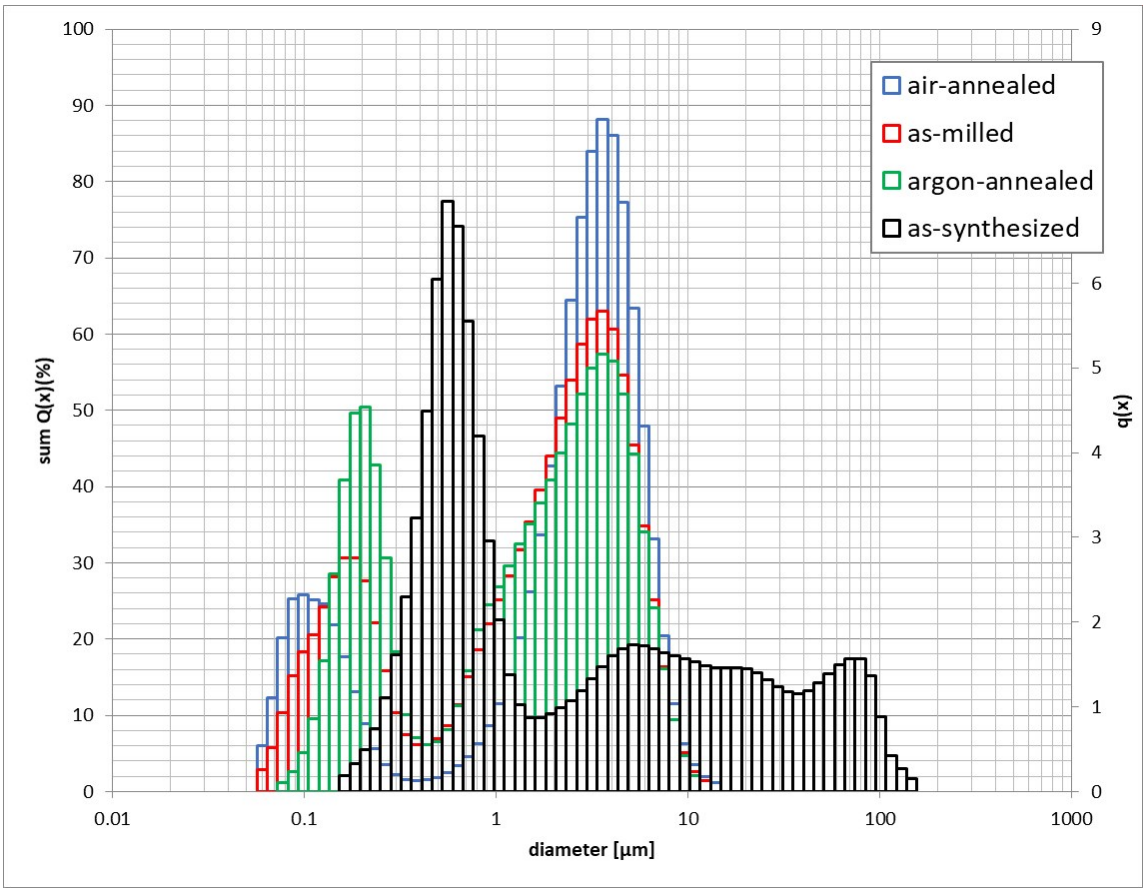
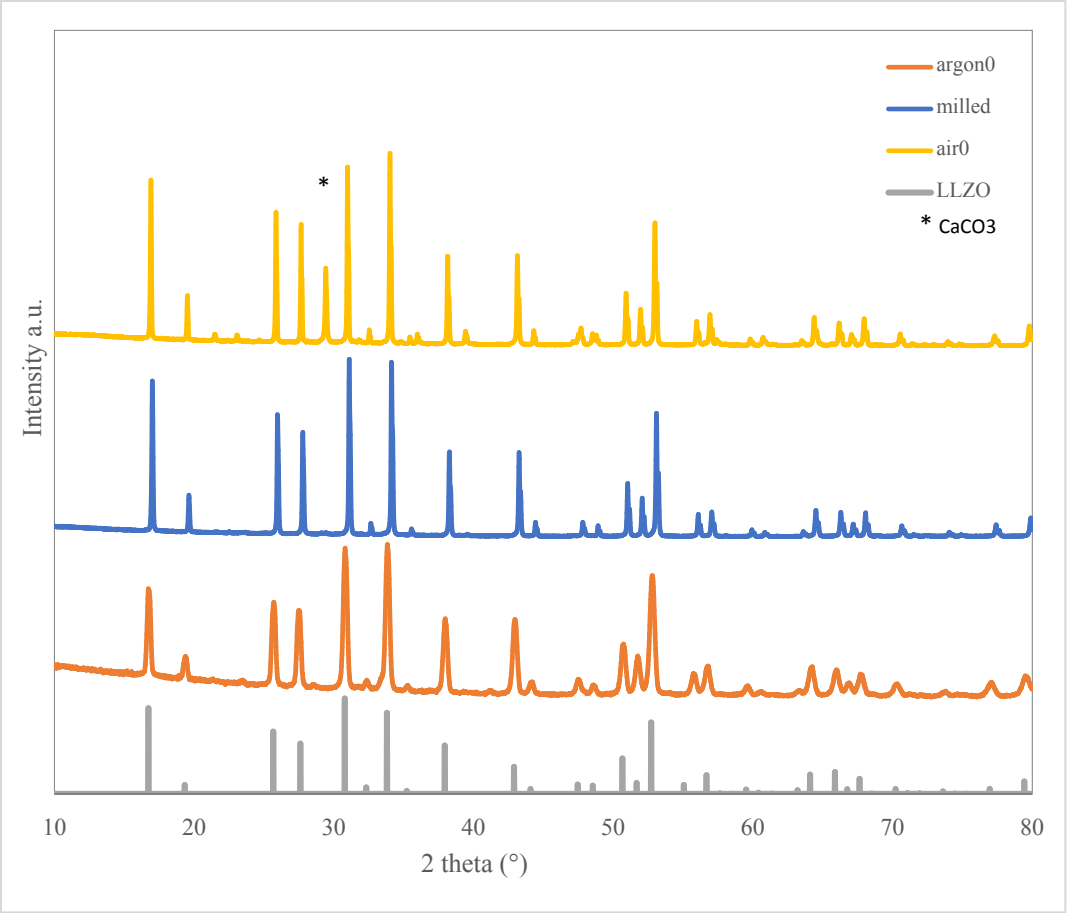
