

Bulk ionic conductivity and crystallization of lithium thiophosphate solid electrolytes

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Abstract

Lithium solid electrolytes are important for safe energy storage and have the possibility to operate at wider electrochemical windows than liquid electrolytes. For energy storage devices, it is important to understand whether bulk or surface conduction dominates ionic transport within a given solid electrolyte. Recent work by Liu et al. (Ref. 1) suggests that surface conduction may be dominant in 95% dense, nanoporous compacts.

We present results to support that bulk conduction dominates in the $x \text{Li}_2\text{S} + (1-x) \text{P}_2\text{S}_5$ (mol fraction) system. A study on the dependence of compact density on ionic conductivity on $x = 0.70, 0.75$, and 0.80 compositions was performed on $x \text{Li}_2\text{S} + (1-x) \text{P}_2\text{S}_5$. Mechanically milled powders were cold-pressed ($\sim 75\%$ dense) and pressed near their glass transition temperatures ($\sim 95\%$ dense). Higher density compacts had higher ionic conductivity with little change in the activation energy for conduction in a given composition.

From our literature review, the $0.80 \text{Li}_2\text{S} + 0.20 \text{P}_2\text{S}_5$ composition seems to exhibit good cycleability within the lithium thiophosphate system. The low glass transition temperature ($\sim 190^\circ\text{C}$) allows the possibility to pressure-form a low ESR electrolyte-electrode interface (Ref. 2). Furthermore, if the system is lithium-deficient, there is less of a detrimental decrease in conductivity at $x = 0.80$ than in the higher conductivity $x = 0.70$ composition (Ref. 3).

We report new impedance spectroscopy characterization on dense, crystallized samples below room temperature. Results support that bulk lithium loss may limit the benefit from the crystallization in “oversintered” glass-ceramics. Between a cold-pressed x-ray amorphous compact with residual Li_2S and a dense, crystalline compact, there is a 40% conductivity benefit from densification and a 60% benefit from crystallization at room temperature (Fig. 1).

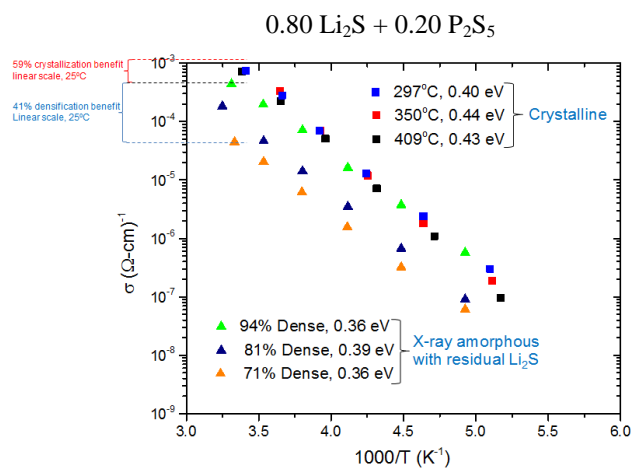


Figure 1. Arrhenius plot of the \log_{10} of ionic conductivity vs. inverse temperature for $x = 0.80$ at different densities and heat treatments. Activation energies are indicated. The average activation energy for the x-ray amorphous samples with residual Li_2S is 0.37 eV , while the average activation energy for crystallized samples is 0.42 eV . Note that conductivity benefit values are reported on a linear scale, even though they are shown on the vertical log axis.

References

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