Oxygen substitution effects in $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ solid electrolyte

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ABSTRACT

For the lithium super-ionic conductor $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$, the partial substitution of sulfur by oxygen is achieved via a solid-state reaction. The solid-solution range of oxygen is found to be $0 \leq x < 0.9$ in $\text{Li}_{10}\text{GeP}_2\text{S}_{12-x}\text{O}_x$. Structure refinements using synchrotron X-ray diffraction data confirm the preference for oxygen substitution in the PS_4 tetrahedra. The local structural change in the $\text{P}(\text{S/O})_4$ tetrahedra upon substitution is also indicated by Raman spectroscopy. Ionic conduction properties are maintained even after the oxygen substitution in $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$; the ionic conductivity of $\text{Li}_{10}\text{GeP}_2\text{S}_{12-x}\text{O}_x$ ($0.3 \leq x \leq 0.6$) ranges from 1.03×10^{-2} to $8.43 \times 10^{-3} \text{ S cm}^{-1}$ at 298 K. No redox current is observed by cyclic voltammetry from nearly 0 to 10 V versus Li/Li^+ except for that due to the lithium deposition/dissolution reactions. All-solid-state batteries using $\text{Li}_{10}\text{GeP}_2\text{S}_{12-x}\text{O}_x$ ($x = 0.3$ and 0.6) as solid electrolytes with Li metal anodes show discharge capacities exceeding 100 mAh g^{-1} and better cycling performance compared to batteries using the original $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$. The partial substitution of oxygen for sulfur in $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ affords a novel solid electrolyte, $\text{Li}_{10}\text{GeP}_2\text{S}_{12-x}\text{O}_x$, with high conductive properties and electrochemical stability.

Keywords: lithium ion conductor, all-solid-state battery, oxysulfide, $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$

1. Introduction

Lithium-ion conducting solids, as key materials for solid electrolytes in all-solid-state lithium batteries, have great potential for improving the safety, reliability, energy density, and power density of lithium battery systems [1]. Among the reported solid electrolytes, sulfide-based materials are attractive due to their superior properties compared to their oxide counterparts. One of the most remarkable advantages of sulfides is their notable ionic conductivity, which can be as high as 10^{-3} – 10^{-2} S cm⁻¹ [2–5]. Moreover, the grain-boundary resistance of sulfides is easily reduced, which is suitable for application in bulk-type all-solid-state batteries [6–8]. Furthermore, a wide range of solid solutions, and thus, material properties, are accessible through the substitution of elements in the system [2,9]. Therefore, sulfide-based solid electrolytes have been intensively studied as promising components of all-solid-state lithium batteries. Li₁₀GeP₂S₁₂ (LGPS), belonging to the sulfide family, exhibits an extremely high ionic conductivity of 1.2×10^{-2} S cm⁻¹, a value comparable to those of the liquid electrolytes used in commercial lithium-ion batteries [10]. However, LGPS is not stable against Li metal, which provides the

highest battery voltage, because it decomposes at the low voltage triggered by the reduction of Ge [11]. Therefore, it would be significant to develop new solid electrolytes having both high ionic conductivity and high electrochemical stability.

In the design of new ionic conductors, one approach is to modify existing materials with suitable frameworks for ionic conduction. The discovery of LGPS afforded a structural template for exploring new solid electrolytes. After this discovery, many kinds of new solid electrolytes belonging to the LGPS family, such as $\text{Li}_{10}\text{SiP}_2\text{S}_{12}$, $\text{Li}_{10}\text{SnP}_2\text{S}_{12}$, and $\text{Li}_{11}\text{AlP}_2\text{S}_{12}$, were predicted by first principles calculations [12]. The subsequent synthesis of several of these materials [13–17] shows that a wide range of solid-solutions in the LGPS family would be available through the appropriate selection of elements (anions and cations). Given that the chemical bonds between Ge/P-O are stronger than those of Ge/P-S, oxygen substitution would be expected to enhance thermodynamic stability. Density-of-states (DOS) results from first principles calculations also predict that O-substituted LGPS-type LMPO materials would exhibit greater intrinsic redox stability than LMPS compounds [12]. For example, oxysulfide systems are reported to achieve higher electrochemical stabilities [18–20]: the LGPS-type Ge-free Li-P-S-O system with

enhanced stability in the low voltage region was proposed, however, its conductive properties were decreased to 10^{-4} – 10^{-5} S cm⁻¹ [20]. Therefore, based on the concept of developing LGPS-type ionic conductors, oxygen introduction into the LGPS crystal structure would be expected to improve electrochemical stability while maintaining relatively high ionic conductivity [21].

