Electrochemical behaviors of Li^+ ion conductor, Li_3PO_4–Li_2S–SiS_2

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Abstract

There are great interests on sulfide glasses because of their high lithium ion conductivity. We synthesized a new lithium ion conductive solid electrolyte, Li_3PO_4–Li_2S–SiS_2 to obtain a solid electrolyte with high ionic conductivity and electrochemical stability. Its conductivity at room temperature was 7.6×10^{-4} S/cm, and proved to be stable against electrochemical reduction. We also investigated the electrochemical behaviors of spherical graphite with this electrolyte as a preliminary study for solid-state batteries and proved that spherical graphite seems a good candidate for negative electrode material in the solid-state batteries.

Introduction

Lithium batteries are promising to reply the great demands of batteries for their high voltage and high energy densities. On the contrary to their validity, we can not get rid of anxiety about safety completely because of their combustible organic electrolytes accompanied by high chemical energy inherent in them. When the high chemical energy is not under control in some unexpected cases, the battery with combustible liquids would be ignited. To solve this problem, incombutible electrolyte, i.e., solid electrolyte must be developed.

There have been many kinds of lithium ion conductive solid electrolytes studied e.g., lithium nitride, lithium oxysalts, lithium halides, and their derivatives, but few of them have been put into practical use. Most of them have high decomposition potentials, but their ionic conductivities are rather poor comparing with nonaqueous electrolytes. On the contrary to that, lithium nitride is a lithium ion conductive solid electrolyte with high ionic conductivity, but its decomposition potential is rather low (about 0.445 V versus Li^+/Li) [1].

Lithium chalcogenide glasses, e.g., Li_2S–SiS_2 [2], Li_2S–P_2S_5 [3] and Li_2S–B_2S_3 [4], etc., are well known lithium ion conductive solid electrolytes with high ionic conductivity in the magnitude of order of 10^{-4} S/cm. Kennedy *et al.* [5] proposed lithium halide-doped Li_2S–SiS_2 to improve its ionic conductivity. They reported that the glasses doped with lithium iodide indicate high ionic conductivity (1.32×10^{-3} S/cm at ambient temperature for $0.28SiS_2$–$0.42Li_2S$–$0.30LiI$). They also pointed out that the glass is unstable in contact with lithium metal.

We attempted to improve the ionic conductivity of Li_2S–SiS_2 glasses by doping with Li_3PO_4 [6]. The reasons are:

(i) Li_3PO_4 exhibits high Li^+ ionic conductivity at high temperature. The local structure at high temperature, that causes high Li^+ ionic conductivity, might remain down to ambient temperature in quenched glass state.

(ii) Conductivity is expressed in the product of mobility by carrier density. Li^+ ion content can be higher by Li_3PO_4 doping. If the lithium ions are mobile, they might improve the ionic conductivity.

We tried to synthesize Li_3PO_4–Li_2S–SiS_2 glasses and investigated their ionic conductivity and the stability toward electrochemical reduction. The preliminary study for application of this glass to solid-state lithium batteries will be also discussed.

Glass-forming region of Li_3PO_4–Li_2S–SiS_2

Preparations of Li_3PO_4-doped Li_2S–SiS_2 glass

Lithium ion conductive glasses doped with Li_3PO_4 were synthesized as follows. First Li_2S–SiS_2 base glasses were synthesized. Special purity grade Li_2S and SiS_2 were mixed in appropriate molar ratios. The mixture was heated in a vitreous carbon crucible in a vertical tube furnace at 950 °C under argon gas flow for 2 h. The melt was quenched by dropping it into liquid N_2 to yield noncrystalline base glass. After that, Li_3PO_4 was doped to the base glass. Li_3PO_4 was mixed with the ground base glass in several mol% ratio. The mixture was heated and quenched as above.

