Fraunhofer IKTS

LLZO SEPARATOR SHEETS MANUFACTURED BY A TAPE CASTING PROCESS AND THEIR ELECTROCHEMICAL CHARACTERIZATION

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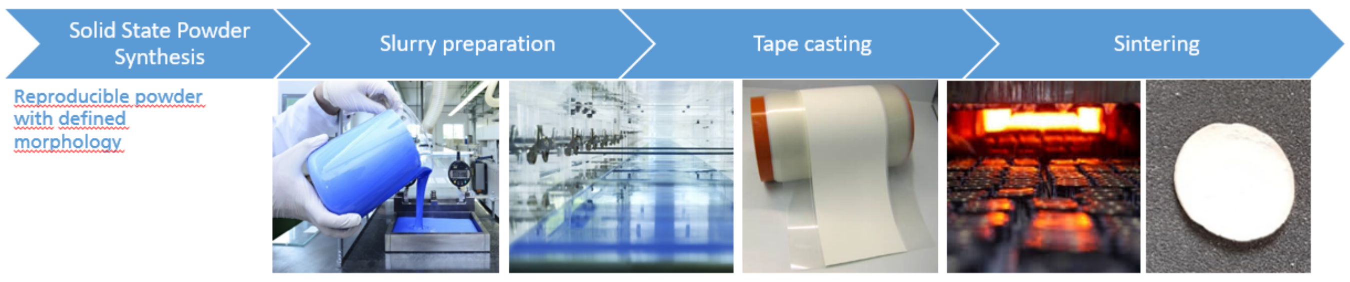
MOTIVATION

The solid state electrolyte LLZO has faced a lot of interest within research society since its discovery in 2007 [1]. The ionic conductivity of the material as well as its sinterability can be improved strongly by different doping strategies and powder properties optimization.

However, besides material optimisation it is crucial to develop scalable manufacturing techniques to enable the possibility to use LLZO in an industrial scale. Within the funded project 'ARTEMYS' the aim is to develop a tape casting and sintering process for LLZO.

EXPERIMENTAL



- A LLZO powder with the nominal composition $Li_{6.16}La_3Al_{0.28}Zr_2O_{12}$ was manufactured by lab-scale solid state synthesis and was milled in Isopropanol.
- The isopropanol based tape casting slurry was prepared with the LLZO powder and Li_2CO_3 as additive
- The green tape was casted in a pilot-plant scale.
- The tape was cut into pieces, which were sintered at 1230 °C in a powder bed on a spinel support.
- The density of the sintered tapes was measured by Archimedes method. The average tape was measured by SEM images of the tape cross section.
- Impedance measurement was conducted using blocking Cu electrodes as well as Li electrodes. The frequency range was 100 mHz–1 MHz.
- The Cu and Li electrodes were applied by physical vapor deposition with a thickness of ~250 nm. Li chips were applied on top of the lithium coating without pressure or heat. After the first impedance measurement, the stack was heated to 175 °C in argon for better contact and measured again.

RESULTS

Characterization of sintered LLZO tape

- The density of the sintered LLZO tape is 4.94 g/cm³ (97 %) when using Li_2CO_3 as sintering additive.
- The additive strongly affects the microstructure by increasing the sintering activity: A pure LLZO tape, in comparison, has hardly developed particle-particle contacts.
- The high porosity of the pure LLZO tape could be reduced. The particles of the LLZO-Li_2CO_3 tape form an almost dense structure with plenty smaller pores and few very large pores, which may have arisen from sample preparation.
- The sintered tapes have a Li-ion conductivity of > 10^{-6} S/cm. Two semi-circles are visible in the Nyquist plot. The first semi-circle correlates with the bulk conductivity (E_A = 0.49 eV) and the second with the grain boundary conductivity (E_A = 0.60 eV).
- The conductivity of a pressed and sintered reference pellet of the same powder is ~10^{-4} S/cm.

