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Recent progress of glass and glass-ceramics as solid electrolytes for lithium secondary batteries

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Abstract

In recent years many new glass-based solid electrolytes with high Li^+ conductivity have been developed. In the present paper, we review the preparation and characterization of Li_2S-based oxysulfide glasses and sulfide glass-ceramics on the basis of two strategies of enhancing Li^+ conductivity: the utilization of "mixed-anion effect" by combining sulfide and oxide anions, and the precipitation of superionic metastable crystals by careful heat-treatment of glasses. The superior Li^+ conducting solid electrolytes with the highest conductivity and the lowest activation energy for conduction have been achieved in the Li_2S–P_2S_5 glass-ceramics. The use of these glass-ceramic solid electrolytes leads to the development of a bulk-type all solid-state lithium secondary battery with excellent cycling performance.

Keywords: Glass; Glass-ceramic; Lithium ion conductivity; Solid electrolyte; All-solid-state; Battery

1. Introduction

Realization of fast ion conduction in solids is indispensable to producing all-solid-state devices such as batteries and chemical sensors with high safety and reliability. Inorganic ionic conductors, namely solid electrolytes, have been extensively studied in two types of solids: crystal and glass. The ionic conductivity of glassy materials is, in general, higher than that of the corresponding crystals [1–4]. In the system AgI–Ag_2O–P_2O_5, the ambient temperature conductivity of glasses is 10^{-2} S cm^{-1}, which is higher by 1–2 orders of magnitude than the conductivity of crystals. These glasses are named "superionic conducting glasses". The advantage of glass in conductivity is explained by the structure of glass, which is very similar to that of the corresponding melt with high conductivity and low activation energy for conduction. In ionic conductors, Ag^+ ions are known to show higher conductivity than alkali ions in spite of the fact that Ag^+ ions have a large ionic radius and atomic weight. The electronic configuration of the ions, *i.e.* the $4d^{10}$ configuration in the outermost orbital, plays an important role as well as the ionic radius in achieving high ion conductivities [3–5].

The most favorable ion species is Li^+ because lithium secondary batteries have superior features such as high energy density and low weight. Three important discoveries for creating high Li^+ conducting electrolytes have been obtained: (1) the change of an oxide matrix to a sulfide one, (2) the utilization of so-called the "mixed-anion effect" by combining sulfide and oxide anions, and (3) the precipitation of superionic metastable crystals by careful heattreatment of glasses. First of all, the development of Li^+ ion conducting glasses has been achieved by changing the glass matrix from oxides to sulfides. Li^+ ions acting as a "hard acid", which is classified from a viewpoint of the "hard and soft acids and bases theory" by Pearson [6], would be more compatible to sulfide ions acting as a "soft base" [7]. In fact, the conductivity of Li_2S–SiS_2 sulfide glasses is in the order of 10^{-4} S cm^{-1} at room temperature, which can be compared with the conductivity of 10^{-7} S cm^{-1} for the corresponding Li_2O–SiO_2 glasses [5,8].

In this paper, we focus on the other two strategies for developing Li^+ conductivity of glass-based solid electrolytes and review the preparation and characterization of Li_2S-based

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oxysulfide glasses and sulfide glass-ceramics. The rapid quenching method using a twin-roller apparatus and the mechanochemical method using a planetary ball mill apparatus were used for preparation of glasses. All-solid-state lithium secondary batteries with glasses and glass-ceramics as a solid electrolyte were fabricated, and their performance is reported here.

2. Experimental

2.1. Preparation of glass-based solid electrolytes

Li_2S-based sulfide and oxysulfide glasses were prepared by melt-quenching and mechanical milling techniques. In the former case, the mixture of staring materials such as Li_2S, SiS_2, and Li_4SiO_4 in the composition of $(100-x)(0.6Li_2S\cdot 0.4SiS_2)\cdot xLi_4SiO_4$ (mol%) was melted in a carbon crucible at 1000–1100 °C for 2 h in a dry N_2-filled glove box. The molten samples were rapidly cooled using a twin-roller quenching apparatus to prepare flake-like glasses with a thickness of 20 μm. The glasses were also prepared by the mechanochemical method using a planetary ball mill apparatus (Fritsch Pulverisette 7). The mechanochemical treatment using an Al_2O_3 pot and balls was performed for the mixture of Li_2S and P_2S_5 crystals. Fine glassy powders were obtained after mechanical milling for several hours at a constant rotation speed of 370 rpm. All the processes were carried out at room temperature in a dry Ar-filled glove box. Glass-ceramic materials were prepared by heating the mechanically milled glasses over their crystallization temperatures.

