Preparation and characterization of lithium ion conductive Li_3SbS_4 glass and glass-ceramic electrolytes

Takuya Kimura, Atsutaka Kato, Atsushi Sakuda, Akitoshi Hayashi, Masahiro Tatsumisago
Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University, 1-1 Gakuencho, Naka-ku, Sakai, Osaka 599-8531, Japan

E-mail: syb02037@edu.osakafu-u.ac.jp

The demand of high-energy rechargeable batteries is increasing for larger scale application. Commercially available lithium ion batteries use organic liquid electrolytes, which may cause leakage and fire in severe conditions. The risks are able to reduce by replacing the liquid electrolytes with non-flammable inorganic solid electrolytes. Various solid electrolytes (SEs) have been discovered and applied to all-solid-state batteries. In the past decade, oxide SEs with high conductivity at room temperature such as $Li_7La_3Zr_2O_{12}$ ($> 10^{-4}$ S cm^{-1}) were found [1]. However, the formability of the oxide SEs is poor, thus it is necessary to be sintered at high temperature and densified to achieve high ionic conductivity. On the other hand, sulfide SEs have a good formability and can be densified just by cold pressing. In addition, the conductivity of the sulfide SEs, such as Li_3PS_4 glass and glass-ceramic ($> 10^{-4}$ S cm^{-1}) [2] is higher than that of the oxide SEs. However, most of sulfide electrolytes are generally unstable in air and generate H_2S. Recently, the Na_3SbS_4 crystal is reported to have a high sodium ion conductivity ($> 10^{-3}$ S cm^{-1}) and good dry air stability; this sulfide material become $Na_3SbS_4 \cdot 9H_2O$ without generating H_2S from the electrolyte [3]. It is anticipated that lithium ion conductors in the system Li-Sb-S have high conductivity and air stability.

In this study, Li_3SbS_4 glass and glass-ceramic were prepared *via* a mechanochemical process. Raman spectra showed that the glass and glass-ceramic electrolytes contained the SbS_4^{3-} ions. The conductivity of the pelletized Li_3SbS_4 glass was 1.5×10^{-6} S cm^{-1} at 25°C, which was higher than that of its glass-ceramic. In order to clarify the conduction mechanism in Li_3SbS_4 glass-ceramic, Rietveld refinement was done for Li_3SbS_4 glass-ceramic heated at 500ºC. The Li_3SbS_4 has a similar structure to γ-Li_3PS_4 crystal. The amount of H_2S generated from the Li_3SbS_4 glass was measured by flowing humid air with 70% of relative humidity at room temperature. The amount of H_2S generated from Li_3SbS_4 glass was considerably lower than that of Li_3PS_4 glass, indicating that Li_3SbS_4 glass is more stable to the humid air.

References:

[1] R. Murugan *et al*., Angew. Chem. Int. Ed., 46 (2007) 7778-7781.
[2] F. Mizuno *et al*., Solid State Ionics, 177 (2006) 2721-2725.
[3] A. Banerjee *et al*., Angew. Chem. Int. Ed., 55 (2016) 9634-9638.