New methodology to investigate grain and grain boundaries resistivity in LLZO garnet

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The commercial future of solid state lithium-ion batteries with high energy and power densities could be related to solid Li-garnet electrolytes. This class of materials has shown relatively high ionic conductivity (10^{-3} $S \cdot cm^{-1}$ at room temperature) and high thermodynamic and electrochemical stability. In addition, in a battery set up, lithium metal can be employed as anode increasing the theoretical specific battery capacity [1]. The major unsolved problem for employing lithium garnet is the battery short life-time during cycling caused by the fast formation of lithium dendrites in the garnet material [2]. The dendrite formation is believed to be faster in the garnet grain boundaries compared to the grains. Few is known about garnet grain boundaries chemical composition and resistivity. In the literature Rgb values of Li-garnet diverge greatly, from several points percent to 40% of the total resistance [3]. Such a large difference in the Rgb values is believed to originate from the variation in the chemical composition of the grain boundaries and the grain microstructure.

For this reason we developed a new methodology in the attempt of unequivocally measure the lithium garnet grain and grain boundaries conductivities. Cubic Al-doped $Li_{6.4}Al_{0.2}La_3Zr_2O_{12}$ (LLZO) solid electrolyte has been prepared by citrate acid route in a glove box with controlled atmosphere, to avoid the undesired reaction of the garnet with the water or carbon dioxide present in the atmospheric air [4]. The test-sample has been thermally etched to reveal grain and grain boundaries features. The particular citric acid route utilised, allowed to obtain samples with a mean grain size of around 250 microns, large enough to fulfill our purpose. FIB-SIMS analysis has been employed in order to study the chemical composition of grain and grain boundaries and to perform in situ electrochemical characterisation within grains and grain boundaries. This analysis revealed a higher Al concentration in the grain boundaries compared to the grain, confirming an Al preferential segregation [5]. Test on Ga- and Ge-doped LLZO garnet prepared with the same citric method will be also performed to explore the influence of the dopant on the conductivity behavior of the grain boundaries.

References:

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