Local conductivities in Li ion conducting garnet-based ceramics measured by microelectrodes.

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Energy storage and energy conversion with a high efficiency are key issues for future mobile devices and transportation technology. Secondary elements like lithium ion batteries are already state of the art for a large number of mobile applications. Despite the good performance of current lithium ion batteries, safety and stability problems as well as limitations in the energy density are related to the standard organic electrolytes. Being able to surpass these problems would open further options, e.g. for applications.

In the past years new solid material classes came into the focus of electrolyte research. Cubic Li$_7$La$_3$Zr$_2$O$_{12}$ (LLZO) garnets and it variants are among the most promising candidates for future solid electrolyte systems because of their very high lithium conductivity (about $10^{-4}$ - $10^{-3}$ S cm$^{-1}$ [1]). Doping of the garnet is a crucial factor to achieve high conductivities. However, many details on the effects of dopants and on the role of the exact Li stoichiometry, but also on degradation phenomena are still not understood.

In this contribution, we present an electrochemical impedance spectroscopy (EIS) study of LLZO doped with different elements. To achieve a better fundamental understanding of the electrochemical processes and diffusion of lithium ions, we performed, besides overall conductivity measurements using blocking electrodes, measurements on microelectrodes of different composition and size. Varying doping materials (Ga, Al, Mo, ...) and changing temperature lead to very different impedance responses in the complex impedance plane. From these measurements information on the local bulk conductivity can be determined and blocking layers near to the surface can be identified.