In this study, the substitution of oxygen for sulfur in the LGPS structure was examined; new solid electrolytes with the compositions Li₁₀GeP₂S_{12-x}O_x ($0 < x \leq 1.5$) were synthesized, and their crystal structures, ionic conductivities and electrochemical stabilities were investigated. The battery performance of the all-solid-state cells using the newly developed Li₁₀GeP₂S_{12-x}O_x solid electrolytes was also examined.

2. Experimental

The oxygen-substituted LGPS materials were fabricated based on the composition Li₁₀GeP₂S_{12-x}O_x. The starting materials, Li₂S (Nihon Kagaku Kogyo, >99.9% purity), GeS₂ (Mitsuwa Chemical, 99.9% purity), Li₂O (Kojundo Chemical Laboratory Co., Ltd., >99.9% purity), and P₂S₅ (Aldrich, > 99.9% purity), were weighed in stoichiometric ratios in an Ar-filled glove box, and then mixed mechanically in a ZrO₂ pot with ZrO₂ balls ($\phi = 10$ mm). The mixing process was

conducted using a planetary ball milling apparatus at 380 rpm for 20 h. The product mixture was pelletized under 120 MPa pressure, sealed in a quartz tube at ~10 Pa, and heated at 823 K for 24 h. Then, the samples were slowly cooled to room temperature.

X-ray diffraction patterns of the synthesized powders were collected using an X-ray diffractometer (Rigaku Smartlab) with Cu K α radiation. The diffraction data were collected at a 0.01° step width over a 2θ range from 10 to 50°. Synchrotron X-ray diffraction measurements were performed using the BL02B2 beamline at SPring-8, with an X-ray wavelength of 0.5 Å. The specimens were sealed under Ar atmosphere in Lindemann glass capillaries (~0.3 mm inner diameter), and a Debye-Scherrer diffraction camera was employed for the measurements. Diffraction data were collected in 0.01° steps from 3 to 70° at room temperature. Refinements for the structural parameters were conducted using the RIETAN-FP program [22]. Raman spectral measurements were performed to observe the local structure in the Li_{3.35}Ge_{0.35}P_{0.65}S_{4-x}O_x using a confocal Raman microscope (Raman 11, Nanophoton Corp.) with an excitation wavelength of 532 nm.

Ionic conductivity was measured by the alternating current (AC) impedance method with an applied voltage of 20 mV in the frequency range from 100 Hz to 15 MHz

using a frequency response analyzer (National Instruments, NF) in an Ar-gas-cycled atmosphere over the temperature range 298–398 K. For the measurements, pellets of the solid electrolytes (diameter $\approx$ 10 mm; thickness 1–2 mm) were prepared by the cold-press method under 168 MPa and then sintered at 823 K for 12 h. Both surfaces of the sintered pellets were coated with Au powder to form blocking electrodes. The electrochemical stability was evaluated by cyclic voltammetry. The measurements were conducted in a Li/solid electrolyte (SE)/Au cell at a scan rate of 1 mV s^{-1} between -0.5 to 10 V using a Solartron 1287 electrochemical interface.

The fabrication of two-electrode all-solid-state batteries using the prepared solid electrolytes was conducted under Ar atmosphere. Composite electrodes incorporating LiCoO_2 powders (Nippon Kagaku) with a 10 nm-thick LiNbO_3 coating (Powrex, MP-01) [23,24] and $\text{Li}_{10}\text{GeP}_2\text{S}_{12-x}\text{O}_x$ ($x = 0, 0.3, 0.6$) were used as cathodes. The LiCoO_2 and $\text{Li}_{10}\text{GeP}_2\text{S}_{12-x}\text{O}_x$ powders were weighed in a 70:30 weight ratio and mixed using a vortex mixer for 10 min. Li metal and the $\text{Li}_{10}\text{GeP}_2\text{S}_{12-x}\text{O}_x$ pellet were used as the anode and solid electrolyte, respectively. To make the solid electrolyte layer, 100 mg of the $\text{Li}_{10}\text{GeP}_2\text{S}_{12-x}\text{O}_x$ powder was pressed into a pellet with a diameter of 10 mm. Lithium foil (thickness, 0.1 mm; diameter, 10 mm) with a Cu mesh current

collector and the cathode composite with Al mesh and Al foil current collectors were pressed onto opposite sides of the solid electrolyte pellet. The electrochemical properties of the cells were evaluated using a TOSCAT-3100 (Toyo System). Cycling tests were carried out between 2.5–4.2 V for the Li anode at an applied current of 7 mA g⁻¹ at 298 K.

