

# Electrical and electrochemical properties of $\text{Li}_2\text{S}-\text{P}_2\text{S}_5-\text{P}_2\text{O}_5$ glass–ceramic electrolytes

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## Abstract

The electrical and electrochemical properties of the  $\text{Li}_2\text{S}-\text{P}_2\text{S}_5-\text{P}_2\text{O}_5$  glass–ceramic electrolytes were investigated. The  $80\text{Li}_2\text{S} \cdot (20-x)\text{P}_2\text{S}_5 \cdot x\text{P}_2\text{O}_5$  (mol%) glass–ceramics were prepared by a mechanical milling and a subsequent heat treatment. The  $80\text{Li}_2\text{S} \cdot 19\text{P}_2\text{S}_5 \cdot 1\text{P}_2\text{O}_5$  glass–ceramic showed the high lithium ion conductivity of  $7.4 \times 10^{-4} \text{ S cm}^{-1}$  at room temperature and the low activation energy of  $34 \text{ kJ mol}^{-1}$  for conduction. The addition of a small amount of  $\text{P}_2\text{O}_5$  to the  $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$  sulfide system lowered the electronic conductivity and enhanced the electrochemical stability of the glass–ceramic electrolytes. All-solid-state In/LiCoO<sub>2</sub> cells with the  $80\text{Li}_2\text{S} \cdot 19\text{P}_2\text{S}_5 \cdot 1\text{P}_2\text{O}_5$  glass–ceramic as a solid electrolyte worked as lithium secondary batteries at room temperature. The cells maintained high discharge capacity of about  $100 \text{ mAh g}^{-1}$  for 10 cycles.

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**Keywords:** Solid electrolyte; Lithium ion; Glass–ceramic; Mechanical milling; All-solid-state battery

## 1. Introduction

Lithium ion conducting solid electrolytes have attracted a strong interest for their potential application to all-solid-state lithium secondary batteries with high energy densities. All-solid-state batteries have some advantages, such as no leakage of electrolytes and an easy miniaturization. Solid electrolytes require a high ionic conductivity, a low electronic conductivity and a good electrochemical stability over a wide potential range. Sulfide glasses in the systems  $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$  and  $\text{Li}_2\text{S}-\text{SiS}_2$  are one of the highly lithium ion conductive solid electrolytes [1,2].

We have reported that the  $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$  glasses prepared by using a mechanical milling technique show lithium ion conductivities of more than  $10^{-4} \text{ S cm}^{-1}$  at room temperature [3]. The crystallization of the glasses enhanced the conductivity and the obtained glass–ceramic materials showed high conductivity of about  $10^{-3} \text{ S cm}^{-1}$  at room temperature [4].

The enhancement of the conductivity was brought by a precipitation of a highly conductive crystal, which was analogous to thio-LISICON phase in the  $\text{Li}_{3+x}\text{P}_{1-x}\text{Ge}_x\text{S}_4$  system [5].

The addition of a small amount of ortho-oxosalts to the  $\text{Li}_2\text{S}-\text{SiS}_2$  sulfide systems has been reported to improve electrical and thermal properties of glassy electrolytes [6,7]. Results of solid-state NMR and X-ray photoelectron spectroscopy suggested that these glasses mainly contained  $\text{SiOS}_3$  tetrahedral units with three non-bridging sulfur atoms and a bridging oxygen atom, which works as a weaker trap for lithium ions than a non-bridging oxygen atom. The increase in the conductivity by adding oxides was also observed in the mechanically milled  $\text{Li}_2\text{O}-\text{Li}_2\text{S}-\text{P}_2\text{S}_5$  glasses; the conductivity of the  $7.5\text{Li}_2\text{O} \cdot 67.5\text{Li}_2\text{S} \cdot 25\text{P}_2\text{S}_5$  (mol%) glass exhibited the conductivity of  $2.7 \times 10^{-4} \text{ S cm}^{-1}$  at room temperature [8]. Thus, the addition of a small amount of oxides to pure sulfide glasses is one of the effective ways to increase ionic conductivity.