Glass-forming region

Figure 1 indicates the region where the glasses were formed; (O); (△) and (×) in Fig. 1 indicate the composition with which the samples were completely glassy, partially glassy, and crystallized, respectively. Li_2S–SiS_2 glasses were formed in the region with $(Li_2S):(Li_2S + SiS_2)$ ratios less than 0.61. But Li_3PO_4–Li_2S–SiS_2 quasi-ternary glasses can be yielded in the different composition ratio of Li_2S and SiS_2. For example, glasses were yielded in the region with Li_2S composition up to 0.7 when Li_3PO_4 was doped.
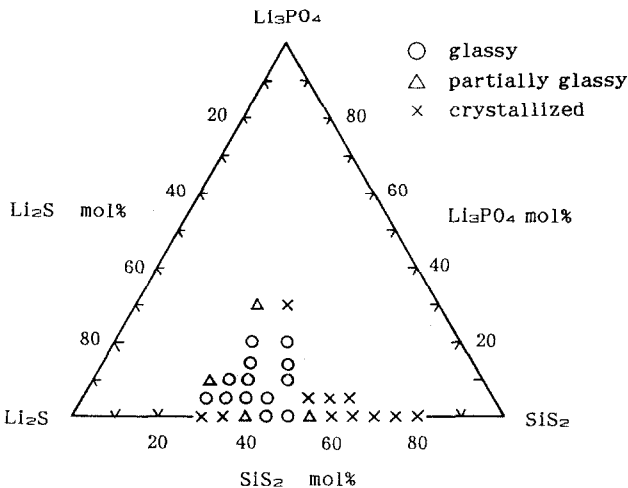

Fig. 1. Glass-forming region of Li_3PO_4–Li_2S–SiS_2 glasses.

The reason has not been proved yet, but we can suppose that Li_3PO_4 would also play a part in glass forming in the quasi-ternary system. As well known, PO_4^{3-} ions can be glass-forming ions in silver ion conductive glassy solid electrolytes, e.g., $AgI-Ag_4P_2O_7$ and $AgI-AgPO_3$ [7]. The quasi-ternary glass would be constructed by not only SiS_4^{4-} ions but also PO_4^{3-} ions.

Ionic conductivity of Li_3PO_4–Li_2S–SiS_2

Measurement method for ionic conductivity

Ionic conductivity of the obtained glass was measured by a.c. impedance measurement.

Obtained Li_3PO_4-doped glass was ground and pressed into a 10 mm diameter pellet inside an insulator tube (a polyimide resin tube) with platinum plates as electrodes on both faces.

Complex impedance was measured with a Solartron 1186 electrochemical interface and 1170 frequency response analyzer. The signal across the sample was 10 mV and the frequency range was from 10^5 to 10^{-3} Hz.

Ionic conductivity

Figure 2 indicates the electric conductivity versus Li_3PO_4. Base glasses were Li_2S–SiS_2 with the compositions Li_2S:SiS_2 = 50:50, 60:40, and 61:39. The horizontal axis indicates Li_3PO_4 content x in xLi_3PO_4–$(1-x)(yLi_2S$–$(1-y)SiS_2)$. Electric conductivity of the Li_3PO_4-doped glasses increased with increasing content of Li_3PO_4. A maximum value is reached at $x = 0.02 \sim 0.03$. After that, the conductivity decreases with increasing Li_3PO_4 beyond $x = 0.03$ because of their crystallization. Figure 2 shows that doped Li_3PO_4 improves the ionic conductivities in the glass-forming region.

Figure 3 indicates the ionic conductivity of Li_3PO_4-doped $0.65Li_2S$–$0.35SiS_2$ glasses. Glassy sample was not obtained when Li_3PO_4 was not doped. Electric conductivity of the crystallized $0.65Li_2S$–$0.35SiS_2$ was so poor that we could not measure the conductivity. Glassy samples could be obtained by doping Li_3PO_4 to $0.65Li_2S$–$0.35SiS_2$. The highest conductivity was obtained at 1% Li_3PO_4-doped composition. This phenomenon also
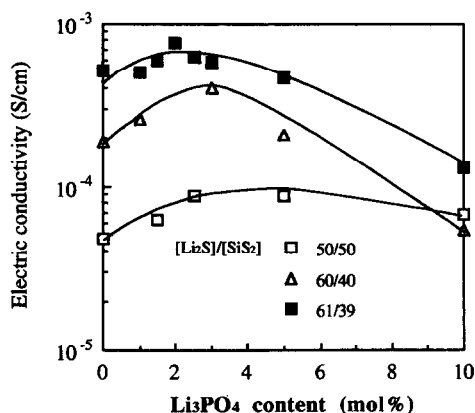

