesting that these glasses are one of the most promising candidates of solid electrolytes for solid-state lithium secondary batteries.

In order to obtain superior solid-state secondary batteries with good cyclelife performance, solid electrolytes with flexibility, which can absorb volume changes accompanied by charge–discharge processes, are required.[4,5] However, the glassy electrolytes are brittle and have poor mechanical flexibility. The addition of a flexible polymer to a glassy electrolyte is efficient to overcome the lack of flexibility. The glass–polymer composite electrolytes are expected to have the following advantages: (1) an improvement of a mechanical flexibility which is very important to obtain sheet-like flexible solid batteries, (2) an increase in a packing density of an electrolyte, in which voids among glass particles are filled with polymers, leading to an enhancement of conductivity due to a decrease of grain boundary resistance, and (3) an achievement of an excellent solid–solid interfacial contact between electrolyte and electrode materials in order to realize smooth electrochemical reactions in the solid-state batteries.

Several composite materials with ion conducting inorganic materials and poly(oxyethylene) (POE)-based polymers have so far been reported.[4–7] In the lithium ion conducting polymer electrolytes, a high molecular weight branched POE with $LiClO_4$ as lithium salts exhibited high conductivity over 10^{-4} S cm^{-1} at room temperature.[8,9] Recently, we prepared the glass–polymer composites from the lithium ion conducting oxysulfide glass and those branched POE without lithium salts and examined their electrical conductivity.[10] In the present study, high lithium ion conducting composite electrolytes of the oxysulfide glasses with an addition of small amounts of comb-shaped POE polymers with $LiClO_4$ are prepared. Their electrical and electrochemical properties and thermal stability against lithium metal are investigated.

The $95(0.6Li_2S \cdot 0.4SiS_2) \cdot 5Li_4SiO_4$ (mol%) oxysulfide glass was prepared from reagent-grade Li_2S and SiS_2 and crystalline Li_4SiO_4 using a twin-roller quenching technique in a dry N_2-filled glove box ([H_2O] < 1 ppm).[2,3] The obtained glass was ground to fine powders using a planetary ball mill; the average size of the particles was a few μm in diameter. The structural unit mainly present in the oxysulfide glass[11,12] is illustrated in Figure 1 (a). The synthesized high molecular weight branched POE ($M_n = 1.3 \times 10^5$) with 19 mol% copolymer units of branching, which is named as TEC-19 as shown in Figure 1 (b), was used as a polymer.[9,10] The polymer with $LiClO_4$ as a lithium salt was also prepared; the concentration of $LiClO_4$ was fixed to be [Li]/[-O-] = 0.10, where “-O-” means the ether oxygen.

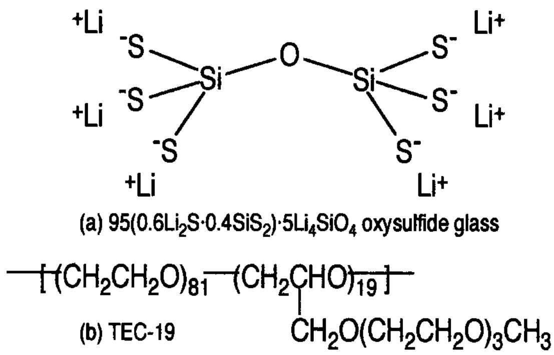

Figure 1. (a) Main structural unit in the oxysulfide glass and (b) chemical structure of TEC-19 polymer.

The glass–polymer composites were prepared by mixing and grinding the mixture of x vol% TEC-19 polymer (x = 2, 10, and 18) and (100 – x) vol% oxysulfide glass powder in a mortar and pestle. The polymers were dried at 80 °C under high vacuum over one week before use. The glass–polymer mixtures were pressed into pellets (ϕ = 10 mm) under 5550 kg/cm^2 for 5 min and then kept at 80 °C for 2 h to ensure the polymer flow into the voids among glass particles. The obtained composite electrolytes are flexible even in the case of the addition of only 2 vol% TEC-19 to the oxysulfide glass, suggesting that TEC-19 used in this study is a good polymer binder and introduces mechanical flexibility to the high ion conductive oxysulfide glass powders.

The electrical conductivity for the pelletized composites was measured in a dry Ar atmosphere by the ac impedance method in the temperature range 30–200 °C and the frequency range 1 Hz–10 MHz. Figure 2 shows temperature dependence of electrical conductivities of the glass–polymer composites. The conductivities of the bulk and pelletized $95(0.6Li_2S \cdot 0.4SiS_2) \cdot 5Li_4SiO_4$ oxysulfide glasses are also shown in Figure 2. Closed and open marks respectively denote the composites of TEC-19 with and without $LiClO_4$. The conductivity value of the bulk