Recently, we have examined a combination of (i) the precipitation of the high lithium ion conductive crystal and (ii)

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the addition of a small amount of oxides in order to increase conductivities of solid electrolytes. The  $\text{Li}_2\text{S}$ – $\text{P}_2\text{S}_5$  glasses and glass–ceramics with a small amount of  $\text{Li}_2\text{O}$  or  $\text{P}_2\text{O}_5$  were prepared by the mechanical milling and their local structure and lithium ion conductivity were investigated [9]. These glasses and glass–ceramics contained  $\text{PO}_n\text{S}_{4-n}$  ( $n=1$ – $3$ ) tetrahedral units, in which a phosphorus atom was coordinated with both sulfur and oxygen atoms. The  $\text{Li}_2\text{S}$ – $\text{P}_2\text{S}_5$ – $\text{P}_2\text{O}_5$  glass–ceramics exhibited lower activation energies for conduction than the  $\text{Li}_2\text{S}$ – $\text{P}_2\text{S}_5$  glass–ceramic and maintained high conductivities. The precipitation of the thio-LISICON analog was confirmed by XRD patterns of the  $\text{Li}_2\text{S}$ – $\text{P}_2\text{S}_5$ – $\text{P}_2\text{O}_5$  glass–ceramics.

In the present study, the electrical and electrochemical properties of the  $\text{Li}_2\text{S}$ – $\text{P}_2\text{S}_5$ – $\text{P}_2\text{O}_5$  glass–ceramics were investigated. An all-solid-state secondary battery with this glass–ceramics was assembled and the performance of the battery was characterized.

## 2. Experimental

Reagent-grade  $\text{Li}_2\text{S}$  (Furuuchi Chem., 99.99%),  $\text{P}_2\text{S}_5$  (Aldrich, 99%) and  $\text{P}_2\text{O}_5$  (Aldrich, 99.99%) crystalline powders were used as starting materials. The  $80\text{Li}_2\text{S}\cdot(20-x)\text{P}_2\text{S}_5\cdot x\text{P}_2\text{O}_5$  (mol%) glasses were prepared by using the mechanical milling technique. The  $\text{Li}_2\text{S}$  content in these glasses was fixed to be 80 mol% because the  $80\text{Li}_2\text{S}\cdot 20\text{P}_2\text{S}_5$  glass–ceramic exhibited the highest conductivity at room temperature in the  $\text{Li}_2\text{S}$ – $\text{P}_2\text{S}_5$  glass–ceramics [4]. A mixture of the starting materials was loaded into an alumina pot in 45 mL volume with 10 alumina balls of 10 mm in diameter. The pot was mounted in a planetary ball mill apparatus (Fritch Pulverisette 7) and milled at a rotating speed of 370 rpm for 20 h. The  $\text{Li}_2\text{S}$ – $\text{P}_2\text{S}_5$ – $\text{P}_2\text{O}_5$  glass–ceramics were prepared by a heat treatment of the milled glasses at 230 °C, which was higher than their crystallization temperatures [9].

The conductivities of the glass–ceramics were determined for pellets obtained by a cold press of the glass–ceramics under  $3700\text{ kg cm}^{-2}$ ; the diameter and thickness of the pellets were 10 mm and about 1 mm, respectively. A carbon paste was painted as electrodes on both faces of the pelletized glass–ceramics. The electrical conductivities were obtained by AC impedance measurements using a Solartron 1260 impedance analyzer in a temperature range from 25 °C to 230 °C and in a frequency range from 100 Hz to 15 MHz. DC conductivities of the glass–ceramics were also examined. Lithium foils as non-blocking electrodes or stainless-steel plates (SUS-316) as blocking electrodes were attached to both faces of the pelletized glass–ceramics. The DC conductivities were calculated from the current values obtained by applying a constant DC voltage of 1 V to the pellets at room temperature. The electrochemical stability of the pelletized glass–ceramics was investigated by cyclic voltammetry. A stainless-steel as a working electrode plate was attached on one face of the pellet. A lithium foil as counter and pseudoref-

erence electrodes was also attached on the other face of the pellet. The potential sweep was performed using a Solartron 1286 potentiostat at room temperature with a scanning rate of  $5\text{ mV s}^{-1}$ .

