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Improved chemical stability and cyclability in Li_2S–P_2S_5–P_2O_5–ZnO composite electrolytes for all-solid-state rechargeable lithium batteries

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ABSTRACT

Sulfide glasses with high Li^+ ion conductivity are promising solid electrolytes for all-solid-state rechargeable lithium batteries. This study specifically examined the chemical stability of Li_2S–P_2S_5-based glass electrolytes in air. Partial substitution of P_2O_5 for P_2S_5 decreased the rate of H_2S generation from glass exposed to air. The addition of ZnO to the Li_2S–P_2S_5–P_2O_5 glasses as a H_2S absorbent reduced the H_2S gas release. A composite electrolyte prepared from 90 mol% of $75Li_2S{\cdot}21P_2S_5{\cdot}4P_2O_5$ (mol%) glass and 10 mol% ZnO was applied to all-solid-state cells. The all-solid-state In/$LiCoO_2$ cell with the composite electrolyte showed good cyclability as a lithium secondary battery.

1. Introduction

All-solid-state rechargeable lithium batteries have attracted much attention because of their high energy density and long cycle life [1,2]. All-solid-state batteries with sulfide solid electrolytes were fabricated by compressing powders without sintering at high temperatures, and the batteries operated as a rechargeable lithium battery at room temperatures [3–6]. Sulfide-based solid electrolytes in Li_2S–P_2S_5 and Li_2S–P_2S_5–GeS_2 systems offer superior properties such as high lithium ion conductivity from 10^{-3} to 10^{-2} S cm^{-1} at room temperature and an electrochemical window that is wider than 5 V [7–12]. All-solid-state batteries with the Li_2S–P_2S_5 sulfide electrolytes exhibited excellent cycle performance. Batteries using a $LiCoO_2$ positive electrode or a $Li_4Ti_5O_{12}$ negative electrode were charged and discharged for 500–700 cycles without remarkable capacity fading [13,14]. An important shortcoming of sulfide electrolytes is their hygroscopic nature. Sulfide solid electrolytes should be treated in inert gas atmosphere to prevent the hydrolysis of sulfides by moisture in air, which generates H_2S gas. Our recent examination of the chemical stability of Li_2S–P_2S_5 glass electrolytes in air revealed that glass with the composition of 75 mol% Li_2S generated the least H_2S of any Li_2S–P_2S_5 binary system [15]. Furthermore, the addition of metal oxides to the $75Li_2S{\cdot}25P_2S_5$ (mol%) glass as a H_2S absorbent reduced H_2S gas release to air. Ball-milled mixtures of the sulfide glass and a metal oxide such as Fe_2O_3, ZnO, or Bi_2O_3 suppressed the H_2S gas generation effectively [16]. These secure electrolytes are favorable for application to all-solid-state batteries. The modification of glass structures is important for additional improvement of the chemical stability of sulfide glass electrolytes because the amount of H_2S generated from Li_2S–P_2S_5 binary glasses depends on the glass composition and glass structure [15]. Very recently, we have reported that a partial substitution of Li_2O for Li_2S in the Li_2S–P_2S_5 glasses enhances their chemical stability in air [17].

This study specifically examined the chemical stability of the Li_2S–P_2S_5–P_2O_5 oxysulfide glass electrolytes. The effects on chemical stability and ionic conductivity of glass structure modification were investigated when replacing a part of P_2S_5 with P_2O_5. Furthermore, H_2S generation from the prepared electrolytes was suppressed by the addition of ZnO, which was effective in reducing H_2S generation from the sulfide electrolytes [16]. The developed electrolytes were applied to all-solid-state cells. Then the electrochemical performance of the cells was investigated.

2. Experimental

The $75Li_2S{\cdot}(25-x)P_2S_5{\cdot}xP_2O_5$ (mol%; $0 \leqslant x \leqslant 10$) glasses were prepared by mechanical milling. Reagent-grade Li_2S (99.9%; Idemitsu Kosan Co. Ltd.), P_2S_5 (>99.9%; Aldrich Chemical Co. Inc.) and P_2O_5 (99.99%; Aldrich) crystalline powders were used as starting materials. A mixture of these materials was mechanically milled at room temperature using a planetary ball mill apparatus (Pulverisette 7; Fritsch GmbH) with a zirconia pot (45 ml volume) and 500 zirconia balls (4 mm

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diameter). The rotation speed was 510 rpm. The milling period was 35 h. All processes were performed in a dry Ar atmosphere. X-ray diffraction measurements for the prepared samples produced a halo pattern with no diffraction peak attributable to the starting materials. The prepared amorphous samples exhibited glass transition phenomena at 220–240 °C on differential thermal analysis. It was therefore confirmed that the $75Li_2S{\cdot}(25-x)P_2S_5{\cdot}xP_2O_5$ ($0 \leqslant x \leqslant 10$) glasses were obtained by mechanical milling. Composite electrolytes were also prepared from the $75Li_2S{\cdot}(25-x)P_2S_5{\cdot}xP_2O_5$ glass powder and ZnO (99.9%, Aldrich) crystalline powder. The mixtures of the glass and ZnO were mechanically milled at 230 rpm for 2 h to obtain the composite electrolytes.

