# Neutron Quasi Elastic Scattering Study of Glassy Sulfide Electrolytes

K. Ohara[A], S. Hiroi[A], K. Kobayashi[A], Y. Ohmasa[B], T. Endou[B], H. Akiba[B], and O. Yamamuro[B]

[A] Shimane Univ., [B]ISSP-NSL, Univ. of Tokyo

Controlling Li ion transport in glasses at atomic and molecular levels is key to realising all-solid-state batteries. Based on previous theoretical study,[1] we found that the Li ions of the $Li_3PS_4$ glass, a promising solid electrolyte candidate, have a characteristic correlation of 4.0 ~ 5.0 Å from the analysis for the charge state of the Li ions.[2] In this study, we aim to understand the mechanism of Li ion conduction in the glassy structures through experimental evidence of Li ion dynamics in sulfide glass electrolytes. Quasi elastic neutron scattering (QENS) experiment is very useful for this aim. The QENS study was already used to examine $Li_7P_3S_{11}$ glass ceramics.[3] The observed QENS component can be regarded as the self-diffusion of Li ions. The half-width at half-maximum of the QENS peak $\Gamma$ was reproduced well by the following equation of the jump-diffusion model:

$$\Gamma = \hbar \frac{D_s Q^2}{1 + D_s \tau_0 Q^2} \qquad (1)$$

where $D_s$ is the self-diffusion constant and $\tau_0$ is the residence time. $D_s$ is related to the mean jump length $<l>$ by the following equation:

$$D_s = \frac{\langle l \rangle^2}{6\tau_0} \qquad (2)$$

The self-diffusion coefficient for the $Li^+$ ions ($D_{S\_Li}$) was $5.7 \times 10^{-6}$ cm²/s, the mean residence time $\tau_0$ was $5.5 \times 10^{-11}$ s, and the mean jump length $<l>$ was 4.3 Å. [3] In addition, the ionic conductivity of this system was $1.7 \times 10^{-2}$ S/cm. In contrast, using the ⁷Li pulsed field-gradient (PFG) NMR technique, the value of $D_{S\_Li}$ was determined to be $9.0 \times 10^{-10}$ cm²/s in β-$Li_3PS_4$,[4] and its macroscopic Li ion conductivity was estimated to be $1.0 \times 10^{-4}$ S/cm, which is consistent with that obtained experimentally from the impedance results (i.e., $2.0 \times 10^{-4}$ S/cm). Hence, finding the key parameters that lead to improvements in $D_{S\_Li}$ and in the Li distribution and will be expected lead to more ionic conductivity in glassy electrolytes.

We performed the QENS experiments for the $Li_3PS_4$ glasses at AGNES. Figure 1 shows the QENS spectra at $Q = 0.67$ Å⁻¹ of $Li_3PS_4$ glass at three different temperatures 3 K, 200 K, and 420 K. The QENS width is broader at 420 K than that at 200 K. This indicates that the relaxation time of the $Li^+$ ions becomes shorter as in high temperature. It should be noted that QENS of $Li^+$ ions can be clearly observed using AGNES. In the future, we will obtain the jump length of Li ions in $Li_3PS_4$ glass from the QENS data and understand the relationship between the anion framework structure and the dynamics of Li ions.

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[2] H. Yamada et al., Energy & Environment. Materials, **7(3)**, e12612 (2023).
[3] K. Mori et al., Physical Review Applied, **4(5)**, 054008 (2015).
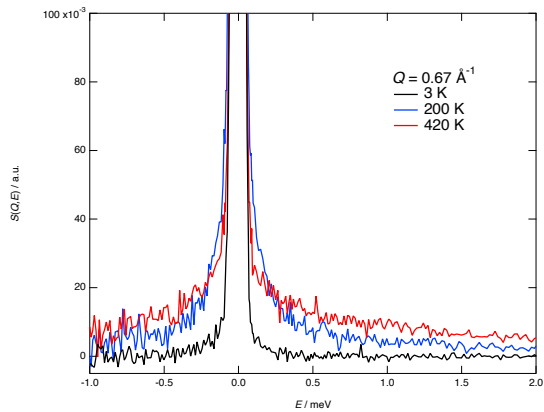[4] H. Stöffler et al., Journal of Physical Chemistry C, **122(28)**, 15954 (2018).

Fig. 1. Quasi elastic neutron scattering spectra at $Q$=0.67Å⁻¹ of $Li_3PS_4$ glass at three different temperatures 3K (black), 200K (blue) and 420K (red).