An all-solid-state cell with the glass–ceramics as solid electrolytes was assembled to evaluate the cell performance as a lithium secondary battery. A positive electrode was formed by mixing of the three powders of  $\text{LiCoO}_2$ , the glass–ceramic and vapor grown carbon fiber (VGCF) in a weight ratio of 38:58:4. An indium foil was used as a negative electrode. These two electrodes and glass–ceramic powder as an electrolyte were placed together in an insulator tube ( $\Phi = 10\text{ mm}$ ), and then were pressed at  $3700\text{ kg cm}^{-2}$ . The cell was charged and discharged under a constant current density of  $64\text{ }\mu\text{A cm}^{-2}$  at room temperature. All the processes were performed in a dry Ar-filled glove box ( $[\text{H}_2\text{O}] < 1\text{ ppm}$ ).

## 3. Results and discussion

Fig. 1 shows composition dependences of the electrical conductivity at 25 °C ( $\sigma_{25}$ ) and activation energy ( $E_a$ ) for conduction of the  $80\text{Li}_2\text{S}\cdot(20-x)\text{P}_2\text{S}_5\cdot x\text{P}_2\text{O}_5$  glass–ceramics. Solid circles and triangles denote  $\sigma_{25}$  and  $E_a$ , respectively. Changes in  $\sigma_{25}$  and  $E_a$  against the composition are not monotonous. The glass–ceramic with 1 mol%  $\text{P}_2\text{O}_5$  retains high  $\sigma_{25}$  of  $7.4 \times 10^{-4}\text{ S cm}^{-1}$  and exhibits lower  $E_a$  of  $34\text{ kJ mol}^{-1}$  compared to the pure sulfide glass–ceramic. Further increasing  $\text{P}_2\text{O}_5$  content results in decreasing  $\sigma_{25}$  and increasing  $E_a$ . We reported that the  $\text{Li}_2\text{S}$ – $\text{SiS}_2$  glasses added with a small amount of ortho-oxosalts mainly contained  $\text{SiOS}_3$  units, and such structural units probably brought an increase of the conductivity at room temperature and a decrease of the activation energy for conduction [7]. We confirmed from  $^{31}\text{P}$  MAS-NMR measurements that the  $80\text{Li}_2\text{S}\cdot 19\text{P}_2\text{S}_5\cdot 1\text{P}_2\text{O}_5$  glass–ceramic contained  $\text{PO}_n\text{S}_{4-n}$  ( $n=1$ – $3$ ) units. The presence of  $\text{PO}_n\text{S}_{4-n}$  units might be one factor of lowering  $E_a$  and retaining high  $\sigma_{25}$ . A small amount of  $\text{P}_2\text{O}_5$  added to the  $\text{Li}_2\text{S}$ – $\text{P}_2\text{S}_5$  system plays a significant role to migrate lithium ions smoothly in the glass–ceramics.

Fig. 2 shows DC conductivities calculated from the current observed by applying a constant DC voltage of 1 V to

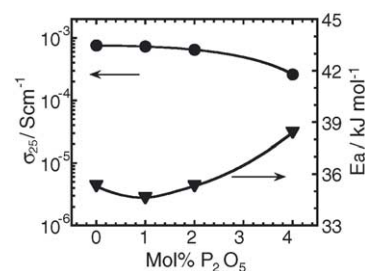


Fig. 1. Composition dependences of the conductivity at 25 °C and the activation energy for conduction of the  $80\text{Li}_2\text{S}\cdot(20-x)\text{P}_2\text{S}_5\cdot x\text{P}_2\text{O}_5$  (mol%) glass–ceramics. Solid circles and triangles denote the conductivity and the activation energy for conduction, respectively.

