Impact of field stress on electrochemical properties of LLZO

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Conventional Li-ion batteries use organic solvents as electrolytes, which are known to cause safety issues. Replacing the liquid, organic electrolytes by inorganic, solid electrolytes could eliminate these problems. Further, solid electrolytes enable the use of Li-metal as electrode material, resulting in higher possible energy densities. The garnet-type oxide $Li_7La_3Zr_2O_{12}$ (LLZO) has received much attention as a solid electrolyte for all solid state batteries due to its high Li-ion bulk conductivity of up to 10^{-3} S cm^{-1} at room temperature [1]. The application of LLZO, however, requires a deeper understanding of its properties, including its stability and the interaction with electrodes.

In this work, we investigated the impact of field-stress on LLZO polycrystalline pellets and single crystals and its dependence on the electrode material. Voltages of up to a few V were applied using (partly) ion blocking or reversible electrodes at elevated temperatures in different gas atmospheres (nitrogen and air). The electrochemical processes induced by field-stress were investigated by a combination of impedance spectroscopy and chemical analysis. Local conductivities were determined using circular thin film micro-electrodes prepared by photolithography and ion-beam etching. Laterally resolved elemental compositions of the samples were measured by laser-induced breakdown spectroscopy (LIBS). Further, the electrochemical properties of interfaces between LLZO and common electrode materials, such as $LiMn_2O_4$ and $Li_4Ti_5O_{12}$ are investigated by means of impedance spectroscopy and DC-cycling.

[1] V. Thangadurai, S. Narayanan, D. Pinzaru, Chem. Soc. Rev. 43, 4714–4727 (2014).