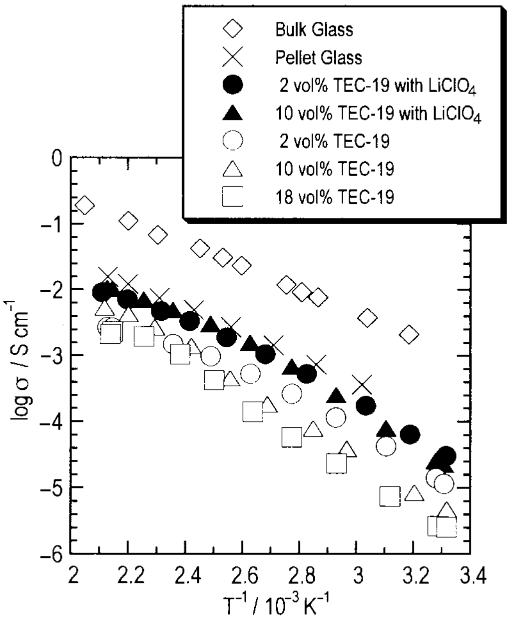

Figure 2. Temperature dependence of the electrical conductivities of the glass–polymer composite electrolytes of the $95(0.6Li_2S{\cdot}0.4SiS_2){\cdot}5Li_4SiO_4$ oxysulfide glass and TEC-19 polymer with or without $LiClO_4$.

glass is 1×10^{-3} S cm^{-1} at 25 °C and that of the pelletized glass is 1×10^{-4} S cm^{-1}.[3,13] The conductivity of the glass–polymer composites of TEC-19 without $LiClO_4$ decreases with an increase in TEC-19 content from 2 to 18 vol%. The conductivity values of the composites with 2 and 18 vol% TEC-19 are respectively 1×10^{-5} and 3×10^{-6} S cm^{-1} at 30 °C. These values are one or two orders of magnitude lower than that of the pelletized glass without polymer. This is because the lithium ion concentration in the composites decreases with an increase in additional polymers without lithium ions; these polymers must also prevent lithium ion conduction. The $LiClO_4$ doping to TEC-19 increases the conductivity of the composites. The composite consisting of 98 vol% oxysulfide glass and 2 vol% TEC-19 with $LiClO_4$ exhibits similar conductivities to the pelletized glass in the high temperature range over 80 °C; the conductivities of this composite are 1×10^{-3} at 100 °C and 3×10^{-5} S cm^{-1} at 30 °C. The conductivities of the composite with 10 vol% TEC-19 (▲) are almost the same as those with 2 vol% TEC-19 (●). The conductivities of the bulk and pelletized glasses follow the Arrhenius equation, while the temperature dependence of the glass–polymer composites exhibits convexly curved profiles. These curved profiles are usually observed in the amorphous polymer electrolytes, which are expressed semi-quantitatively by the WLF or VTF equation.[8] Therefore, the total conductivity of the composites is mainly controlled by the lithium ion conduction in the TEC-19 polymer added to the oxysulfide glass.

Cyclic voltammetry was performed with a scanning rate of 5 mV/s for the electrochemical cell with the pelletized composite as a solid electrolyte, an SUS plate as a working electrode, and a lithium foil as a counter electrode, which is also used as a reference electrode. Figure 3 shows the cyclic voltammograms for the glass–polymer composite with 2 vol% TEC-19 doped with $LiClO_4$. The measurements were performed from the rest potential to the cathodic direction and then to the anodic direction to 4.5 V vs Li^+/Li. The cathodic current due to lithium

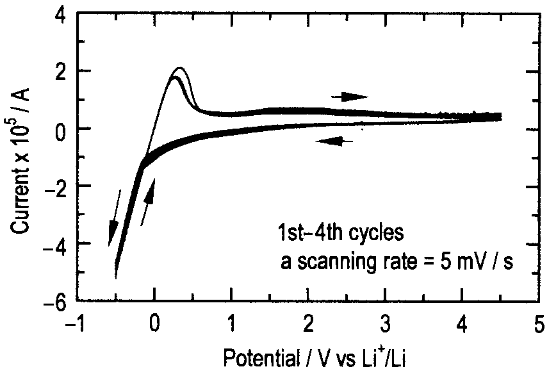

Figure 3. Cyclic voltammograms for the glass–polymer composite electrolyte with 2 vol% TEC-19 doped with $LiClO_4$.

deposition ($Li^+ + e^- \rightarrow Li$) and the anodic one due to the lithium dissolution ($Li \rightarrow Li^+ + e^-$) are observed at –0.5 to 1 V. The composite exhibits good cycling performance in the potential range –0.5 to 4.5 V for 4 cycles. We confirmed that the large anodic current was observed in the potential over 5 V and the cycling performance became worse, suggesting that this composite has at least a 4 V stable potential window vs Li^+/Li.

In conclusion, the flexible glass–polymer composite materials were obtained from the oxysulfide glass powder and TEC-19 polymer. The composites exhibited the conductivity over 10^{-5} S cm^{-1} at room temperature and a 4 V stable potential window vs Li^+/Li. The flexible glass–polymer composites prepared in this study are promising solid electrolytes for solid-state lithium secondary batteries.

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