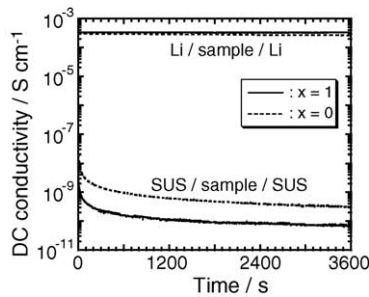


Fig. 2. Conductivities calculated from the current obtained by applying a constant DC voltage of 1 V to the  $80\text{Li}_2\text{S}\cdot(20-x)\text{P}_2\text{S}_5\cdot x\text{P}_2\text{O}_5$  glass–ceramics at room temperature for 1 h. Solid and dotted lines denote the compositions of  $x=1$  and 0, respectively.

the  $80\text{Li}_2\text{S}\cdot(20-x)\text{P}_2\text{S}_5\cdot x\text{P}_2\text{O}_5$  glass–ceramics ( $x=0$  and 1) at room temperature. Solid and dotted lines denote  $x=1$  and 0, respectively. When lithium metal foils were used as non-blocking electrodes, the conductivities of the both glass–ceramics retained constant current with time, and exhibited almost the same conductivity of  $3.0 \times 10^{-4} \text{ S cm}^{-1}$ . These conductivities are in good agreement with those calculated from resistances obtained by an AC impedance technique using stainless-steels (SUS) as blocking electrodes. When stainless-steel electrodes were used, a large polarization initially occurred, and then the current became almost constant. The conductivities of the glass–ceramics with and without  $\text{P}_2\text{O}_5$  after 3600 s are  $7.0 \times 10^{-11} \text{ S cm}^{-1}$  and  $3.0 \times 10^{-10} \text{ S cm}^{-1}$ , respectively. The conductivity of the glass–ceramic with  $\text{P}_2\text{O}_5$  measured by the use of blocking electrodes is about a half of magnitude lower than that of the glass–ceramic without  $\text{P}_2\text{O}_5$ , suggesting that the addition of a small amount of  $\text{P}_2\text{O}_5$  leads to decrease the electronic conductivity of the glass–ceramics. A self-discharge property of batteries is expected to decline when the  $\text{Li}_2\text{S}\text{--}\text{P}_2\text{S}_5\text{--}\text{P}_2\text{O}_5$  glass–ceramics are applied to lithium secondary batteries. The DC conductivities obtained using stainless-steel electrodes are about six orders of magnitude lower than those obtained using lithium electrodes in the glass–ceramics with and without  $\text{P}_2\text{O}_5$ . Therefore, the electronic conductivity of the glass–ceramics is at least six orders of magnitude lower than the ionic conductivity, suggesting that the lithium ion transport number of the glass–ceramics proves to be almost unity.

Fig. 3 shows cyclic voltammograms of (a) the  $80\text{Li}_2\text{S}\cdot 20\text{P}_2\text{S}_5$  glass–ceramic and (b) the  $80\text{Li}_2\text{S}\cdot 19\text{P}_2\text{S}_5\cdot 1\text{P}_2\text{O}_5$  glass–ceramic. The cyclic voltammetry was carried out in a potential range from  $-0.10 \text{ V}$  to  $+5.0 \text{ V}$  versus  $\text{Li}^+/\text{Li}$ . In both the cases (a) and (b), a cathodic current is observed at around  $0 \text{ V}$  on a cathodic sweep from an open circuit potential to  $-0.10 \text{ V}$ , and then an anodic current is observed at around  $0 \text{ V}$  on an anodic sweep. The lithium deposition ( $\text{Li}^+ + \text{e}^- \rightarrow \text{Li}$ ) and lithium dissolution ( $\text{Li} \rightarrow \text{Li}^+ + \text{e}^-$ ) reactions occur in a potential range from  $-0.1 \text{ V}$  to  $+0.1 \text{ V}$  versus  $\text{Li}^+/\text{Li}$  in the cyclic voltammograms. Insets in this figure show the magnified voltammograms on the anodic sweep after lithium disso-

