Superior sintering behavior and ionic conductivity: Facile coating methods for improved electrolyte materials

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Introduction

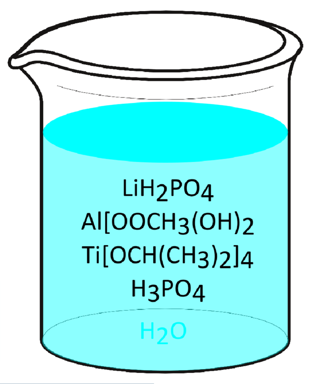
Solid-state batteries are intensively investigated as a disruptive energy storage technology. Oxide and phosphate-based Li-ion conductors such as $Li_{1.5}Al_{0.5}Ti_{1.5}(PO_4)_3$ (LATP), which crystallizes in the rhombohedral $NaZr_2(PO_4)_3$ structure [1], and $Li_{6.45}La_3Zr_{1.6}Ta_{0.4}Al_{0.05}O_{12}$ (LLZ), with a garnet structure [2] show properties like improved safety, high ionic conductivities (0.1 – 1 mS/cm [3,4]); and electrochemical stability compared to incumbent Li-ion battery technologies, but also require treatment at elevated temperatures.

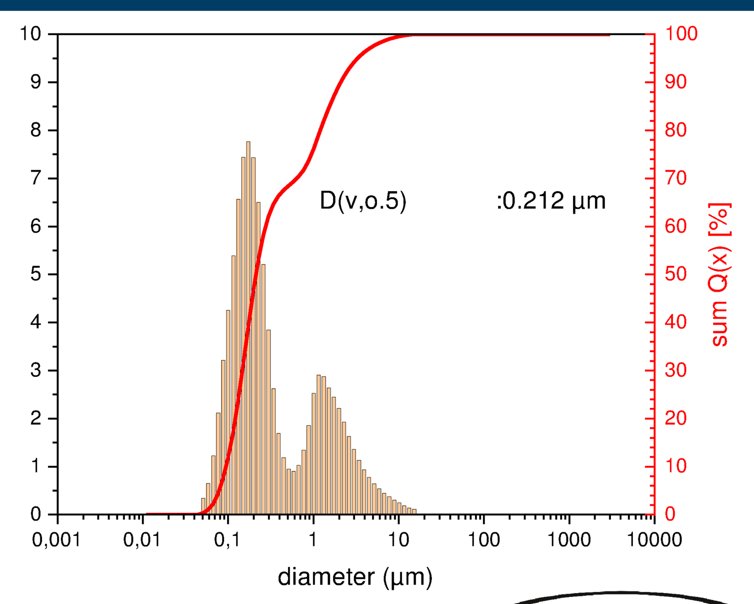
We present advanced processing methods for these ceramic electrolyte materials. By applying various surface coatings on electrolyte particles and electrode-electrolyte interfaces we aim to improve the sintering behavior and the electrode compatibility.

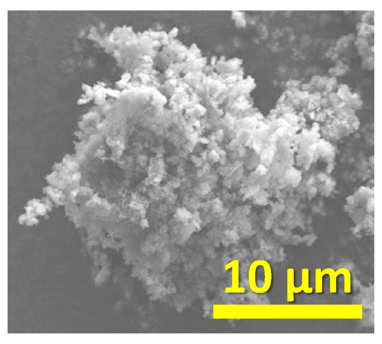
Experimental

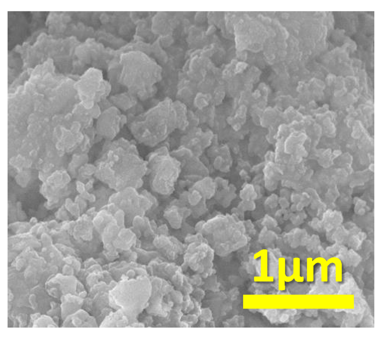
LATP

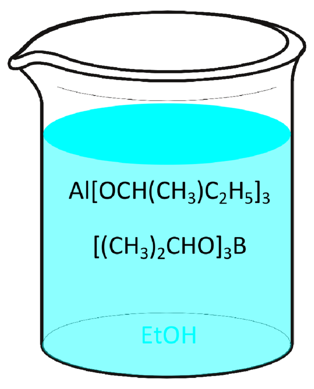
Stirring of dispersion → Drying → Calcination → Ball milling → Dispersing in solvent, addition of sol precursors → Gelation and Drying → Pressing discs and testing