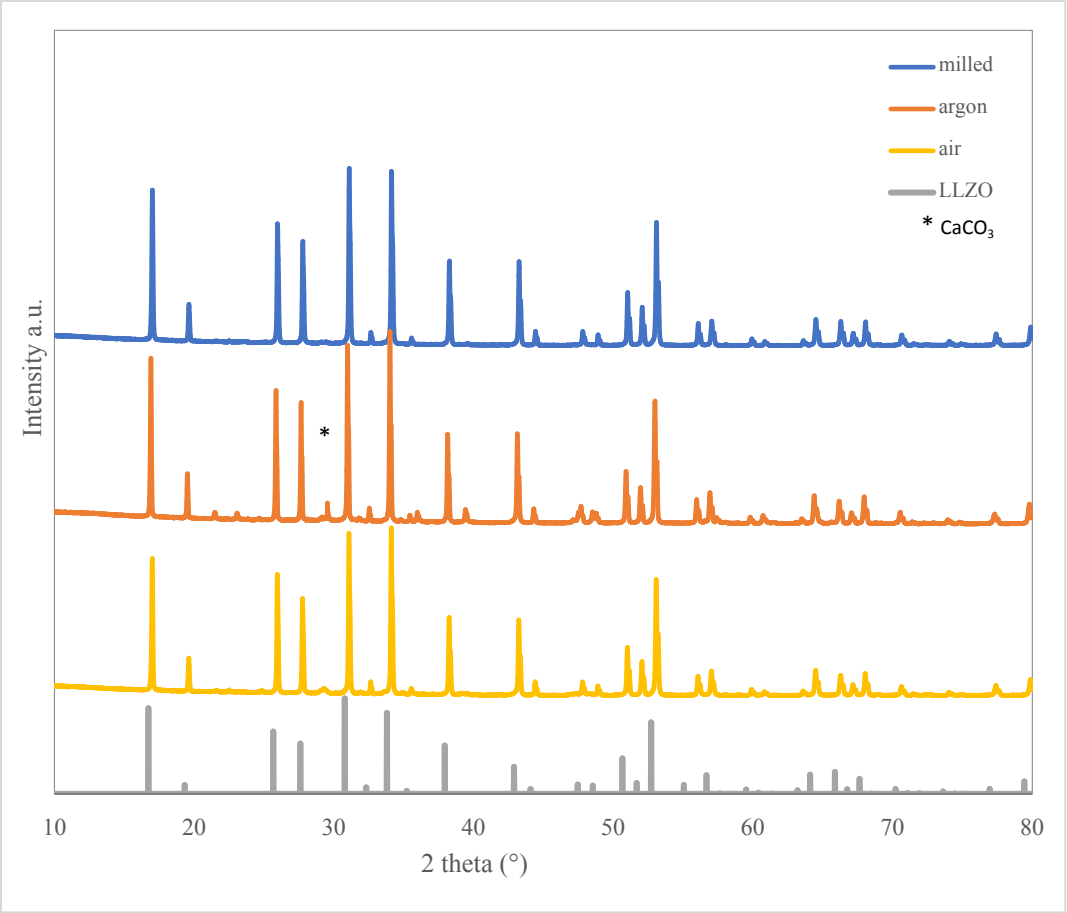


