Synthesis and Electrochemical Properties of Solid Lithium Ion Conductors in $Li_{4+x}Al_xSi_{1-x}S_4$ System

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Lithium conducting solids with high ionic conductivity attract much attention as solid electrolytes for developing all-solid-state batteries [1, 2]. However, searching for novel materials is still necessary to satisfy the strict demands of practical electrochemical devices such as electrochemical/chemical stability, low cost, and abundant materials. This study systematically investigates the synthesis and electrochemical properties of solid lithium ion conductors in the $Li_{4+x}Al_xSi_{1-x}S_4$ system. The relationship of ionic conductivity, thermal stability, and phase-types in the binary Li_5AlS_4–Li_4SiS_4 system is elucidated. The samples in the $Li_{4+x}Al_xSi_{1-x}S_4$ (x = 0 ~ 1.0) system were synthesized using stoichiometric amounts of Li_2S, Al_2S_3, and SiS_2 powders as starting materials. The powders were ground by vibration-milling apparatus, pressed into a pellet, and then sealed in a quartz tube. Solid-state reaction and melt-quenching methods were used for stable and metastable phases search, respectively. X-ray diffraction measurements were conducted to identify the synthesized phases. The ionic conductivities of the obtained samples were evaluated by AC impedance method. A phase diagram of this system was determined by differential thermal analysis method, with the corresponding phases identification. In this study, a new thio-LISICON phase formation was confirmed at x = 0.5 by solid-state reaction, with a relatively high ionic conductivity (2×10^{-6} S cm^{-1} at R.T.). Further, novel phases with the argyrodite structure [3] in HT– and LT–modifications were obtained by a melt-quenching method at x = 0.08 ~ 0.17. The ionic conductivity of the HT–argyrodite phase (x = 0.1) was calculated from the impedance plot (inset of **Fig.** 1); the highest conductivity (2.5×10^{-4} S cm^{-1} at R.T.) in all the examined samples with the activation energy 40 KJ cm^{-1} was confirmed, which was three order of magnitude higher than that of the reported solid solutions in the $Li_{4+x}Al_xSi_{1-x}S_4$ system [4]. Further work in an optimization of the synthesis processes and compositions might improve the ionic conductivity of the $Li_{4+x}Al_xSi_{1-x}S_4$ system.

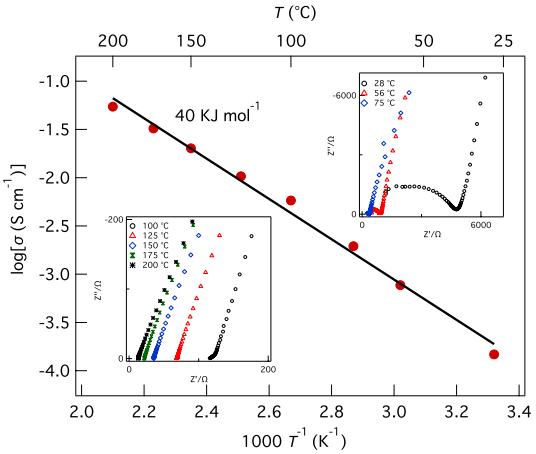

Fig.1 Arrhenius plot of ionic conductivity for $Li_{4.1}Al_{0.1}Si_{0.9}S_4$ with HT–Argyrodite structure.

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