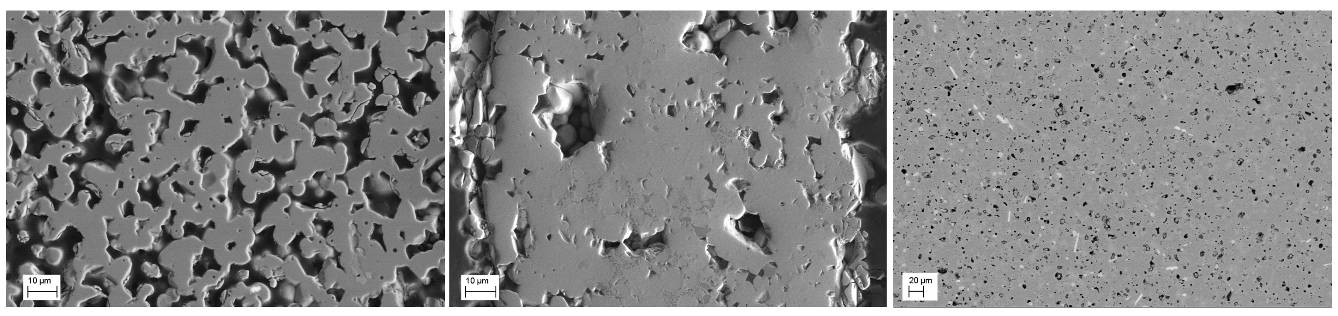


Figure 1: Influence of Li_2CO_3 as sintering additive on the microstructure of LLZO tapes; left: pure LLZO tape; middle: LLZO-Li_2CO_3 tape; right: LLZO pellet as reference, which was manufactured from the same powder like the tapes.

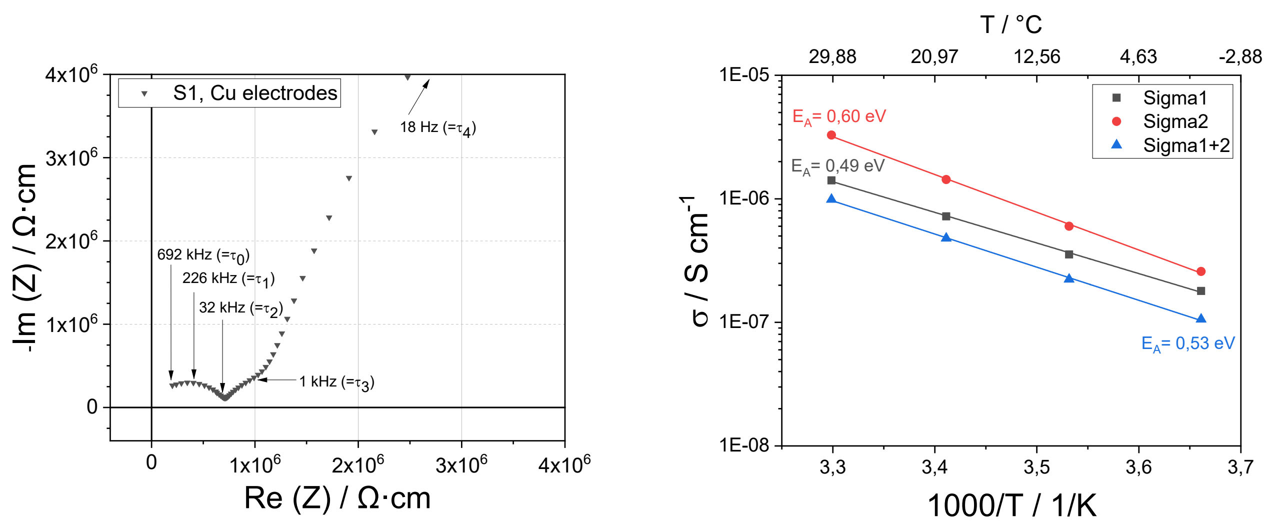


Figure 2: Left: impedance spectrum of a LLZO tape ("S1") with Cu electrodes; right: logarithmic plot of the conductivities according to the equivalent circuit consisting of 2 RC elements (Sigma 1 and Sigma 2) and one CPE element for the blocking electrodes.

GOALS AND …

- Densification of the LLZO by sintering
- Substrate with high lithium-ion conductivity (>10^{-5} S/cm)
- Homogenous microstructure
- Transfer of the manufacturing process of pressing and sintering to scalable methods (tape casting)

CHALLENGES

- High sintering temperature of LLZO
- Lithium loss during sintering at high temperatures
- Complete densification of LLZO without pores or phase transition due to lithium loss

RESULTS

Impedance spectroscopy with lithium electrodes

- Impedance spectroscopy with Li electrodes (figure 3) was measured in comparison to the measurement with Cu electrodes (figure 2).
- After attaching the Li electrodes without pressure or heat, the spectrum consists of three semicircles on the first sight, which is in accordance to the expectation to see one semicircle for the bulk, for the grain boundary and the interface resistance, respectively.
- After heating the sample stack, only two semicircles are visible by eye. Since one would expect three semicircles to appear, the question regarding the physical interpretation arises.

