Li$^+$ Ion Diffusion in Solid State Electrolyte Li$_3$InCl$_6$ measured by ^{7}Li 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 ^{7}Li 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,

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

$$< z^2 > = 6D\Delta$$ (2)

in which Δ is the diffusion time. In this study, the Li$^+$ diffusion mechanisms in Li$_3$InCl$_6$ are studied as a function of treatment condition. Li$_3$InCl$_6$ 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$_3$InCl$_6$ 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.

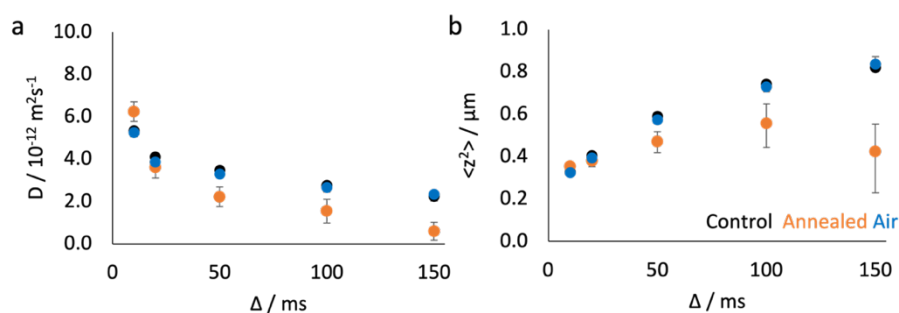

Figure 1: a) D is plotted as a function of diffusion time (Δ). b) The mean squared displacement, $<z^2>$ is plotted as a function of Δ. When Δ is short (Δ= 10 ms), D reflects conductivity. In comparison to the control sample, ^{7}Li $D(\Delta$= 10) ms increases after annealing and shows no change when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