2.2. Characterization of glass-based solid electrolytes

Differential thermal analysis (DTA) was carried out using a thermal analyzer (Rigaku, Thermo-plus 8110) for the glassy powders sealed in an Al pan in order to determine their glass transition temperature (T_g) and crystallization temperature (T_c). Electrical conductivities were measured for the flake-like glasses or pelletized glasses for the powders obtained by mechanical milling. AC impedance measurements were carried out in dry Ar atmosphere using a Solartron 1260 impedance analyzer in a frequency range of 100 Hz to 15 MHz. X-ray diffraction (XRD) measurements (CuKα) were performed using a diffractometer (M18XHF^{22}-SRA, MAC Science) to identify crystals in glass-ceramics.

2.3. Fabrication of all-solid-state batteries

The composite positive electrode materials were prepared by mixing $LiCoO_2$, the glass-ceramics and acetylene-black with the weight ratio of 20:30:3. The composite powder (20 mg) acting as a positive electrode and the glass-ceramics powder (80 mg) acting as a solid electrolyte were placed in a polycarbonate tube ($\varphi = 10$ mm) and pressed together under 3.6×10^8 Pa, and then an indium foil with a thickness of 0.1 mm as a negative electrode was pressed under 2.5×10^8 Pa on the pellet. The obtained In/$LiCoO_2$ cells were charged and discharged at room temperature in an Ar atmosphere.

3. Results and discussion

3.1. Li_2S-based oxysulfide glassy electrolytes — the utilization of mixed-anion effect

Ionic conducting glasses are commonly prepared by the melt-quenching method. A large number of studies revealed that increase in lithium ion concentration in glassy materials is a key point to achieve higher electrical conductivity and lower activation energy for Li^+ transport. A rapid quenching technique using a twin-roller apparatus is useful to expand the glass-forming region, and thereby oxide and sulfide glasses with large amounts of lithium ions have been prepared. One of the techniques to improve Li^+ conductivity is the utilization of "mixed-anion effect" [9,10]. The "mixed-anion effect" is defined as the phenomenon that the enhancement or maximum in composition dependence of conductivity is observed when two different types of anions are mixed. For example, the ionic glasses in the system Li_4SiO_4–Li_3BO_3 exhibit the maximum conductivity at the composition with the equal mole of two anions: SiO_4^{4-} and BO_3^{3-}. On the basis of the oxide mixed-anion systems, the oxysulfide glasses with combining SiS_4^{4-} and SiO_4^{4-} anions have been prepared, and the mixing effects of the two anions on electrical properties and local structure have been investigated.

Fig. 1 shows the composition dependence of electrical conductivities at 25 °C (σ_{25}) and $T_c - T_g$ of the oxysulfide glasses in the systems $(100-x)(0.6Li_2S\cdot 0.4SiS_2)\cdot xLi_xMO_y$ (M = Si, P, Ge, B, Al, Ga and In) (mol%) prepared by the twin-roller quenching technique [8,11,12]. The solid lines are a guide to the eye. The addition of 5 mol% of Li_xMO_y (M = Si, P, Ge, B, and

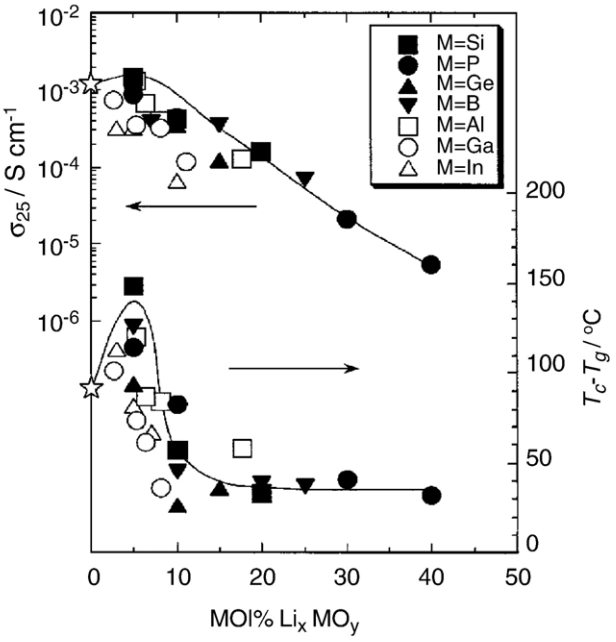

Fig. 1. Composition dependence of the ambient temperature conductivity (σ_{25}) and $T_c - T_g$ of the oxysulfide glasses in the $(100-x)(0.6Li_2S\cdot 0.4SiS_2)\cdot xLi_xMO_y$ (Li_xMO_y = Li_4SiO_4, Li_3PO_4, Li_4GeO_4, Li_3BO_3, Li_3AlO_3, Li_3GaO_3 and Li_3InO_3) systems.