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著者(和文)	LIYUXIANG
Author(English)	Yuxiang Li
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OUTLINE

In order to fabricate all-solid-state batteries with high power density and energy density, Li–Si–P–S based phases with $Li_{10}GeP_2S_{12}$ (LGPS)-type structure and high ionic conductivity and Li–P–S phases with a new crystal structure and high electrochemical stability were explored and characterized by diffraction and electrochemical measurements. A new solid solution of LGPS-type phase was obtained in the Li–Si–Ge–P–Br–O system. At $Li_{9.54}(Si_{0.6}Ge_{0.4})_{1.74}P_{1.44}S_{11.1}Br_{0.3}O_{0.6}$, bulk conductivity was estimated to be 37.4 mS cm^{-1}. For the Li–P–S system, a phase with a new crystal structure having layered PS_4 units and P_2S_7 units was obtained at the composition of $Li_{3.2}PS_4$. The cycle performance of solid-state-cell using the new $Li_{3.2}PS_4$ indicated a high electrochemical stability of this phase. The relationships between properties and compositions were clarified in the Li–*M*–P–S–*X*–O (*M* = Si, Ge, Sn; *X* =F Cl, Br, I) and Li–P–S systems.