3. Results and Discussion

3.1 Phase identification of Li₁₀GeP₂S_{12-x}O_x and structural analysis

Figure 1 shows the XRD patterns of the synthesized samples, which have the general formula Li₁₀GeP₂S_{12-x}O_x ($0 \leq x \leq 1.5$). To confirm the characteristic peaks of the LGPS-type phase and Li₃PO₄ as impurity, magnified patterns around 29.5° and 22.5°, respectively, are also presented. The system can be divided into two composition regions depending on the peak shift, with additional peaks due to Li₃PO₄. For the composition $0 \leq x < 0.9$, a gradual peak shift toward higher angle is observed with increasing x , although no peaks due to Li₃PO₄ are observed. Accordingly, LGPS-type single phases, namely, Li₁₀GeP₂S_{11.7}O_{0.3} and Li₁₀GeP₂S_{11.4}O_{0.6}, are obtained in this region. The XRD peak shift indicates the substitution of oxygen into

the solid solution. The incorporation of oxygen, with its smaller ionic radius than sulfur, could contribute to a reduction in the lattice parameters of the LGPS-type phase. For compositions in which $x \geq 0.9$, the XRD peaks can be indexed as the LGPS-type phase and Li_3PO_4 . The relative intensities of the Li_3PO_4 peaks increase gradually as x changes from 0.9 to 1.5, indicating the growth of the impurity phase ratio in the samples. In addition, the diffraction lines of the LGPS-type phase shift to a lower angle, indicating the lattice expansion of the LGPS-type phase. This behavior could be due to the impurity phase, because the P content in the LGPS-type phases is decreased by Li_3PO_4 formation, and a higher Ge:P ratio leads to larger lattice parameters [16]. From these results, the solid-solution range for oxygen substitution was found to be limited to within $0 \leq x < 0.9$. The narrowness of this range could be due to the large difference between the ionic radii of the S ($r = 1.84 \text{ \AA}$) and O atoms ($r = 1.38 \text{ \AA}$).

Fig. 1 XRD patterns of $\text{Li}_{10}\text{GeP}_2\text{S}_{12-x}\text{O}_x$ ($0 \leq x \leq 1.5$) along with the XRD patterns of Li_3PO_4 (ICSD #79427) and LGPS (ICSD #188887). The magnified patterns around 29.5° and 22.5° are characteristic peaks for LGPS-type phases and Li_3PO_4 .

Synchrotron Rietveld refinements were performed for $\text{Li}_{10}\text{GeP}_2\text{S}_{12-x}\text{O}_x$ ($x = 0.3$ and 0.6). Space group $P4_2/nmc$ was used for the refinements, and the initial parameters were taken from the structural model reported for the LGPS phase [16]. In addition, atomic positions, occupancies, and atomic displacement parameters for the Li atoms were fixed at the values reported from the neutron diffraction data for LGPS.

A representative fitting pattern and the refinement parameters are shown in Fig. 2 and Tables 1 and 2, respectively. Well-fitted results were obtained using a single-phase

