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Li^+ Ion Diffusion in Solid State Electrolyte Li_3InCl_6 measured by ^7Li Liquid State NMR

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Conventional lithium-ion batteries have changed modern life. However, concerns remain about their energy density limit and safety risks introduced by flammable liquid electrolytes. One alternative is all-solid-state Li batteries (ASSBs) which are not only safer but also can achieve higher energy densities. One of the most vital components of ASSBs is the solid-state electrolyte (SSEs). The optimization and design of SSEs is still underway, of which ion conductivity, Li^+ diffusion mechanisms, and their stability are key. For the study of ion conduction mechanisms and Li^+ diffusion, pulsed gradient spin echo (PGSE) NMR methods are ideal. The PGSE method provides diffusion time dependent ^7Li apparent diffusion coefficients (*D)* and distances on the scale of 0.2-10 µm. In the short diffusion time limit, the electrical conductivity is directly proportional to *D* via the Nernst-Einstein equation,

$$\sigma = \frac{DNe^2}{kT}, \tag{1}$$

in which σ is the electrical conductivity, *N* is the number of carrier ions, *e* is the elementary charge, *k* is the Boltzmann constant, and *T* is the temperature. In the long diffusion time limit, *D* scales with tortuosity and restricted motion, such as the effect of grain boundaries, and the mean squared displacement can be calculated as

$$< z^2 > = 6D\Delta \tag{2}$$

in which Δ is the diffusion time. In this study, the Li^+ diffusion mechanisms in Li_3InCl_6 are studied as a function of treatment condition. Li_3InCl_6 is a halide-based SSEs with a stable monoclinic crystal structure and good ionic conductivity. It is known that the ionic conductivity increases after annealing; however, the mechanism by which conductivity increases is unknown. The results indicate that the SSEs is stable when exposed to air and that the Li^+ *D* is enhanced by annealing while the presence of intraparticle restrictions increase. The Li_3InCl_6 samples are also characterized by *D*-T_2, T_2, T_2-T_2, and T_1 measurements as well as FESEM, TEM/STEM and XRD.

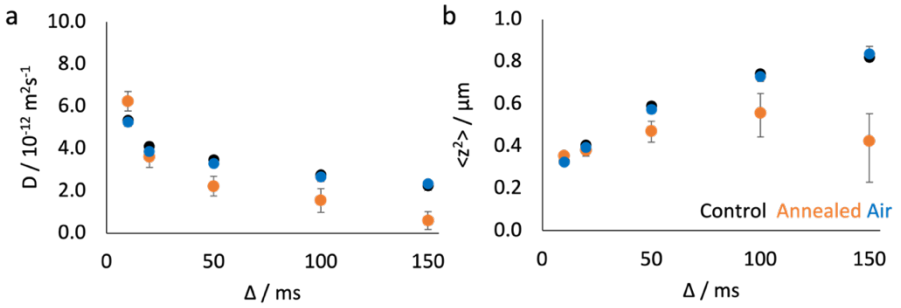

Figure 1: a) *D* is plotted as a function of diffusion time (Δ). b) The mean squared displacement, $<z^2>$ is plotted as a function of Δ. When Δ is short (Δ= 10 ms), *D* reflects conductivity. In comparison to the control sample, ^7Li *D*(Δ= 10) ms increases after annealing and shows no change when the sample is exposed to air. When Δ is long, (Δ= 150 ms), *D* reflects long range mobility and tortuosity. In comparison to the control sample, ^7Li *D*(Δ= 150 ms) decreases after annealing and shows no change when the sample is exposed to air.