Elucidating the Role of Microstructure in Thiophosphate Electrolytes
– a Combined Experimental and Theoretical Study of β-Li3PS4

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Since the number of electric vehicles (EVs) is growing rapidly, the interest in developing an appropriate battery is immense. The state-of-the-art lithium-ion battery (LIB) proved to be an efficient energy storage system, so far, however, crucial safety risks arise from the flammable liquid electrolyte. In this context, the focus nowadays is set on solid-state Li metal batteries (SSBs) with nonflammable solid electrolytes (SEs), which are potentially safer and offer higher energy and power densities.[1,2] For SSBs, polymeric and inorganic solid electrolytes are of interest as well as a combination of both resulting in flexible hybrid solid electrolytes.[1,3,4] This work concentrates on the use of inorganic electrolytes. Among the classes of SE available, sulfides are particularly promising, such as lithium thiophosphate (LPS) having a comparably low density, and thus can increase the cell energy more efficiently.[5] Further, sulfides offer high ionic conductivity and can be processed in slurry-type sheet-batteries showing promising results.[6] Another advantage of sulfides is the possibility of being densified at room temperature owing to their ductility.[7] This last aspect often leads to the assumption that highly dense SE layers can be easily obtained by cold pressing, thus discouraging a systematic investigation on the role of SE’s microstructure. Therefore, here we investigate for the first time the microstructure of a thiophosphate SE LPS. Four batches of β-Li3PS4 with different particle morphologies are systematically studied. It is found out that differences in pellet porosities are originating from single-particle intrinsic features, especially, the particle size and porosity. The batches with larger SE particles showed overall better performance even though the porosities of the pressed SE pellets were between 30-40%, whereas the denser SE pellets made of smaller sized SE particles delivered lower ionic conductivities and higher interface resistance with Li. Modelling results suggest that the grain boundary resistance may play a crucial role not only for oxide SE [8], but also in the case of sulfides. Larger SE particles seem to be more attractive, as their grain boundary contribution is lower than that of denser pellets prepared using smaller β-LPS particles. Our unexpected findings mean, that striving for a dense SE separator may become irrelevant, as long as the microstructure allows for low grain boundary resistance. This certainly represents a paradigm shift and may open new possibilities in the field of SSBs, including the design of highly porous, low density solid electrolytes.

**References**

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