

Phase identification of new solid electrolyte in the Li–P–S–Cl system

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All-solid-state battery (ASSB) is a promising energy storage technology that uses a solid electrolyte instead of a liquid electrolyte. The property of inorganic solid electrolyte is the key materials to the practical use of ASSB. Recently, sulfide solid electrolytes have been developed with high Li ionic conductivity. Especially $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ and its structural analogous to $\text{Li}_{10}\text{MP}_2\text{S}_{12}$ ($M = \text{Si}, \text{Sn}$) have attracted interest because of their high ionic conductivity of 10^{-3} – $10^{-2} \text{ S cm}^{-1}$ [*Adv. Energy Mater.* **10**, 42, 2002153 (2020)]. However, their low electrochemical stability hinders the practical use of Li metal anode in ASSB. The specific capacity of Li metal (3860 mA h g^{-1}) is more than 10 times that of graphite (372 mA h g^{-1}); thus, it is possible to improve the energy density by utilizing Li metal anode. Halogen-substituted sulfide electrolytes have been developed with high ionic conductivity and electrochemical stability. In this context, the new solid electrolyte with a high ionic conductivity of $10^{-3} \text{ S cm}^{-1}$ was synthesized in the Li–P–S–Cl system (LPSCl). However, the phase identification and structural analysis of LPSCl have not been performed. To identify minor phases (such as the residual Li_2S and LiCl phases) and thereby elucidate lattice system of the main phase, the neutron powder diffraction (NPD) experiment of LPSCl was performed. The result was analyzed in conjunction with synchrotron X-ray diffraction (SXRDX) experiment at the BL02B2 beamline of the SPring-8. NPD.

The NPD measurement was conducted using high efficiency high resolution measurements (HREMES) installed at JRR-3, ISSP. The utilization of NPD is essential for obtaining information about Li sites and distinguishing between sulfur and chlorine. Distinguishing between sulfur and chlorine with SXRDX is challenging, whereas it is feasible with NPD because of the significant difference in neutron scattering length (coherent scattering length S:

2.85, Cl: 9.58).

Figure shows SXRDX and NPD patterns of LPSCl. Peaks derived from Li_2S were not observed both in SXRDX and NPD. The identification of LiCl using SXRDX was challenging due to the angular dependence of X-ray atomic scattering amplitude. As the measurement angle (θ) of XRD increases over $2\theta > 40^\circ$ peak intensity decreases. Furthermore, the two peaks of LiCl at $2\theta = 30.1^\circ$ and 35.0° overlapped with LPSCl pattern, hindering the distinction of LiCl. Meanwhile, with NPD data the minor LiCl phase was clearly identified. Atomic scattering length of neutron does not show any angle-dependent parameter; thereby, the presence of LiCl, which showed peaks at $2\theta = 50.3^\circ$ and 59.7° , could be identified.

Based on the above phase identifications, peak indexing of LPSCl was performed for SXRDX data to reveal that it possesses a hexagonal unit cell. These results will help future research to synthesize monophasic LPSCl for the detailed structural analysis.

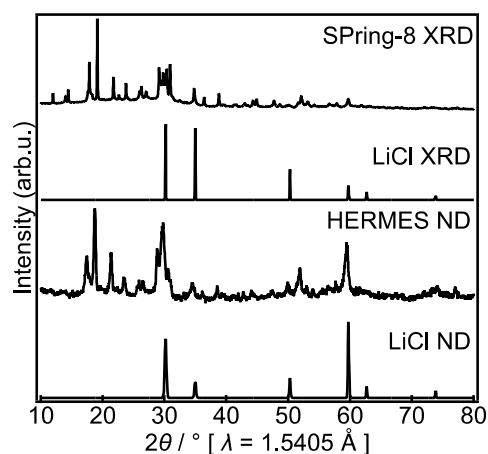


Fig. Synchrotron XRD and NPD patterns of LPSCl and LiCl. The wavelengths of XRD and NPD were converted to $\text{CuK}\alpha_1$ for comparison. The diffraction patterns of LiCl were referred to ISCD-26909.