Supp 1 Particle size distribution of the LLZO powders before milling, after milling and after annealing

The difference in particle size distribution for LLZO powders with different pre-treatments are minor. The differences are not expected to have a significant influence on the rheological behaviour of the slurry or sintering behaviour of the green tapes.



Supp 2 XRD pattern of LLZO powders after pre-treatment



Supp 3XRD pattern of LLZO tapes with different pre-treatment after sintering

All samples show cubic LLZO. Additional peaks in the argon sample can be attributed to $CaCO_3$ in the sample holder.

Supp Tab. 1 Sample overview with electrochemical properties of LLZO and interface properties

Sample	Pre-treatment	storage	Conductivity 25°C [S cm^{-1}]	Critical current density 50°C [µA cm^{-2}]	Interface resistance [Ohm]
Argon0	Argon	-	$1.89 \cdot 10^{-4}$	5.1	290
Argon0,1	Argon	1 day ethanol	$2.20 \cdot 10^{-4}$	35.7	310
Argon1	Argon	1 day air	$2.66 \cdot 10^{-4}$	<5.1	1900
Argon7	Argon	7 days air	$2.75 \cdot 10^{-4}$	114.6	345
Argon1,7	Argon	7 days ethanol	-	-	
Air0	Air	-	**$3.90 \cdot 10^{-4}$**	**318.5**	132
Air0,1	Air	1 day ethanol	$2.08 \cdot 10^{-4}$	35.7	350
Air1	Air	1 day air	$1.19 \cdot 10^{-4}$	127.4	178
Air7	Air	7 days air	$7.87 \cdot 10^{-6}$	-	
Air1,7	Air	7 days ethanol	-	-	
Milled	as-milled	-	$1.09 \cdot 10^{-4}$	127.4	186

Interface resistance was carefully checked for all samples prior to CCD measurements.

In comparison to free-sintered LLZO pellets, the CCD of tape-cast separators is lower. However, in case of thick and dense pellets, the sample surface is usually fine polished, and the metallic anode is applied with high pressures. This allows for a well-defined, defect-free sample surface and good wetting. Fully optimized LLZO pellets can reach interface resistances close to 0 Ohm and therefore approach the limiting range of the CCD values, which is no longer governed by the LLZO layer, but by the diffusion of lithium to the interface.

Unfortunately, polishing as well as the application of high pressures is not possible for thin layers obtained by tape-casting, thus the CCD is expected to be lower.

Supp Tab. 2 Composition of the LLZO powders with varied pre-treatment by ICP-OES, normalized for Zr 1.6

Pre-treatment	Li	La	Zr	Ta	Al
Milled	7.77	3.22	1.6	0.41	0.20
Air	7.71	3.18	1.6	0.41	0.17
Argon	7.75	3.15	1.6	0.40	0.20
target	6.45	3.00	1.6	0.40	0.05

ICP-OES shows Al-uptake from the crucibles during the high-temperature treatments. Differences in La-content are within the error of the method for ICP-OES. Excess Lithium is present in all LLZO powders after pre-treatment.