model of the LGPS for both samples; low R_{wp} values of 6.399 and 6.845 were

obtained for $x = 0.3$ and $x = 0.6$, respectively. The lattice parameters for $\text{Li}_{10}\text{GeP}_2\text{S}_{11.7}\text{O}_{0.3}$ and $\text{Li}_{10}\text{GeP}_2\text{S}_{11.4}\text{O}_{0.6}$ were determined to be [$a = 8.65898$ (12) Å, $c = 12.5503$ (4) Å] and [$a = 8.65065$ (13) Å, $c = 12.5397$ (3) Å], respectively. With increases in the oxygen content, the lattice parameters decreased slightly, compared to LGPS ($a = 8.7177$ Å and $c = 12.6345$ Å) [10]. These results clearly indicate that S atoms ($r = 1.84$ Å) are partially substituted by O atoms ($r = 1.38$ Å). The lattice parameters of the obtained phases are plotted as a function of the oxygen content x in Fig. 3. The refined lattice parameters of the $\text{Li}_{10}\text{GeP}_2\text{S}_{12-x}\text{O}_x$ changed with x ; the a and c values decrease from 8.7177 to 8.6506 Å and from 12.635 to 12.540 Å, respectively. These results indicate the formation of solid solutions with the oxygen substitution in $\text{Li}_{10}\text{GeP}_2\text{S}_{12-x}\text{O}_x$ ($0 \leq x \leq 0.6$).

Fig. 2 Synchrotron X-ray Rietveld refinement pattern for $\text{Li}_{10}\text{GeP}_2\text{S}_{11.4}\text{O}_{0.6}$. Observed data points are indicated by cross marks (+), and solid lines overlaying the data were obtained via Rietveld refinement analysis. Vertical markers below the patterns indicate the positions of possible Bragg reflections of space group $P4_2/nmc$ for the LGPS-type phases (green). Differences between the observed and calculated intensities are plotted below the data on the same scale.

Table 1 Rietveld refinements of synchrotron XRD data for $\text{Li}_{10}\text{GeP}_2\text{S}_{11.7}\text{O}_{0.3}$ at 298 K

Atom	Site	g	x	y	z	B ($\text{\AA}^2$)
Li(1)	16h	0.53	0.2338(15)	0.2623(15)	0.1751(15)	7.90
Li(2)	4d	1	0	1/2	0.9408(18)	5.05
Li(3)	8f	0.69	0.2462(13)	=x(Li(3))	0	9.65
Li(4)	4c	0.54	0.0	0.0	0.2468(14)	5.14
Ge(1)	4d	0.525	0	1/2	0.6914(2)	1.20(6)
P(1)	4d	0.475	=x(Ge(1))	=y(Ge(1))	=z(Ge(1))	=B(Ge(1))
P(2)	2b	1	0	0	1/2	2.27(7)
S(1)	8g	0.9560(2)	0	0.1879(3)	0.4065(2)	2.72(9)
S(2)	8g	0.9694(9)	0	0.2965(3)	0.0975(2)	2.15(9)
S(3)	8g	0.9995(7)	0	0.7008(3)	0.7916(2)	2.04(9)
O(1)	8g	=1- $g(\text{S}(1))$	=x(S(1))	=y(S(1))	=z(S(1))	=B(S(1))
O(2)	8g	=1- $g(\text{S}(2))$	=x(S(2))	=y(S(2))	=z(S(2))	=B(S(2))
O(3)	8g	=1- $g(\text{S}(3))$	=x(S(3))	=y(S(3))	=z(S(3))	=B(S(3))

*Note: space group $P4_2/nmc$ (137), $a = 8.65898$ (12) $\text{\AA}$, $c = 12.5503$ (4) $\text{\AA}$, $R_{\text{wp}} = 6.021\%$, $R_e = 5.011\%$, $R_p = 3.520\%$, $R_B = 7.126\%$, $S = R_{\text{wp}}/R_e = 1.202$.

Table 2 Rietveld refinements of synchrotron XRD data for Li₁₀GeP₂S_{11.4}O_{0.6} at 298 K