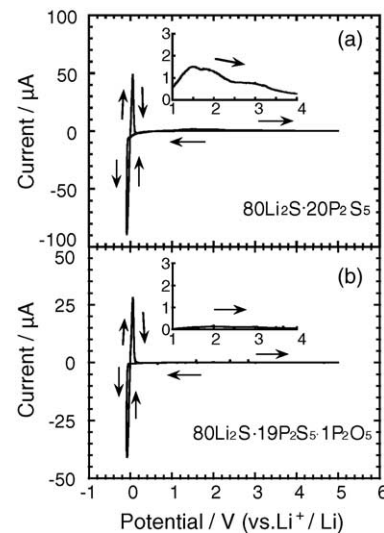


Fig. 3. Cyclic voltammograms of (a) the  $80\text{Li}_2\text{S}\cdot 20\text{P}_2\text{S}_5$  glass–ceramic and (b) the  $80\text{Li}_2\text{S}\cdot 19\text{P}_2\text{S}_5\cdot 1\text{P}_2\text{O}_5$  glass–ceramic. The cyclic voltammetry was performed at a scanning rate of  $5 \text{ mV s}^{-1}$ .

lution. The voltammograms of those two glass–ceramics are somewhat different. A very small anodic current compared to the current due to the lithium dissolution reaction appears in the potential range from  $1.0 \text{ V}$  to  $3.0 \text{ V}$  for the  $80\text{Li}_2\text{S}\cdot 20\text{P}_2\text{S}_5$  glass–ceramic, while no obvious anodic current is observed for the  $80\text{Li}_2\text{S}\cdot 19\text{P}_2\text{S}_5\cdot 1\text{P}_2\text{O}_5$  glass–ceramic. Machida et al. have reported a cyclic voltammogram of the  $67\text{Li}_2\text{S}\cdot 33\text{P}_2\text{S}_5$  milled glass [10]. The  $67\text{Li}_2\text{S}\cdot 33\text{P}_2\text{S}_5$  glass showed a small anodic peak at around  $2.1 \text{ V}$  in its voltammogram and the peak was attributed to an oxidation of free  $\text{S}^{2-}$  ions. The oxidation of the free  $\text{S}^{2-}$  ions, which would be present in the glass–ceramics is one possibility of the anodic current for the  $80\text{Li}_2\text{S}\cdot 20\text{P}_2\text{S}_5$  glass–ceramic as shown in Fig. 3(a). Although the origin of the anodic current in the range from  $1.0 \text{ V}$  to  $3.0 \text{ V}$  has not been clarified at the present stage, the addition of a small amount of  $\text{P}_2\text{O}_5$  to the  $\text{Li}_2\text{S}\text{--}\text{P}_2\text{S}_5$  sulfide system enhances the electrochemical stability of the glass–ceramics.

Fig. 4 shows charge and discharge curves of the all-solid-state cell  $\text{In}/80\text{Li}_2\text{S}\cdot 19\text{P}_2\text{S}_5\cdot 1\text{P}_2\text{O}_5$  glass–ceramic/ $\text{LiCoO}_2$  cell. The charge and discharge measurements were carried out under a constant current density of  $64 \mu\text{A cm}^{-2}$  at room

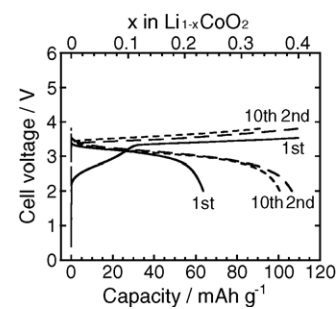


Fig. 4. Charge and discharge curves of the all-solid-state cell  $\text{In}/80\text{Li}_2\text{S}\cdot 19\text{P}_2\text{S}_5\cdot 1\text{P}_2\text{O}_5$  glass–ceramic/ $\text{LiCoO}_2$ . Electrochemical measurements were performed at the current density of  $64 \mu\text{A cm}^{-2}$  at room temperature.

