Separating bulk from grain boundary Li ion conductivity in the sol-gel prepared solid electrolyte $Li_{1.5}Al_{0.5}Ti_{1.5}(PO_4)_3$

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In terms of ionic conductivity lithium aluminium titanium phosphate (LATP) belongs to one of the most promising solid electrolytes. Besides sufficiently high electrochemical stability, its use in lithium-based all-solid-state batteries crucially depends on the ionic transport properties. While many impedance studies can be found in literature that report on *overall* or total ion conductivities, a discrimination of bulk and grain boundary electrical responses via conductivity spectroscopy has rarely been reported so far. Here, we took advantage of impedance measurements that were carried out at low temperatures to separate bulk contributions from the grain boundary responses. It turned out that bulk ion conductivity is by approximately three orders of magnitude higher than ion transport across the grain boundary regions. At temperatures well below ambient, long-range Li ion dynamics is governed by activation energies ranging from 0.26 to 0.29 eV depending on the sintering conditions. As an example, at temperatures as low as 173 K, the bulk ion conductivity, measured in N_2 inert gas atmosphere, is in the order of 8.1×10^{-6} S cm^{-1}. Extrapolating this value to room temperature yields ca. 3.4×10^{-3} S cm^{-1} at 293 K. Interestingly, exposing the dense pellets to air atmosphere over a long period of time causes a significant decrease of bulk ion transport. This process can be reversed if the phosphate is calcined at elevated temperatures again.