Atom	Site	<i>g</i>	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)
Li(1)	16 <i>h</i>	0.53	0.2293(14)	0.2911(15)	0.1761(13)	7.90
Li(2)	4 <i>d</i>	1	0	1/2	0.9514(13)	5.05
Li(3)	8 <i>f</i>	0.69	0.2464(13)	= <i>x</i> (Li(3))	0	9.65
Li(4)	4 <i>c</i>	0.54	0	0	0.2490(15)	5.14
Ge(1)	4 <i>d</i>	0.525	0	1/2	0.6911(3)	1.64(7)
P(1)	4 <i>d</i>	0.475	= <i>x</i> (Ge(1))	= <i>y</i> (Ge(1))	= <i>z</i> (Ge(1))	= <i>B</i> (Ge(1))
P(2)	2 <i>b</i>	1	0	0	1/2	2.79(19)
S(1)	8 <i>g</i>	0.9220(13)	0	0.1879(5)	0.4070(3)	2.52(11)
S(2)	8 <i>g</i>	0.9470(9)	0	0.2956(4)	0.0975(3)	2.02(11)
S(3)	8 <i>g</i>	0.9809(6)	0	0.7011(3)	0.7907(8)	1.67(11)
O(1)	8 <i>g</i>	=1- <i>g</i> (S(1))	= <i>x</i> (S(1))	= <i>y</i> (S(1))	= <i>z</i> (S(1))	= <i>B</i> (S(1))
O(2)	8 <i>g</i>	=1- <i>g</i> (S(2))	= <i>x</i> (S(2))	= <i>y</i> (S(2))	= <i>z</i> (S(2))	= <i>B</i> (S(2))
O(3)	8 <i>g</i>	=1- <i>g</i> (S(3))	= <i>x</i> (S(3))	= <i>y</i> (S(3))	= <i>z</i> (S(3))	= <i>B</i> (S(3))

*Note: space group *P4₂/nmc* (137), *a* = 8.65065 (13) Å, *c* = 12.5397 (2) Å, *R*_{wp} = 6.845%, *R*_e = 4.899%, *R*_p = 4.163%, *R*_B = 9.545%, *S* = *R*_{wp}/*R*_e = 1.397.

Fig. 3 Lattice parameters for the $\text{Li}_{10}\text{GeP}_2\text{S}_{12-x}\text{O}_x$ ($0 \leq x \leq 0.6$) solid solutions.

The Rietveld refinement results indicate that O atoms prefer to occupy specific sites. The LGPS structure has three independent sites where anions are situated; these are termed S(1), S(2), and S(3) in this study. Based on the fitting results, the largest proportion of oxygen atoms are located at S(1) sites, and the occupancy increases from about 4 to 8% with x value. Although the absolute values are smaller than for the S(1) sites, the oxygen occupancies at the S(2) and S(3) sites also increase with x , from 3 to 5% and from 0 to 2%, respectively. As shown in Fig. 4, the tetrahedral PS_4 units are constructed by four S(1) atoms, whereas the tetrahedral $(\text{Ge/P})\text{S}_4$ units are constructed by two S(2) and two S(3) atoms. LiS_6 octahedra are connected to the PS_4 units through shared S(1) atoms, and are connected to the $(\text{Ge/P})\text{S}_4$ units by sharing S(2)–S(2) and S(3)–S(3) edges. In addition, the LiS_6 octahedra units incorporate all

the S(1), S(2), and S(3) sites. Therefore, most of introduced oxygen atoms are contained in the PS_4 tetrahedra rather than the $(\text{Ge/P})\text{S}_4$ and LiS_6 units. According to the hard and soft acids and bases (HSAB) theory, hard acids react preferentially with hard bases, and soft acids are more prone to react with soft bases [25]. Oxygen is a hard base whereas sulfur is soft. Compared with Ge, P is relatively small and non-polarizable, and can be considered a hard acid. Therefore, the introduced oxygen atoms would be prone to bond with P in the LGPS structure.

Fig. 4 Framework structure of $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ and the coordination environments of the sulfur atoms.

To reveal the substitution effects on the structure, the $\text{Li}_{10}\text{GeP}_2\text{S}_{12-x}\text{O}_x$ ($x=0$, 0.3, and 0.6) samples were subjected to Raman spectroscopy. Figure 5 shows the obtained Raman spectra in the frequency range from 200 to 530 cm^{-1} . Two characteristic peaks appear at around 280 and 440 cm^{-1} , indicating the PS_4 tetrahedral unit [26]. As x increases, the peak at around 440 cm^{-1} is split into two peaks from $x = 0.3$. This change may be related to a local structural change (e.g., distortion) in the PS_4 tetrahedral unit due to the introduction of oxygen at the S(1) sites. An additional peak appears at around 390 cm^{-1} for $x = 0.6$. Since the peaks in the range from 330 to

420 cm^{-1} are attributable to Li–S and Ge–S bonding [27–29], this new peak indicates structural changes in the GeS_4 and LiS_6 units. As these polyhedra contain the S(2) and S(3) sites, the occupancy increase of oxygen atoms in these sites may be responsible for the local structural changes of the GeS_4 and LiS_6 units.

