

# Solid electrolytes with $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ -type structure in the Li–Si–P–S–O system; electrochemical properties and structure–composition relationships

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$\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  (LGPS) is a lithium superionic conductor exhibiting conductivity of over  $10 \text{ mS cm}^{-1}$  at  $27^\circ\text{C}$ , and is a potential electrolyte candidate for solid-state batteries [1,2], though the incompatibility with anodes having low potential (0–1 V vs.  $\text{Li}/\text{Li}^+$ ) remains an obstacle to be overcome [3,4]. This study we reports LGPS-type conductors in the Li–Si–P–S–O system, which shows the significant increase in the electrochemical stability but at the cost of tolerable decrease in conductivity [5].

Monophasic LGPS-type phases were obtained at the composition of  $\text{Li}_{9.42}\text{Si}_{1.02}\text{P}_{2.1}\text{S}_{9.96}\text{O}_{2.04}$  (LSiPSO) and  $\text{Li}_{3.2}\text{PS}_{4-z}\text{O}_z$  respectively, both of which were synthesized by heating at the temperature above 1223 K and by subsequently quenching in ice water. X-ray diffraction (XRD) measurements followed by Rietveld refinements revealed that lattice volume of these LGPS-type crystals having space group of  $P4_2/nmc$  varied depending on the Si/P and S/O ratios, which indicated that these phases have solid-solution ranges with regard to Si/P and S/O ratios. Oxygen atoms were found to selectively occupy one of the three sulfur sites (the S1 site). Especially in the case of  $\text{Li}_{3.2}\text{PS}_{4-z}\text{O}_z$  phases, the limit of solid solution range for oxygen atoms is  $z = 1.2$ , which almost corresponds to the composition in which the S1 site is completely occupied by the oxygen atoms. This agreement suggests the relation between selective replacement by oxygen atoms and the solid-solution range limit.

Ionic conductivity values measured by the AC impedance method at  $25^\circ\text{C}$  varied in the range of  $0.05\text{--}1.1 \text{ mS cm}^{-1}$ , depending on the sample composition and preparation. Although these values were lower than that of the original LGPS phase, charge–discharge cycling tests using a solid-state cell (LGPS+ $\text{LiNbO}_3$ -coated  $\text{LiCoO}_2$ / the sample solid electrolyte/ Li) indicated the improved electrochemical stability of LSiPSO and  $\text{Li}_{3.2}\text{PS}_{4-z}\text{O}_z$  phases. The discharge capacity retention at the 5th cycle was more than 98% of the initial capacity for LSiPSO and  $\text{Li}_{3.2}\text{PS}_{4-z}\text{O}_z$  cells, whereas the LGPS cell showed a rapid capacity fading, with the capacity eventually dropping to less than 20% of the initial discharge capacity. We suggest that oxygen doping is an effective technique for increasing the electrochemical stability of sulfide superionic conductors and therefore further material searches is promising in the Li–M–P–S–O system ( $M = \text{Si, Ge and Sn}$ ). This work was supported by grand-in-aid JSPS research fellow.

## References:

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