Characterization of quasi-solid electrolytes based on Li$_3$PS$_4$ glass with organic carbonate additives

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Composite quasi-solid electrolytes comprising Li$_3$PS$_4$ (LPS) glass and various organic carbonates were prepared, and the effects of these carbonates on the glass were investigated. Compared to LPS glass, the conductivity decreased for composites with highly dielectric cyclic carbonates and increased slightly for composites with a poorly dielectric linear carbonate. Scanning electron microscopy observations indicated that the addition of a poorly dielectric linear carbonate slightly improved the formability of LPS glass.

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Lithium-ion batteries (LIBs) are currently used in vehicles (electric, plug-in hybrid, and hybrid electric), power tools, and energy storage systems, as well as portable devices such as smart phones and laptop computers.\(^1\)

The safety aspect of LIBs becomes more critical with an increase in the energy density and the battery size. All-solid-state batteries, which utilize inorganic solid electrolytes, have the potential to be next-generation batteries as they are safer, more reliable, and have a higher energy density than batteries that utilize liquid electrolytes.\(^2\) A simple method for the synthesis of solid electrolytes is necessary for the commercialization of bulk-type all-solid-state batteries. To increase the contact area between the solid electrolyte and the active material, a homogenous electrode slurry is required. To achieve these requirements, researches on the synthesis of solid electrolytes via a liquid-phase process\(^3\) and preparation of electrode slurry used for the coating process\(^12\)-\(^16\) have attracted considerable attention. However, the effects of organic compounds on sulfide solid electrolytes need to be investigated to improve these production processes for all-solid-state batteries.

Here, we focused on organic carbonate compounds typically used as solvents for the electrolytes of LIBs as they are less likely to have a disadvantageous electrochemical influence compared with other solvents. Until now, organic carbonate compounds have only been reported as solvents used for the synthesis of solid electrolytes via liquid-phase processes; the impact of these solvents on the final product has not been reported in the literature.\(^10\) In this study, quasi-solid electrolytes comprising 75Li$_2$S–25P$_2$S$_5$ (mol %) glass (LPS glass) and different kinds of organic carbonates were prepared. The effects of these carbonates on the conductivity and the formability of LPS glass were investigated.

Li-ion conducting LPS glass was prepared through the mechanochemical method.\(^17\) Reagent-grade Li$_2$S (Alfa Aesar, 99.9%) crystalline powders and P$_2$S$_5$ (Aldrich, 99%) were used as starting materials. These materials were mechanically reacted at room temperature (\textasciitilde25°C) using a planetary ball mill apparatus (Fritsch P-7) with a zirconia pot (80 mL volume) and 1,500 zirconia balls (3 mm in diameter). The rotation speed was 510 rpm, and the milling time was 16 h. The obtained LPS glass was mixed with each one of the following organic carbonates: ethylene carbonate (EC), propylene carbonate (PC), 4-fluoro ethylene carbonate (FEC), dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), and diethyl carbonate (DEC) (Ube Industries, Ltd., battery grade). The structural formulas of these carbonates are shown in Fig. 1. The carbonates were combined with the solid electrolyte without volatilization. The carbonates were mixed with the LPS powder in the planetary ball mill using the zirconia pot (internal volume of 80 mL) with 200 zirconia balls (3 mm in diameter). The rotation speed was 210 rpm, and the milling time was 15 min. All the samples were obtained as powders. All the composites were amorphous, and all the processes were performed in a dry Ar atmosphere.

![Fig. 1. Structural formulas of the carbonates used in this study.](http://doi.org/10.2109/jcersj2.20114)
The morphology of LPS glass in the composites. Di
composite at DMC, EMC, or DEC) were prepared. glass and one of the organic carbonates (EC, PC, FEC, composite quasi-solid electrolytes comprising the LPS electrolytes, the e
investigation of the morphology of the obtained composite

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resistances, these components are indistinguishable.
The conductivities of the obtained composites were related
to the dielectric constants of the carbonates. The conductivities of the obtained composites were related to the dielectric constants of the carbonates. As the particle surfaces of the sulfide glass are highly basic and since both cyclic and linear carbonates are decomposed under basic conditions,18) the cyclic carbonates, which had high dielectric constants, were decomposed due to the strong interaction with the sulfide glass.  The linear carbonates, which have low dielectric constants, were only partially decomposed. This is due to the weak interaction between the linear carbonates and the sulfide glass.

**Figure 2** shows the Nyquist plots of LPS glass, 95LPS·5PC (vol/vol) composite, and 95LPS·5DMC (vol/vol) composite at 25 °C.

The temperature dependence of the ionic conductivity of pelletized samples was measured after pressurizing to 360 MPa at ~25 °C. The pellets had a diameter of 10 mm and an approximate width of 0.8 mm. Gold electrodes were prepared by sputtering on both surfaces of the pellets with a quick coater (SC-701MKII Advance). AC impedance measurements were carried out using an impedance analyzer (PARSTAT MC). A frequency range of 10 Hz–1 MHz and an applied voltage of 10 mV were used.