The ^{31}P MAS NMR spectra of the prepared glasses were measured using an NMR spectrometer (Unity Inova 300; Varian Inc.) to analyze the local structure around phosphorus elements. The glass powders were packed into a zirconia spinner with a sealant in a dry Ar-filled glove box. The observed frequency was 121.42 MHz, with 90° pulse length of 2.0 μs, recycle pulse delay of 5.0 s, and spinning speed of 5000 Hz. AC impedance measurements were performed for the glasses in Ar atmospheres using an impedance analyzer (SI-1260; Solartron Analytical). Ionic conductivities of pelletized samples (10 mm diameter; about 1 mm thickness) were measured in the frequency range of 0.1 Hz to 8 MHz. The morphology of the prepared glass particles was observed using a scanning electron microscope (SEM, JSM-5300; JEOL).

The amounts of H_2S generated from 0.1 g of pelletized electrolytes were measured. A H_2S sensor (GBL-HS; Jikco Ltd.) and a fan were placed in a 2000 cm^3 desiccator. A pelletized sample was placed in the desiccator in air. The desiccator lid was then closed. The pellet was then exposed to the air in the desiccator. The time dependence of H_2S concentration was measured after the pellet had been placed in the desiccator. The amounts of generated H_2S were calculated from the H_2S concentration measured using the H_2S sensor. The air temperature was 24–27 °C. The relative humidity was 40–53%.

The $LiCoO_2$ (D-10; Toda Kogyo Co.) and the prepared electrolyte powders with a weight ratio of 70:30 were mixed using an agate mortar to prepare composite positive electrodes. The $LiCoO_2$ particles used for this study were coated with $LiNbO_3$ film in advance because $LiNbO_3$-coated $LiCoO_2$ shows good electrochemical performance in the all-solid-state batteries using sulfide-based solid-electrolytes [18]. Indium foil with 0.1 mm thickness (Furuuchi Chemical Co., 99.999%) was used as a negative electrode. A bilayer pellet consisting of the composite positive electrode (10 mg) and the prepared electrolytes (80 mg) was obtained by pressing under 360 MPa (ϕ = 10 mm). Then indium foil was attached to the bilayer pellet using pressure of 240 MPa. Cells were charged and discharged at 25 °C at the current density of 0.13 mA cm^{-2} in a dry Ar atmosphere using a charge–discharge measuring device (BTS-2004; Nagano Co. Ltd.).

3. Results and discussion

The local structure of the $75Li_2S{\cdot}(25-x)P_2S_5{\cdot}xP_2O_5$ glasses was analyzed using ^{31}P MAS NMR measurements. Fig. 1 shows ^{31}P MAS NMR spectra of the $75Li_2S{\cdot}(25-x)P_2S_5{\cdot}xP_2O_5$ (x = 0 and 10) glasses. Two peaks at about 83 and 109 ppm were observed for the spectrum of the $75Li_2S{\cdot}25P_2S_5$ (x = 0) glass. These peaks are respectively attributable to the PS_4 and P_2S_6 units [19]. In addition to the peaks observed for the x = 0 glass, three new peaks at about 8, 34, and 65 ppm were observed for the spectrum of the $75Li_2S{\cdot}15P_2S_5{\cdot}10P_2O_5$ (x = 10) glass. The peak assignment for ^{31}P MAS NMR spectra of the oxysulfide glasses was reported [20]. Peaks at 8, 34, 65, and 83 ppm are respectively attributable to the PO_4, PSO_3, PS_2O_2, and (PS_3O + PS_4) units. Oxysulfide units such as PSO_3 and PS_2O_2, where a phosphorus atom is coordinated with both sulfur and oxygen atoms, were formed in oxysulfide glass (x = 10) prepared using mechanical milling. Results revealed that the structure of the $75Li_2S{\cdot}25P_2S_5$ sulfide glass was partially modified by the substitution of P_2O_5 for P_2S_5.