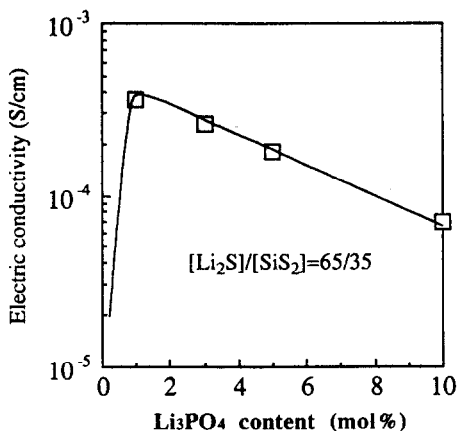Fig. 2. Electric conductivity of Li_3PO_4-doped Li_2S–SiS_2 glasses as a function of Li_3PO_4 compositions.

Fig. 3. Electric conductivity of Li_3PO_4-doped $0.65Li_2S$–$0.35SiS_2$ as a function of Li_3PO_4 compositions.

proves that Li_3PO_4 is not only a glass modifier but also a glass former in the quasi-ternary system, $Li_3PO_4-Li_2S-SiS_2$.

Electrochemical stability of $Li_3PO_4-Li_2S-SiS_2$

Evaluation method for electrochemical stability

Kennedy *et al.* [5] pointed out the instability of Li_2S-SiS_2 and $LiI-Li_2S-SiS_2$ glasses in contact with lithium metal. When the solid electrolytes are in contact with lithium metal, they should be strongly polarized to the potential of lithium electrode. We supposed that the instability is due to the local cell reaction by contacting with lithium metal. We investigated the electrochemical behavior of the glasses by a means of cyclic voltammetry to evaluate the instability against electrochemical reductions.

First of all, $LiI-Li_2S-SiS_2$ glass was synthesized as a comparison. LiI was doped to Li_2S-SiS_2 base glass, instead of Li_3PO_4 to yield the glass with the composition $0.30LiI-0.427Li_2S-0.27SiS_2$.

Three electrode cells were constructed to investigate the electrochemical properties of the glassy electrolytes, i.e., $LiI-Li_2S-SiS_2$ and $Li_3PO_4-Li_2S-SiS_2$. The working electrode was a platinum plate and the counter electrode was a lithium foil. A silver wire was embedded in the electrolyte as a reference electrode. The electrodes and solid electrolyte glass were pressed together at 4000 kg/cm^2 to contact each other.

Cyclic voltammograms were obtained with appropriate scanning rates. The electrochemical cells were put in a desiccator filled with dry argon gas and with P_2O_5 as a desiccant in it, at room temperature.

Electrochemical stability of $Li_3PO_4-Li_2S-SiS_2$

Figure 4 shows the cyclic voltammograms for a $0.5Li_2S-0.5SiS_2$ glass and a 3% Li_3PO_4-doped glass at a scanning speed 2 mV/s. The electrode area was 0.785 cm^2.

Only cathodic and anodic current corresponding to lithium deposition/dissolution reactions were observed. Neither an anodic current corresponding to electrolyte decomposition nor current corresponding to electronic conduction was observed in this potential range from -3 to 2 V versus Ag, which corresponds to the potential range from -1 to 4 V versus Li^+/Li.
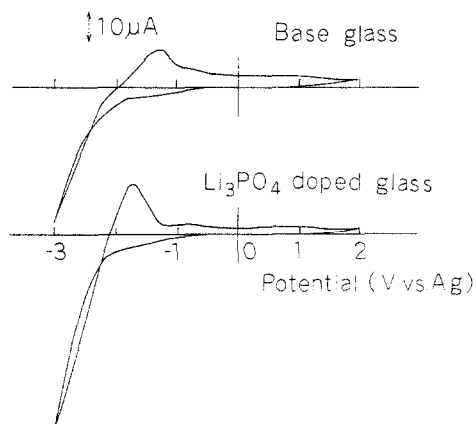

