Mechanochemical Synthesis of Hexagonal $Li_{4+2x}Sn_{1-x}M_xS_4$ solid electrolytes

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Some sulfide-based solid electrolytes show high ionic conductivities of over 10^{-2} S cm^{-1} at 25°C [1, 2]. They also have the advantage of being relatively ductile, resulting in the preparation of dense pellets with low porosity and favorable contact with an electrode simply by pressing at room temperature [3].

Because of their high conductivities and chemical stability in air, Li_2S–SnS_2 solid electrolytes have attracted attention [4-7]. Kaib *et al.* and Sahu *et al.* have reported orthorhombic Li_4SnS_4 [4-5]. Recently, we reported that hexagonal Li_4SnS_4, a metastable phase of Li_4SnS_4, can be obtained by mechanochemical synthesis [7]. Hexagonal Li_4SnS_4 showed higher conductivity than orthorhombic Li_4SnS_4. Choi *et al*. have also reported the preparation of similar materials by liquid phase synthesis [6]. In this study, we developed novel solid electrolytes by partial substitution of divalent Mg^{2+} and Ca^{2+} for tetravalent Sn^{4+} in hexagonal Li_4SnS_4 to enrich lithium compositions.

Hexagonal Li_4SnS_4 and $Li_{4.2}Sn_{0.9}M_{0.1}S_4$ (M=Mg or Ca) solid electrolytes were synthesized by mechanical milling of Li_2S, SnS_2 and MgS or CaS and subsequent heat treatment above the crystallization temperatures.

The materials with low crystalline hexagonal Li_4SnS_4 phase were prepared *via* mechanochemistry in each sample and subsequent heat treatments increased the crystalliny. By the substitution of Mg^{2+} and Ca^{2+} for Sn^{4+}, the diffraction peaks in the XRD patterns shifted to the lower angle side on the basis of the difference of the ionic radius, indicating that solid solutions of hexagonal Li_4SnS_4 with Mg and Ca were successfully prepared. The lithium-ion conductivities of Mg- and Ca-substituted Li_4SnS_4 were both 1.4×10^{-4} S cm^{-1} at 25°C, which were slightly higher than that of hexagonal Li_4SnS_4. The amount of H_2S gas generated from hexagonal Li_4SnS_4 and $Li_{4.2}Sn_{0.9}M_{0.1}S_4$ was considerably smaller than that from the Li_3PS_4 glass-ceramic electrolyte.

It is expected to discover novel solid electrolytes with high conductivity and high chemical stability in air in a series of materials with hexagonal Li_4SnS_4 structure.

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