Fig. 2 shows the composition dependence of conductivity at 25 °C (σ_{25}) and activation energy (E_a) for conduction of the pelletized $75Li_2S{\cdot}(25-x)P_2S_5{\cdot}xP_2O_5$ ($0 \leqslant x \leqslant 10$) glasses. The conductivity of the $75Li_2S{\cdot}25P_2S_5$ (x = 0) glass was 5×10^{-4} S cm^{-1}, which is somewhat higher than that of our previous paper (2×10^{-4} S cm^{-1}) [21]. The difference in conductivity might result from different milling conditions. An alumina pot and balls were used and the rotation speed was 370 rpm in the previous paper. In contrast, a zirconia pot and balls were used and the rotation speed was 510 rpm in this study. Homogeneous glass at the composition of $70Li_2S$ $30P_2S_5$ was obtained using the latter milling condition [10]. The glass also showed higher conductivity than that reported in a previous paper [21]. The conductivity decreased monotonically with increased P_2O_5 content, while the activation energy increased. The formation of oxysulfide units and PO_4 units with non-bridging oxygens, which act as a strong trap for Li^+ ion conduction, are expected to be responsible for the decrease in conductivity.

Fig. 3 shows SEM images of the $75Li_2S{\cdot}(25-x)P_2S_5{\cdot}xP_2O_5$ (x = 0 and 10) glass particles. The glass particles were mainly aggregated. The secondary particle size for the x = 10 glass was about a few micrometers, which is somewhat smaller than that of the x = 0 glass (*ca.* 5–10 μm).

Fig. 4 shows the H_2S gas amounts generated from the pelletized $75Li_2S{\cdot}(25-x)P_2S_5{\cdot}xP_2O_5$ (x = 0 and 10) glasses after exposure to air. The maximum amount of H_2S generated from the x = 10 glass was similar to that from the x = 0 glass. However, the exposure time for reaching the maximum H_2S amount for the x = 10 glass was longer than that for the x = 0 glass. The rates for H_2S generation from x = 0 and 10 glass were calculated respectively as about 8×10^{-5} and 2×10^{-5} cm^3 s^{-1} g^{-1}. The substitution of 10 mol% P_2O_5 for P_2S_5 decreased the rate of H_2S generation. The x = 10 glass particles were smaller than those of the x = 0 glass, as depicted in Fig. 3, suggesting that the surface area exposed to moisture is larger in the x = 10 glass than in the x = 0 glass. In light of the fact that the maximum amount of H_2S did not change by the substitution of P_2O_5, the glass with P_2O_5 has better tolerance for moisture.

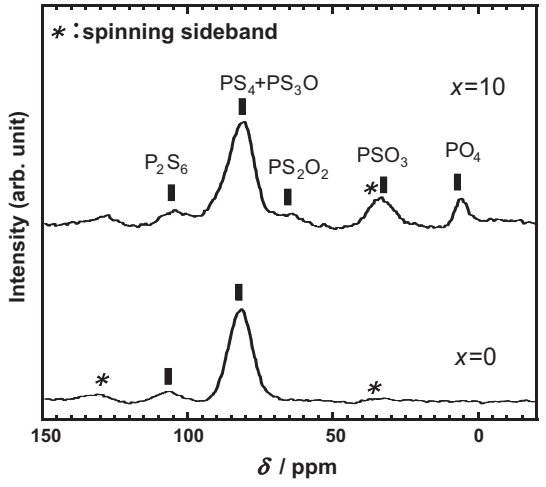

Fig. 1. ^{31}P MAS NMR spectra of the $75Li_2S{\cdot}(25-x)P_2S_5{\cdot}xP_2O_5$ (x = 0 and 10) glasses.

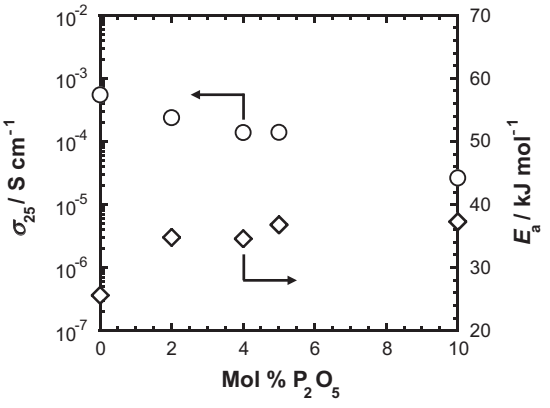

Fig. 2. Composition dependence of conductivity at 25 °C (σ_{25}) and activation energy (E_a) for conduction of the pelletized $75Li_2S{\cdot}(25-x)P_2S_5{\cdot}xP_2O_5$ glasses.