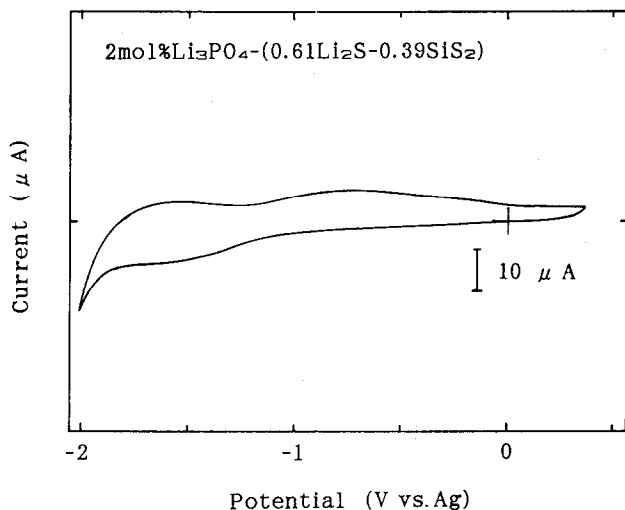Fig. 4. Cyclic voltammograms for 2% Li_3PO_4-doped $0.61Li_2S-0.39SiS_2$ glass.

Fig. 5. Cyclic voltammograms for 30% LiI-doped 0.61Li$_2$S–0.39SiS$_2$ glass.

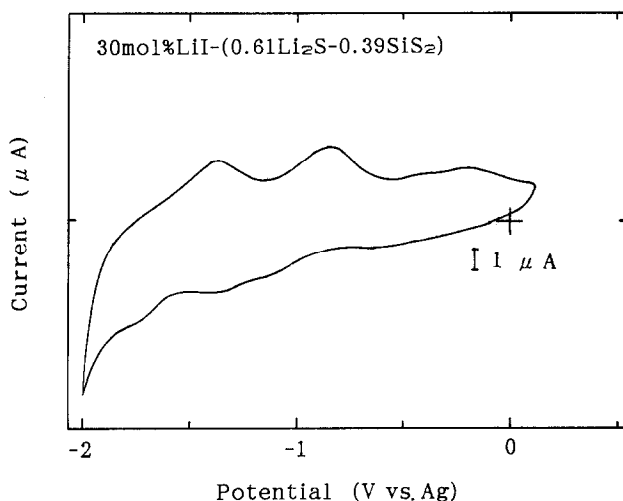Fig. 6. Cyclic voltammograms for spherical graphite as a working electrode.

Figure 5 shows the voltammogram for the 0.02Li$_3$PO$_4$–0.59Li$_2$S–0.39SiS$_2$ glass. The voltammogram was obtained at a 1 mV/s scanning speed in the range from -2 to $+0.35$ V versus Ag ($0 \sim 2.35$ V versus Li$^+$/Li).

Reduction reactions were observed by cathodic sweep, and oxidation reactions were observed by anodic sweep. The coulombic efficiency y was calculated from the voltammogram. y is defined as Q_a/Q_c, where Q_a and Q_c are electrical charges in the anodic reactions and cathodic reactions during a cycle, respectively. Coulombic efficiency y for this glass is almost 1 ($y = 0.98$).

Cyclic voltammogram for LiI–Li$_2$S–SiS$_2$ is indicated in Fig. 6. Peaks, which were not observed in the voltammogram for Li$_3$PO$_4$–Li$_2$S–SiS$_2$, were observed. Coulombic

efficiency for this glass was 0.78 and this value largely deviates from 1 in the potential region. From this result, it is concluded that irreversible electrochemical reactions occur in the potential region. The glass would be undergoing the irreversible reduction reaction while the glass is in contact with lithium metal. The reduction reactions are inferred to result in the degradation of the glass.

From these results, Li_3PO_4-doped glass is supposed to have stability against lithium metal. Their high conductivities and chemical stability against lithium metal made these glasses good candidates as electrolytes for rechargeable solid-state lithium batteries.

Preliminary studies for application of Li_3PO_4–Li_2S–SiS_2 to lithium batteries

We must find out electrode materials to be applied to the solid electrolyte to solid-state lithium batteries. Intercalation materials are generally expected to be favorable as electrode materials in case of constructing batteries with solid electrolytes. When using metals as electrodes with solid electrolytes deposition and dissolution reactions, which caused by charge/discharge operation of the battery, should destroy the interface between electrodes and solid electrolytes, which are connected just by pressing each other. For this reason, lithium insertion materials are preferred to lithium metal as a negative electrode material. The stability against electrochemical reduction described above enables us to investigate the electrochemical properties of spherical graphite, which is known as negative electrode material in lithium batteries with nonaqueous electrolyte.

