Silicone as a binder in composite electrolytes

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Abstract

A liquid silicone was used as a binder to make composite solid electrolytes from lithium-ion conductive inorganic solid electrolytes (ISEs): an oxysulfide glass, $0.01Li_3PO_4$–$0.63Li_2S$–$0.36SiS_2$ and/or a lithium germanium thio-phosphate, $Li_{3.25}Ge_{0.25}P_{0.75}S_4$. Ionic conductivities of the composites were of the order of 10^{-4} Scm^{-1}, even when the silicone was enriched to 10% (v/v). On the other hand, the composite with styrene–butadiene block co-polymer (SBR) or polypropylene oxide–polyethylene oxide (PO–EO) co-polymer as binder showed much lower conductivity. In the composite electrolyte, the silicone rubber must partly cover the surface of the ISE particles because the composite electrolyte is molded before the vulcanization of the fluid liquid silicone; and thus, it must rarely interfere with the conduction between the ISE particles. Hydrocarbons were found to be suitable in the preparation process of the composite solid electrolyte (CSE).
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1. Introduction

The attempts to make the best use of inorganic solid electrolytes (ISEs) are of particular interest, because lithium batteries will be manufactured in the absence of flammable organic liquid electrolytes [1]. Sulfide glasses [2–7] and a sulfide crystalline material [8], have been reported to have ionic conductivity as high as of the order of 10^{-3} Scm^{-1} at room temperature. Their processibility is also very important for their practical application to lithium batteries as well as their high ionic conductivity, because the ISE should be formed into a thin layer with a wide area in the batteries in order to generate large current. However, the ISEs are brittle and thus too poor in the processibility to shape them into such thin layers. Mixing ISE with polymer-binder into composite solid electrolyte (CSE) is a promising method to obtain highly-processible solid electrolytes.

In our previous paper [9,10], we prepared CSE by mixing the oxysulfide glass, $0.01Li_3PO_4$–$0.63Li_2S$–$0.36SiS_2$, with styrene–butadiene block co-polymer (SBR). We have

obtained highly conductive CSE via dry process. However, when the CSE was prepared from slurry composed of the oxysulfide glass and the SBR solution, i.e. through a wet process, its ionic conductivity was much lower than that of the pristine glass. Textural observation of the dry-processed CSEs showed that SBR did not form films on the ISE particles but formed granular polymer domains among them. In this texture, the domains are considered to adhere ISE particles to each other without interfering with the ionic conduction between them. In the wet-processed CSE, such granular polymer domains were not found, indicating that the polymer might coat the ISE surfaces after the removal of solvent. The SBR, an insulator covering the surface of the ISE particles must reduce the conductivity remarkably.

Although the wet processes decreased the ionic conductivity, they have the advantage of thin-film fabrication for composite electrolytes; because some wet processes, e.g. doctor blade or screen-printing method, are already available for thin-film fabrications. We have succeeded in making a composite electrolyte with a high ionic conductivity via wet process by using silicone as binder [9,10].

In the present study, we prepared some CSEs from different kinds of ISEs and polymers to clearly show that silicone is promising for common use in making CSEs. Solvents used in the process were also optimized.

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2. Experimental

2.1. Materials

The oxysulfide glass, $0.01Li_3PO_4$–$0.63Li_2S$–$0.36SiS_2$ [7], and the lithium germanium thio-phosphate (thio-LISICON), $Li_{3.25}Ge_{0.25}P_{0.75}S_4$ [8], were prepared as reported in the literature. The obtained ISEs were pulverized to 1–3 mm of diameter before use. Four kinds of polymers, i.e. silicone, styrene–butadiene block co-polymer, polypropylene oxide–polyethylene oxide co-polymer (PO–EO), and poly(bis-methacrylate), were attempted as binder to obtain the CSEs. The monomer of the silicone was used as received (CY52-005, Dow Corning Torey Silicone Co. Ltd.). It is liquid and cross-linkable by hydrosilylation reaction [11]. The SBR used was supplied from Denki Kagaku Kogyo K.K. as an experimental sample. Total styrene content and the solution viscosity of the SBR are 39.2 wt.% and 3.4 Pa s, respectively. The solution viscosity was measured for the 5 wt.% solution of the SBR in styrene at 25 °C. The SBR was purified by precipitation from its toluene solution with the addition of methanol. PO–EO (CP-2000, Sumitomo Seika Chemical Co.), containing 20% propylene oxide and 80% ethylene oxide, was dried at 40 °C under vacuum for 24 h. The liquid monomer of poly(bis-methacrylate) (PDE-200, NOF Corp.) was used after drying over molecular sieve (0.3 nm) for a week. All solvents used were dehydrated with common methods and distilled before use.

2.2. Preparations of CSEs

Before the preparation of CSEs, effects of solvents on ISEs were investigated. In argon filled glove box, the oxysulfide glass powder was immersed in toluene, *n*-heptane, acetone (Me_2CO), acetonitrile (MeCN), or ethanol at room temperature. The powder was recovered after the removal of solvent under vacuum for 12 h at room temperature. Its ionic conductivity was measured as mentioned below.

The composites containing the SBR or the PO–EO were prepared by the following procedure. The oxysulfide glass or the thio-LISICON were dispersed into a toluene solution of the polymer, and the obtained slurry was gradually concentrated while stirred, and then the solvent was completely removed in vacuo. The silicone composite was prepared by the same procedure except for the use of *n*-heptane instead of toluene. After the removal of the solvent, the resultant mixture was molded into a pellet under 500 MPa and then heated at 150 °C for 30 min. This heating results in a rapid cross-linking reaction of the liquid silicone and changes it to the solid silicone rubber.