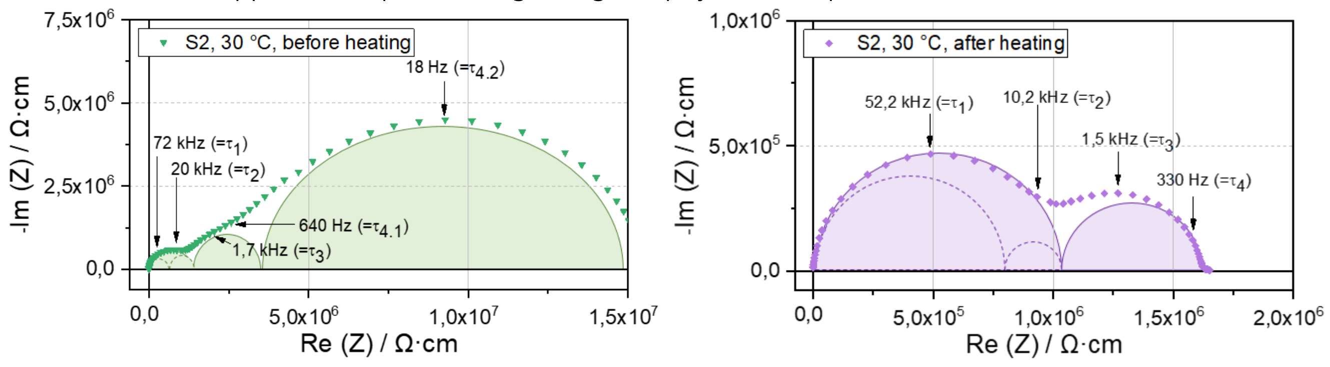


Figure 3: Impedance spectra of one LLZO tape ("S2"), left: Li chip was applied on the Li coating without external pressure; right: the contact between the Li chip and the Li coating was improved by heating the stack to 175 °C.

- Anyhow, the best fitting quality was achieved by using 3 RC elements, assuming that the semicircles 1 + 2 after heating equal the semi-circle 1 before heating.
- The activation energies of semi-circle 1 shifts from 0.51 eV to 0.44 eV after heating, which is comparable to the activation energy of the bulk conductivity (Cu electrodes, figure 2)
- Activation energy of semicircle 2 after heating is the same like that of the grain boundary as well as the interface before heat treatment, both have the same activation energy, what makes it very difficult to separate those processes from each other