An electrochemical cell with three electrodes was constructed as described in the previous section. The working electrode consists of a mixture of spherical graphite and solid electrolyte ($0.03Li_3PO_4$–$0.58Li_2S$–$0.39SiS_2$) instead of a platinum plate. Cyclic voltammetry was performed with the electrochemical cell with a 1 mV/s scanning speed. The working electrode was polarized from -2.05 V, which was the potential of lithium electrode, to 0.50 V versus Ag.
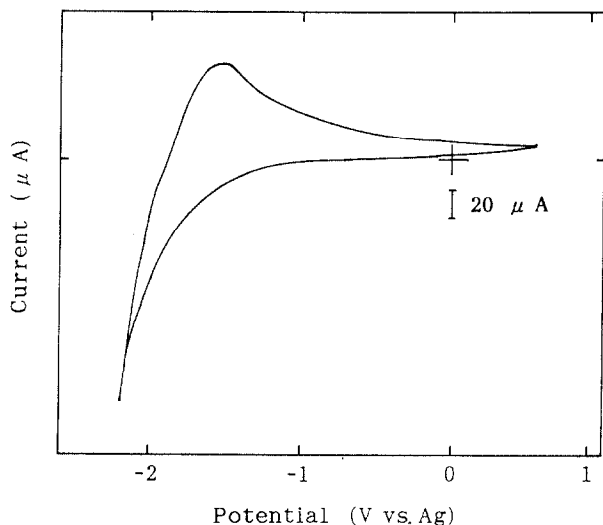

Fig. 7. Charge/discharge cycling properties of the cell, spherical graphite/Li_3PO_4–Li_2S–SiS_2/Li.
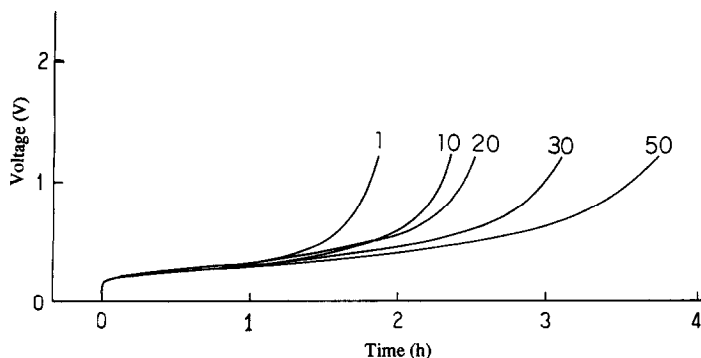
Fig. 8. Charge curves of the cell spherical graphite/Li₃PO₄–Li₂S–SiS₂/Li.

Figure 7 shows the obtained cyclic voltammogram obtained with the electrochemical cell. The coulombic efficiency in a cycle defined by Q_a/Q_c was 1.01.

An electrochemical cell was also constructed as carbon/solid electrolyte/lithium, where solid electrolyte was $0.03Li_3PO_4$–$0.58Li_2S$–$0.39SiS_2$, and carbon was spherical graphite with a weight of about 13 mg. The cell was discharged and charged at constant current (22 μA) between 0 and 1.2 V. Figure 8 indicates the charge curves of the cell, which correspond to the potential curves of the spherical graphite as a negative electrode in a lithium battery during discharging. The electrical charge during the discharge increased with cycle number. It is inferred that interface between the spherical graphite and the solid electrolyte would be improved by the cycling operation. The curves exhibit no deterioration over 50 cycles. This proves that the quasi-ternary solid electrolyte is stable against electrochemical reduction down to lithium deposition-dissolution potential. In addition to that, the electrochemical insertion-deinsertion reaction of lithium ions to spherical graphite was supposed to have excellent reversibility.

These phenomena tell us that spherical graphite seems a good candidate for a negative electrode material in a solid-state rechargeable lithium battery.

Conclusions

The Li_3PO_4–Li_2S–SiS_2 ternary glasses were investigated, and it was found out that:
  (i) Li_3PO_4-doped glasses have good ionic conductivity and the conductivity is maximized at about $0.02Li_3PO_4$–$0.97(Li_2S$–$SiS_2)$ glass composition at each Li_2S–SiS_2 composition.
  (ii) The glassy electrolytes are stable against electrochemical reduction.
  (iii) Spherical graphite seems to be a good candidate for a negative electrode material.

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