The morphologies of the LPS glass and the obtained composites were investigated by scanning electron microscopy (SEM, HITACHI, S4800). Smooth cross-sections of the samples were prepared with a cross-section polisher using an Ar⁺ ion beam (JEOL, IB-09020CP). From the investigation of the morphology of the obtained composite electrolytes, the effect of organic carbonates on the formability of LPS glass itself in the composites was examined. Cross-section polishing is estimated to have little effect on the morphology of LPS glass in the composites. Different composite quasi-solid electrolytes comprising the LPS glass and one of the organic carbonates (EC, PC, FEC, DMC, EMC, or DEC) were prepared.

**Figure 2** shows the Nyquist plots of LPS glass, 95LPS·5PC (vol/vol) composite, and 95LPS·5DMC (vol/vol) composite at ~25 °C. The total resistances of the LPS glass and the 95LPS·5DMC composite were obtained from the intersection of the straight line with the real axis. Although the total resistance consists of bulk and grain boundary resistances, these components are indistinguishable.

**Figure 3** shows the temperature dependences of the total conductivities of the LPS glass and the composites. The temperature dependences of the conductivities obeyed the Arrhenius law, and the activation energies for conductance were calculated from the slopes of the plots.

**Table 1** summarizes the conductivities of the composites at 25 °C, the activation energies of the composites, and the dielectric constants of the carbonates. The conductivities of the composites with a linear carbonate (DMC, EMC, and DEC) were slightly higher than that of the original LPS glass, while the conductivities of the composites with a cyclic carbonate (EC, PC, and FEC) decreased to less than 1 × 10⁻⁴ S cm⁻¹. However, there was no significant difference in the activation energies of the composites. The conductivities of the obtained composites were related to the dielectric constants of the carbonates. As the particle surfaces of the sulfide glass are highly basic and since both cyclic and linear carbonates are decomposed under basic conditions,18) the cyclic carbonates, which had high dielectric constants, were decomposed due to the strong interaction with the sulfide glass. Highly resistive compounds were formed on the particle surfaces of the sulfide glass. The linear carbonates, which have low dielectric constants, were only partially decomposed. This is due to the weak interaction between the linear carbonates and the sulfide glass.

**Figure 4** shows the cross-sectional SEM images of pellets of LPS glass, 95LPS·5PC (vol/vol) composite, and 95LPS·5DMC (vol/vol) composite pressurized to 360 MPa. The addition of PC to the LPS glass increased the number of voids in the pellet [Fig. 4(b)], whereas the addition of DMC had only a slight influence on the formability of the LPS glass [Fig. 4(c)]. This indicated that either PC, with a high dielectric constant, or the reactant of PC with LPS glass inhibited the room temperature pressure sintering of the LPS glass.19) The addition of PC decreased both

![Fig. 2. Nyquist plots of LPS glass, 95LPS·5PC (vol/vol) composite, and 95LPS·5DMC (vol/vol) composite at 25 °C.](image)

![Fig. 3. Temperature dependences of the total conductivity of LPS glass and the 95(LPS)·5(carbonate) (vol/vol) composites.](image)

**Table 1.** Conductivities and activation energies of the 95(LPS)·5(carbonate) (vol/vol) composites and dielectric constants of the carbonates

| Solvents | Dielectric Constant | Conductivity at ~25 °C (S cm⁻¹) | Activation Energy (kJ mol⁻¹) |
|----------|---------------------|-------------------------------|-----------------------------|
| none     | —                   | 4.6 × 10⁻⁴                   | 33                          |
| Cyclic carbonates |          |                               |                             |
| EC       | 95.3                | 7.6 × 10⁻⁶                   | 39                          |
| PC       | 64.4                | 1.0 × 10⁻⁴                   | 36                          |
| FEC      | 78.4                | 7.1 × 10⁻⁵                   | 36                          |
| Linear carbonates |        |                               |                             |
| DMC      | <3                  | 4.7 × 10⁻⁴                   | 32                          |
| MEC      | <3                  | 5.2 × 10⁻⁴                   | 32                          |
| DEC      | <3                  | 5.2 × 10⁻⁴                   | 31                          |
the conductivity and the formability of LPS glass, whereas the addition of DMC slightly increased the formability of LPS glass. Detailed examination is required to fully elucidate the effects of addition of carbonates to LPS glass.

Composite quasi-solid electrolytes based on LPS glass with several kinds of organic carbonates were prepared, and the effects of these carbonates on the properties of the sulfide glass were investigated. The conductivity and the formability at room temperature decreased when cyclic carbonates with high dielectric constants were added. On the other hand, the addition of a linear carbonate with a low dielectric constant slightly improved the formability and the conductivity of the LPS glass. Additionally, the changes in conductivity and formability of the composite quasi-solid electrolytes comprising LPS glass and organic carbonates were related to the dielectric constants of the organic carbonates. By adapting the quasi-solid electrolytes to a separator layer and a composite electrode layer in all-solid-state batteries, it is expected to form the layers with less voids and improve the battery performance.

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