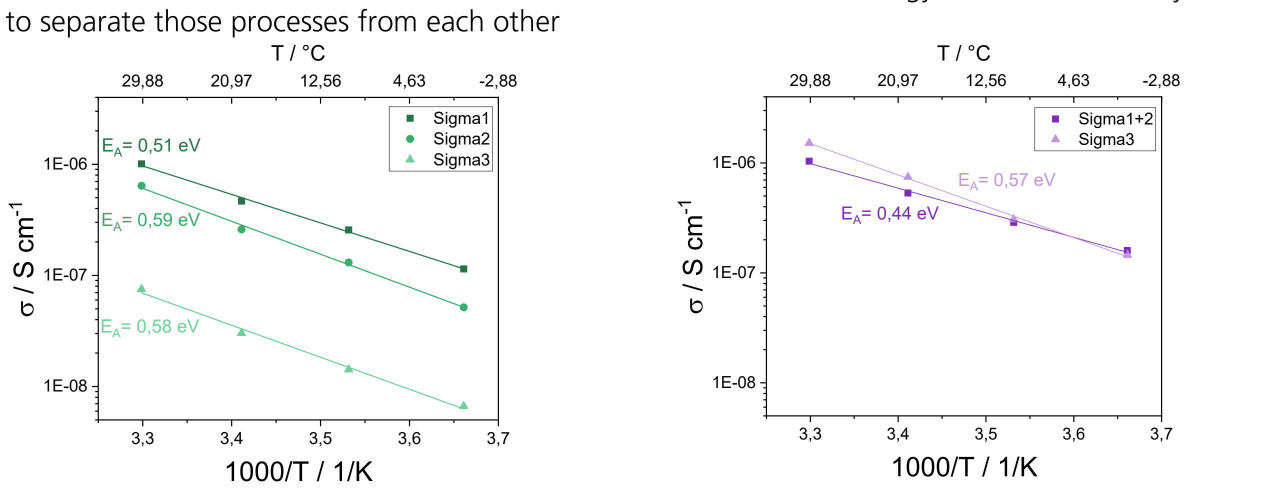


Figure 4: Logarithmic plot of the conductivities according to the equivalent circuit, consisting of 3 RC-elements, left: before heating; right: after heating.

- To get a better understanding of the impedance spectra, a DRT analysis was conducted
- The DRT analysis reveals a high complexity of the spectrum, which could be confirmed by measurements of pressed and sintered LLZO pellets.
- The peak locations can not directly be compared between the Cu and Li-measurements. The peak shift could result from the contact quality, which might be lower with lithium electrodes. Within the Li measurements, τ_1 and τ_3 do not shift (height or location), therefor they can be attributed to the bulk and grain boundary conductivity. The yellow area of $\tau_{4.x}$ contains several peaks, which could be attributed to the interface. τ_2 shifts in height after heating the sample, what implies its dependence of the contacting method. Its physical interpretation needs to be evaluated in further investigations.

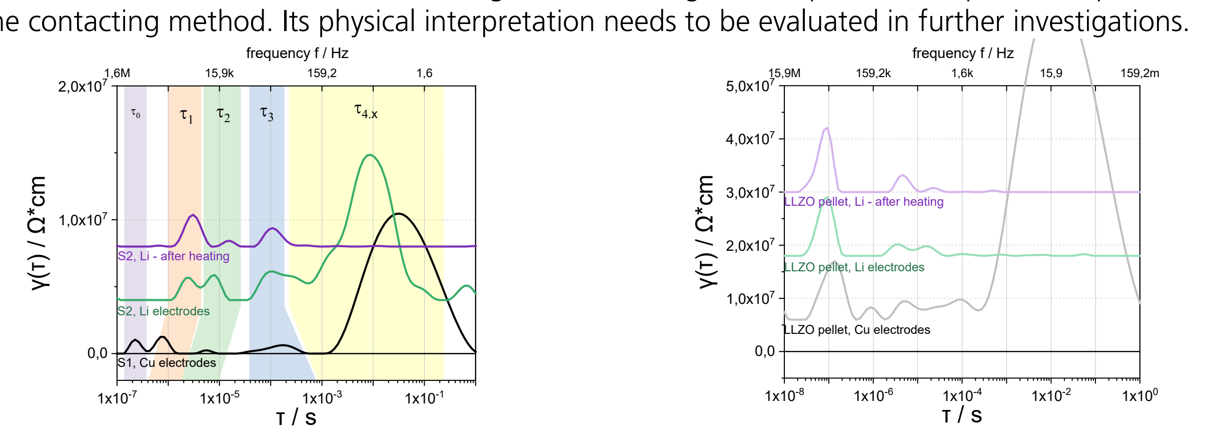


Figure 5: DRT analysis (Distribution of relaxation times); left: analysis of the impedance spectra for LLZO tapes shown in figures 2 and 3; right: reference analysis of a LLZO pellet with Cu- as well as Li electrodes.

SUMMARY

A tape casting process including a slurry recipe, was developed. By the use of Li_2CO_3 as sintering additive, the tape densification could be improved. The overall ionic conductivity of the tape is about $1 \cdot 10^{-6}$ S/cm. Lithium electrodes could be applied as well. By the use of DRT analysis, the impedance spectra could be understood more properly. The bulk conductivity as well as the grain boundary conductivity could be allocated to the segments of the spectra.

OUTLOOK

The slurry and tape composition will be further investigated and adapted to improve the homogeneity of the microstructure as well as the ionic conductivity. It is crucial to understand the impedance spectrum more properly. Additional experiments are planned with laminates and sintered pellets. The contact will be varied systematically. The contact quality should be evaluated by optically.

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[1] Murugan, R.; Thangadurai, V.; Weppner, W. (2007): Fast lithium ion conduction in garnet-type Li(7)La(3)Zr(2)O(12); Angewandte Chemie 46 (41).

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