2.3. Conductivity measurement

Ionic conductivities of the ISEs themselves, the solvent-treated glass, and the CSEs were measured from their pellets by the ac method. Powdery $LiTiS_2$ [12] was used as the reversible electrode for the test cell and was pressed onto both sides of the pellet at 500 MPa. Measurement was performed at 25 °C in the frequency range from 10^7 to 10^{-1} Hz at 10 mV (ac) using a frequency response analyzer (Solartron 1260).

3. Results and discussion

The oxysulfide glass is based on a lithium thio-silicate [13], and thus is considered to act as a base. In fact, the glass reacts with moisture in the air to generate hydrogen sulfide. We have to find solvents suitable for the preparation of the CSE by a wet process from such a highly reactive ISE. Table 1 shows the ionic conductivity at room temperature (σ_{RT}) of the oxysulfide glass after being immersed in various solvents. The glass immersed in ethanol shows astonishing low conductivity. Because ethanol has the acid dissociation constant close to H_2O and is the most acidic among the solvents used in the present study [14], the oxysulfide glass will undergo alcoholysis.

The conductivity of the glass treated with Me_2CO or MeCN is slightly lower than that of the pristine glass. The reason of this decrease has not been cleared yet and is under investigation. In contrast, the glass is quite stable with hydrocarbons such as toluene or *n*-heptane. As the polymers used in this study are soluble in these hydrocarbons, the composites were prepared using *n*-heptane or toluene.

The σ_{RT} of the silicone composite was compared to that of the SBR composite or the PO–EO composite. Fig. 1a shows the composition dependence of the σ_{RT} for the three kinds of composites. Silicone composites show much higher conductivity than the others. Also as shown in Fig. 1b, the σ_{RT} of the thio-LISICON/silicone composite is also higher than that of the SBR or the PO–EO composite.

The silicone composite powder was compressed into pellets at room temperature then heated for the vulcanization. This process is not only used for the conductivity measurement but can also be applicable in the construction of sheet-type batteries with CSEs. As discussed before [9,10], the liquid silicone is fluid unless it is vulcanized

Table 1
Ionic conductivity of oxysulfide glass, $0.01Li_3PO_4$–$0.63Li_2S$–$0.36SiS_2$, after its immersion in some organic solvents

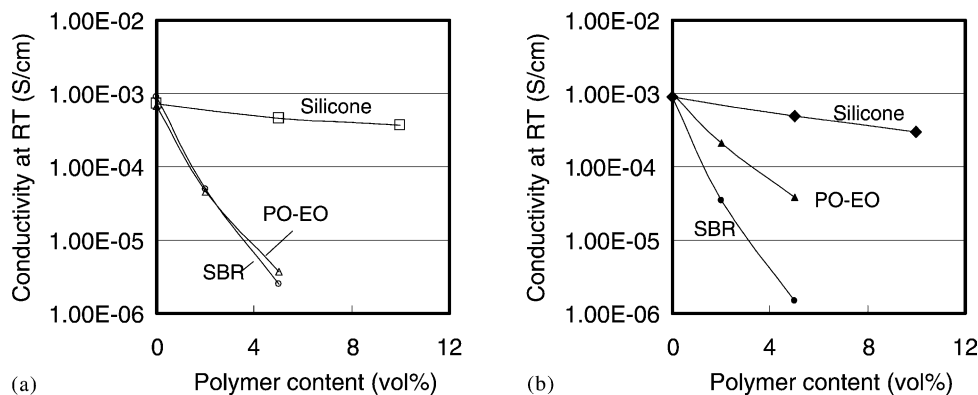| Solvent	σ_{RT} (mScm^{-1})[a]
Intrinsic	1.0
Toluene	1.0
Heptane	1.0
Acetone	0.7
Acetonitrile	0.6
Ethanol	Dissolved

[a] Ionic conductivity at room temperature.

Fig. 1. The conductivity at room temperature of (a) the glass composites and (b) the thio-LISICON composites, as a function of the volume fraction of the polymers.

and will be squeezed into the voids between the ISE particles under compression in the CSE pellets before the heating. The liquid silicone forms granular domains inside the CSEs, and the texture can be maintained even after the cross-linking of the silicone, and thus, does not induce large interference with the ionic conduction between ISE particles. In contrast, SBR or PO–EO cannot flow due to their low fluidity but remain on the surface of ISE particles after the removal of the solvent. These polymers will cover the surface of ISE particles and could interfere with the ionic conduction between the particles, lowering the conductivity of the CSEs.

From the above consideration, a cross-linkable liquid monomer may be preferable for the ISEs' binder. bis-Methacrylate, which has been expected to show the same effect as silicone because of its fluidity, was also examined instead of the silicone. bis-Methacrylate is cured by free radical reaction, which is initiated by the generation of free radical with benzoyl peroxide (BPO). When the bis-methacrylate was heated at 80 °C for 2 h in the presence of the oxysulfide glass, the cure process was not achieved, however the cure had been completed within several minutes in the absence of the glass. One reason can be that BPO is strongly poisoned by the glass, i.e. the glass must act as a radical scavenger.

The silicone used is vulcanized by an addition reaction, which involves addition of a hydrosilane to an unsaturated C–C bond [15]. No radicals are necessary for the cure of the silicone. In addition, the hydrosilylation reaction gives no side reaction products such as ethanol that can lower the conductivity of the ISEs.

4. Conclusion

We prepared some CSEs and measured their ionic conductivities. We concluded that the silicone is a commonly available and useful binder for the ISEs, because (a) the CSE can be prepared by wet process using hydrocarbons, and (b) gives highly conductive CSEs.

Acknowledgements

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