Fig. 5 Unpolarized micro-Raman spectra for the LGPS, $\text{Li}_{10}\text{GeP}_2\text{S}_{11.7}\text{O}_{0.3}$, and $\text{Li}_{10}\text{GeP}_2\text{S}_{11.4}\text{O}_{0.6}$.

3.2 Electrochemical properties of $\text{Li}_{10}\text{GeP}_2\text{S}_{12-x}\text{O}_x$ solid electrolytes

The ionic conductivities at 298 K and activation energies of $\text{Li}_{10}\text{GeP}_2\text{S}_{12-x}\text{O}_x$ ($x = 0.3$ and 0.6), LGPS [10], and $\text{Li}_{10}\text{GeP}_2\text{O}_{12}$ [12] are listed in Table 3. For $\text{Li}_{10}\text{GeP}_2\text{S}_{12-x}\text{O}_x$ ($x = 0.3$ and 0.6), the ionic conductivities are temperature dependent (Fig. 6) and follow the Arrhenius relationship within the measured range (298 to 398 K). The ionic conductivity values for $\text{Li}_{10}\text{GeP}_2\text{S}_{12-x}\text{O}_x$ ($x = 0.3$ and 0.6) at 298 K are 1.03×10^{-2} and $8.43 \times 10^{-3} \text{ S cm}^{-1}$, respectively, and the calculated activation energies values for conduction are typical for superionic conductors (~ 20 and 21 kJ mol^{-1} , respectively). The ionic conductivities of the oxysulfides are slightly lower than that of LGPS, but are much higher than the calculated value for $\text{Li}_{10}\text{GeP}_2\text{O}_{12}$. This trend is also observed in the activation energies. The decrease in ionic conductivity may be due to the slight contraction of the lattice parameters and stronger electrostatic attraction between O atoms and Li ions.

Table 3 Ionic conductivities and activation energies for $\text{Li}_{10}\text{GeP}_2\text{S}_{12-x}\text{O}_x$

Compound	Activation energy $E_a / \text{kJ mol}^{-1}$	Conductivity $\sigma / \text{S cm}^{-1}$
$\text{Li}_{10}\text{GeP}_2\text{S}_{12}$	20	1.2×10^{-2}
$\text{Li}_{10}\text{GeP}_2\text{S}_{11.7}\text{O}_{0.3}$	21	1.03×10^{-2}
$\text{Li}_{10}\text{GeP}_2\text{S}_{11.4}\text{O}_{0.6}$	20	8.43×10^{-3}
$\text{Li}_{10}\text{GeP}_2\text{O}_{12}$	35	3.0×10^{-5}

Fig. 6 Arrhenius plots of ionic conductivity for $\text{Li}_{10}\text{GeP}_2\text{S}_{11.7}\text{O}_{0.3}$ and $\text{Li}_{10}\text{GeP}_2\text{S}_{11.4}\text{O}_{0.6}$ in the temperature range 298–398 K.

The electrochemical stability of $\text{Li}_{10}\text{GeP}_2\text{S}_{12-x}\text{O}_x$ ($x = 0.3$ and 0.6) was evaluated by cyclic voltammetry [10]. Figure 7 illustrates the cyclic voltammograms of Li/SE/Au cells, in which Li metal and Au acted as the reference and working electrodes, respectively. The potential was scanned from -0.5 to 10 V vs. Li/Li^+ at a scan rate of 1 mV s^{-1} . No significant currents are observed except for cathodic and anodic currents due to lithium deposition and lithium dissolution, respectively. Therefore, no significant decomposition of the solid electrolytes was observed in the investigated voltage range.

Fig. 7 Cyclic voltammograms of $\text{Li}_{10}\text{GeP}_2\text{S}_{11.7}\text{O}_{0.3}$ and $\text{Li}_{10}\text{GeP}_2\text{S}_{11.4}\text{O}_{0.6}$ in asymmetric Li/solid electrolyte/Au cells.

