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Crystal Structure, Particle Size, and Ionic Conductivity of Solid-State Electrolytes Studied By Diffusion and Relaxation NMR

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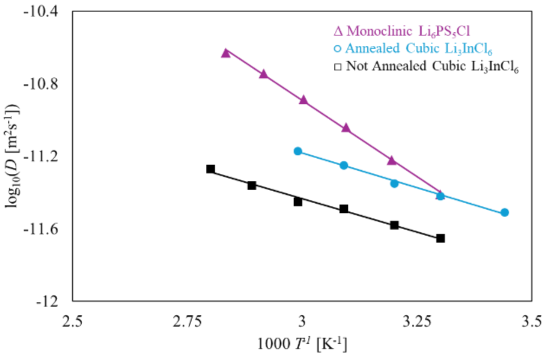
Introduction: Development of new sustainable technologies relies on the development of safer, low cost, and higher energy density batteries, such as all solid-state batteries. In all solid-state batteries, ions migrate from anode to cathode through defects in the crystal structure of the solid-state electrolyte. Diffusion based NMR measurements are a powerful tool for non-invasively characterizing this migration in the crystal structure and across grain boundaries. Diffusion derived from NMR measurements is correlated with electrical conductivity while diffusion measurements as a function of temperature and observation time allow for the measurement of activation energy and mean squared displacement respectively. Relaxation measurements give insight into motion on the atomic scale. In this work, migration of Li in two solid-state electrolyte materials is characterized, cubic Li_6PS_5Cl [1] and monoclinic Li_3InCl_6 [2]. The NMR data is complemented by scanning electroscope microscopy, x-ray diffraction, and electrical impedance spectroscopy to understand the effect of impurities, crystal structure, and grain boundaries on ion migration.

Methods: The powder samples of Li_6PS_5Cl and Li_3InCl_6 in an Argon atmosphere were sealed in 5 mm glass NMR tubes. NMR Measurements, measuring D, T_2, T_1, D-T_2, and T_2-T_2, were acquired using 9.39 and 14.1 T Bruker spectrometers equipped with 5 mm Diffusion Broadband Probes with a maximum gradient strength of 17.4 Tm^{-1} and 28 Tm^{-1}. Data was acquired from -60 to 180^{o}C.

Results and Discussion: To test the effect of defects in the crystal structure on ion migration, which includes ion hopping and long-range motion, monoclinic Li_3InCl_6 was studied before and after annealing. After annealing, the sample showed traces of impurities and larger lattice spacing than before annealing in XRD data. R_2 relaxation rates were faster in the annealed sample, indicating an increased hopping rate of Li between atomic sites in the crystal lattice, due to this increased lattice spacing. $D(T)$ also showed faster diffusion and a smaller activation in the annealed sample, indicating faster long-range motion and improved ion conductivity. To compare the effect of crystal structure, the diffusion in cubic Li_6PS_5Cl Li_3InCl_6 studied. $D(T)$ was faster and had a smaller activation energy in cubic Li_6PS_5Cl than in monoclinic Li_3InCl_6, which corresponds to an improved electrical conductivity, which was confirmed using impedance spectroscopy.



Conclusion: Relaxation and diffusion NMR are powerful tools for measuring the ion motion in solid-state electrolytes that give insight into short range motion and long-range motion. The motion of Li is a key determinant of electrolyte performance.

References: [1] Schlenker, Chem. Mat. (2020). [2] Molaiyan, Mat &. Des. (2023).