temperature. The cell was charged up to  $x = 0.4$  in  $\text{Li}_{1-x}\text{CoO}_2$  ( $110 \text{ mAh g}^{-1}$ ) and discharged to 2.0 V until the second cycle, and then the charge–discharge cycles were repeated between the maximum charge voltage at the second cycle and 2.0 V after the third cycle. The first discharge capacity is about  $70 \text{ mAh g}^{-1}$ , which is smaller than the corresponding charge capacity of  $110 \text{ mAh g}^{-1}$ . At the second cycle, the discharge capacity drastically increases to about  $110 \text{ mAh g}^{-1}$ , which is as large as the charge capacity, and the charge–discharge efficiency approaches to 100%. The cell maintains the discharge capacity of about  $100 \text{ mAh g}^{-1}$  and charge–discharge efficiency of about 100% up to the 10th cycle. The charge–discharge behavior, such as potential plateaux and capacities of the cell, is quite similar to that of the cell with the  $80\text{Li}_2\text{S}\cdot 20\text{P}_2\text{S}_5$  glass–ceramic which showed excellent cycleability for 200 cycles [11].

#### 4. Conclusions

The effects of the addition of  $\text{P}_2\text{O}_5$  on the electrical and electrochemical properties of the  $\text{Li}_2\text{S}\text{--}\text{P}_2\text{S}_5$  glass–ceramics were investigated. It was found that the  $\text{Li}_2\text{S}\text{--}\text{P}_2\text{S}_5$  glass–ceramics containing a small amount of  $\text{P}_2\text{O}_5$  showed some advantages as solid electrolytes for all-solid-state lithium batteries. The  $80\text{Li}_2\text{S}\cdot 19\text{P}_2\text{S}_5\cdot 1\text{P}_2\text{O}_5$  glass–ceramic retained a high electrical conductivity of  $7.4 \times 10^{-4} \text{ S cm}^{-1}$  compared to the pure sulfide glass–ceramic at room temperature, and exhibited a lower activation energy for conduction than the pure sulfide glass–ceramic. Moreover, a lithium ion transport number of the  $80\text{Li}_2\text{S}\cdot 19\text{P}_2\text{S}_5\cdot 1\text{P}_2\text{O}_5$  glass–ceramic proved to be almost unity. The  $80\text{Li}_2\text{S}\cdot 20\text{P}_2\text{S}_5$  glass–ceramic without  $\text{P}_2\text{O}_5$  showed a low electronic conductivity and a wide electrochemical window of 5 V. However, a very small current of about  $1 \mu\text{A}$  due to the oxidation reaction except for the lithium dissolution was observed on the cyclic voltammogram of the pure sulfide glass–ceramic. The addition of 1 mol%  $\text{P}_2\text{O}_5$ , further improved the elec-

trochemical stability of the glass–ceramics and lowered the electronic conductivity. An all-solid-state  $\text{In/LiCoO}_2$  cell using the  $80\text{Li}_2\text{S}\cdot 19\text{P}_2\text{S}_5\cdot 1\text{P}_2\text{O}_5$  glass–ceramic as a solid electrolyte worked as a lithium secondary battery at room temperature. This cell exhibited similar charge–discharge behavior to that with the  $80\text{Li}_2\text{S}\cdot 20\text{P}_2\text{S}_5$  glass–ceramic. The  $\text{Li}_2\text{S}\text{--}\text{P}_2\text{S}_5$  glass–ceramics with a small amount of  $\text{P}_2\text{O}_5$  are promising solid electrolytes for all-solid-state lithium batteries.

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