3.3 All-solid-state battery using $\text{Li}_{10}\text{GeP}_2\text{S}_{12-x}\text{O}_x$ solid electrolytes with Li metal

Since the electrochemical stability of the solid electrolyte for practical use is difficult to evaluate only via CV measurement [11], $\text{Li}_{10}\text{GeP}_2\text{S}_{12-x}\text{O}_x$ ($x = 0.3$ and 0.6) was examined as the electrolyte in an all-solid-state battery. A battery with the LGPS solid electrolyte was also fabricated for comparison. Charge-discharge curves for the batteries and the cycle dependence of their discharge capacities are shown in Fig. 8.

No noteworthy difference in the charge-discharge curves among the batteries can be observed; all show discharge capacities over 100 mAh g^{-1} at the 1st cycle. However, for the battery with the LGPS solid electrolyte, the discharge capacity drastically decreases from the 2nd cycle, finally reaching $\sim 10 \text{ mAh g}^{-1}$ at the 10th cycle. This capacity fading could be due to an increase in the solid electrolyte interphase (SEI) resistance by decomposition of the LGPS solid electrolyte [11] because the combination of the LiNbO_3 -coated LiCoO_2 and the LGPS-type solid electrolyte in the cathode composite does not contribute to the deterioration of the battery [21, 23]. The low redox potential of the Li anode may contribute to the formation of a thick SEI layer at the solid electrolyte/anode interface. When $x = 0.3$, the capacity is maintained until the 3rd cycle, and then rapidly fades in the following cycles. The battery with

$\text{Li}_{10}\text{GeP}_2\text{S}_{12-x}\text{O}_x$ ($x = 0.6$) shows more enhanced cycle capability; the high discharge capacity (over 75 mAh g^{-1}) was maintained until the 7th cycle. Although the battery using the solid electrolyte with the highest oxygen content also showed capacity fading with cycling, these results clearly indicate that the stability of the solid electrolyte against the Li anode was improved with the x value. In other words, Ge reduction in the solid electrolyte could be prevented by the substitution of oxygen for sulfur in the LGPS structure. On the other hand, the observed capacity fading indicates that the oxygen content in the structure is still insufficient to prevent decomposition of the solid electrolyte at the anode/solid electrolyte interface. The further investigation of solid solutions for LGPS-based solid electrolytes could enable the use of Li metal as the anode while maintaining high conductivity (over $10^{-2} \text{ S cm}^{-1}$) in the all-solid-state batteries and providing higher energy density and excellent power characteristics.

Fig. 8 Charge-discharge curves of all-solid-state batteries using (a) LGPS, (b)

Li₁₀GeP₂S_{11.7}O_{0.3}, and (c) Li₁₀GeP₂S_{11.4}O_{0.6} as solid electrolyte layers, and cycle

dependence of the discharge capacity for the batteries (d).

Conclusion

New oxysulfide solid electrolytes belonging to the LGPS family were synthesized in the $\text{Li}_{10}\text{GeP}_2\text{S}_{12-x}\text{O}_x$ system. Since the difference between the radii of S and O atoms is large, a limited solid-solution range for oxygen was observed for $\text{Li}_{10}\text{GeP}_2\text{S}_{12-x}\text{O}_x$ as $0 \leq x < 0.9$. Structural analysis using synchrotron X-ray diffraction and Raman spectroscopy confirmed the preference for oxygen substitution at S(1) positions and local structural changes in the PS_4 unit. The partial substitution of S did not dramatically lower the ionic conductivity from the original $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$; the ionic conductivity of $\text{Li}_{10}\text{GeP}_2\text{S}_{12-x}\text{O}_x$ ($0.3 \leq x \leq 0.6$) ranged from 1.03×10^{-2} to 8.43×10^{-3} S cm^{-1} at 298 K. High electrochemical stability from 0 to 10 V versus Li/Li^+ was also confirmed. Battery evaluations demonstrated that the all-solid-state batteries using $\text{Li}_{10}\text{GeP}_2\text{S}_{12-x}\text{O}_x$ as a solid electrolyte layer and a Li metal anode showed reversible charge/discharge behavior in the initial cycles. Although the discharge capacity decreased with cycling, the introduction of oxygen into the sulfide electrolyte could be a method for combining the high ionic conductivity of sulfides and high electrochemical stability of oxides. This approach holds promise for the exploration of

novel solid electrolytes that incorporate additional oxygen or other anions into the LGPS framework.

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Glossary

AC, alternating current

HSAB, hard and soft acids and bases theory

LGPS, $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$

SEI, solid electrolyte interphase

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