A Micro-contact Electrochemical Impedance Spectroscopy Study of NASICON Type Li$_{1.5}$Al$_{0.5}$Ti$_{1.5}$ (PO$_4$)$_3$ and LiTi$_2$ (PO$_4$)$_3$ Single Crystals

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NASICON-type (NaSuper-Ionic Conductor) solid electrolytes are known for their high Li ion conductivities, in particular systems derived from the LiTi$_2$(PO$_4$)$_3$ (LTP) system have been widely studied. The partial substitution of Ti$^{4+}$ by a subvalent cation such as Al$^{3+}$, Ga$^{3+}$, In$^{3+}$, Y$^{3+}$, La$^{3+}$, Cr$^{3+}$ or Fe$^{3+}$ leads to an increase of Li$^+$ content and forms the high ionic conducting Li$_{1+x}$M$_x$Ti$_{2-x}$(PO$_4$)$_3$ system. Among this group the Li$_{1+x}$Al$_{1-x}$Ti$_{2-x}$(PO$_4$)$_3$ (LATP) composition show the highest Li$^+$ conductivity and one of the highest within the group of inorganic Li$^+$ conducting electrolytes. The additional Li$^+$ occupy sites which are unoccupied in the conventional LTP structure by forming a 3D Li$^+$ network in the NASICON structure. One would expect that the formed Li$^+$ network is responsible for the improved total ionic conductivity, but instead the total ionic conductivity is dominated by the grain boundary conductivity and the grain conductivity plays just a minor role. Nevertheless, the exact contribution of the grain conductivity to the total ionic conductivity and how grain conductivity is related to the crystal chemistry is not at hand.

Therefore we used for the first time micro-contact electrochemical impedance spectroscopy to exactly determine the bulk ionic conductivity of dense LTP and LATP single crystals, which are carefully studied by X-ray single crystal diffraction. This finally enables us to quantify the effect of crystal chemistry on Li-ion transport within the grain. The results of this study will be presented at the conference.