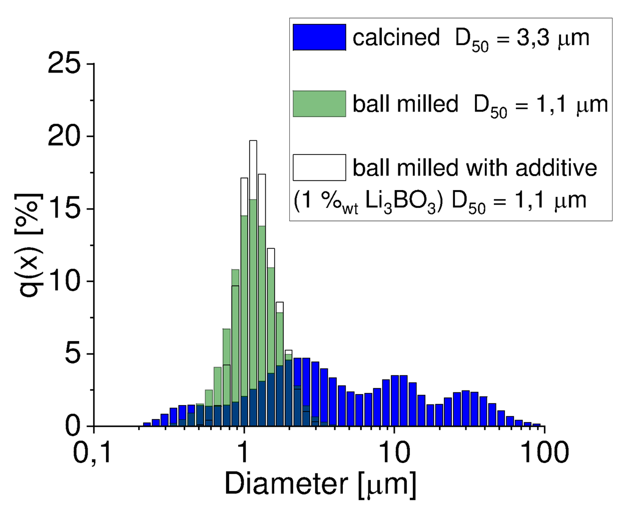


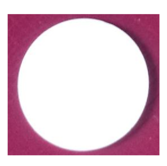


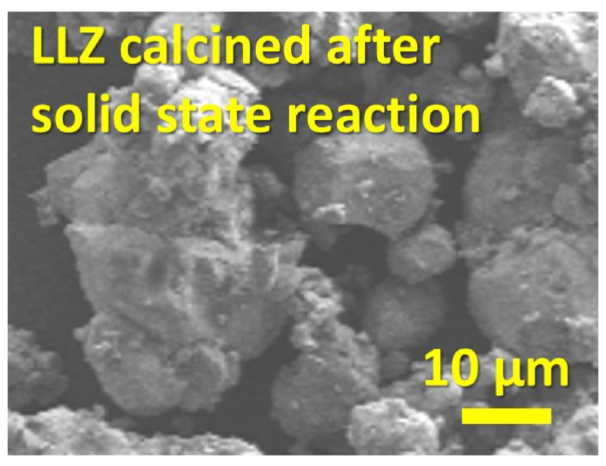
LLZ

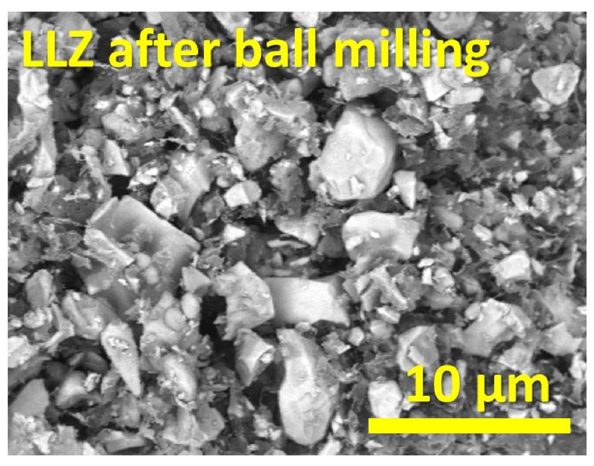
Solid state reaction to form LLZ from oxide-based precursors → Application of sintering additives → Dispersion through ball-milling / LLZ substrate coating by sol-gel process followed by calcination → Preparation of pellets (discs) through uniaxial pressing and sintering → Characterization:

- Crystallographic structure
- Porosity
- Ionic conductivity







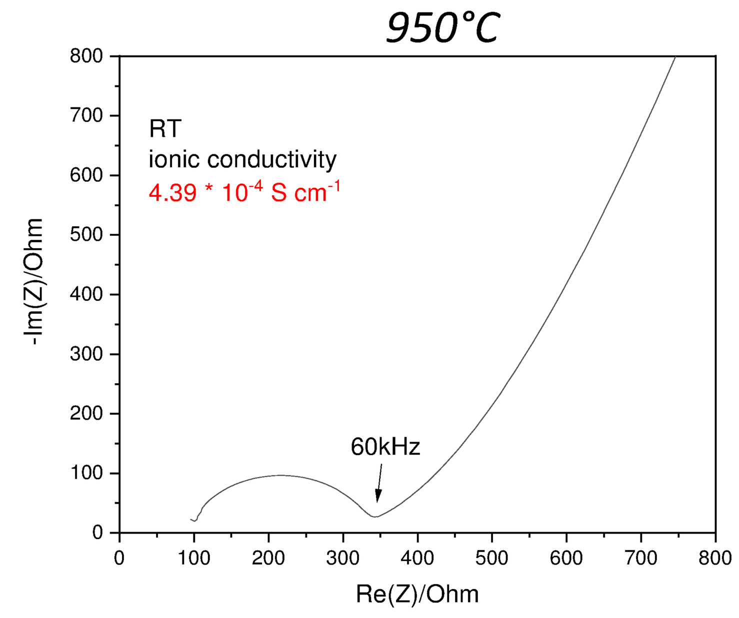


Results

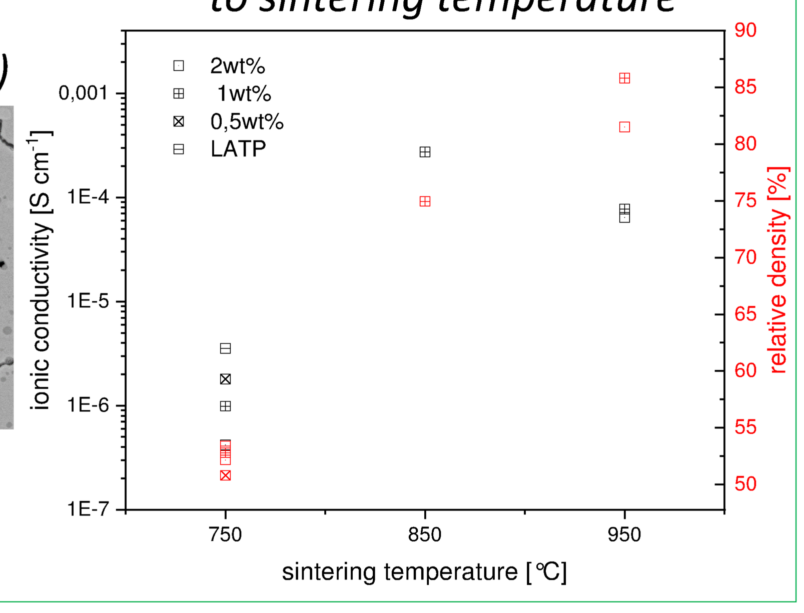
LATP

As expected the relative density increases with rising sintering temperatures and the grain boundary ionic conductivity decreases with lower sintering temperatures. A maximum is present at 850°C in the sample with modification. The SEM images show additional phases for the modified sample. Cracks are also found, which are expected to have a negative effect on the ionic conductivity.
The microstructure is typical for agglomerated primary powders, resulting in large grains and cracks.

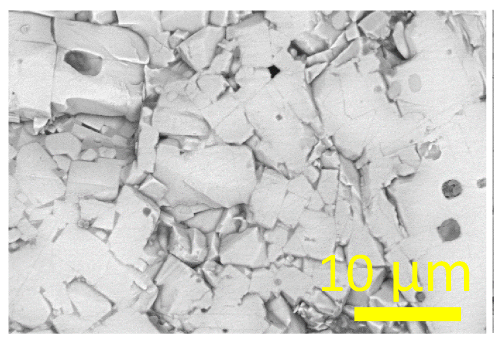
Impedance spectroscopy for unmodified sample sintered at 950°C



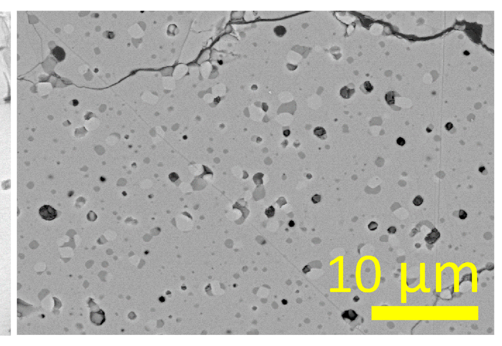
relative density and the ionic conductivity for modified and unmodified samples in relation to sintering temperature



pure LATP disc (sintered at 950°C)



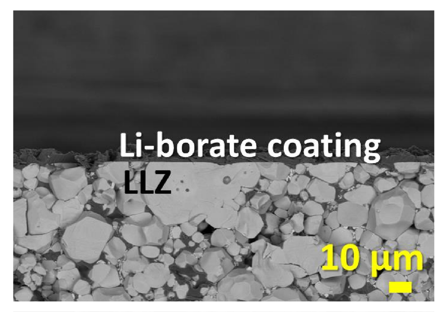
Modified LATP disc (2wt%; sintered at 950°C)

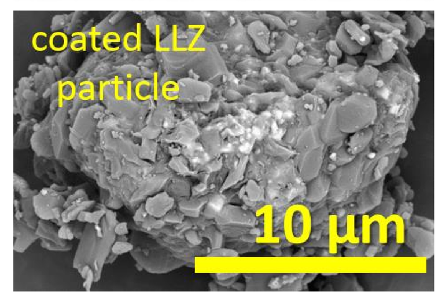


LLZ

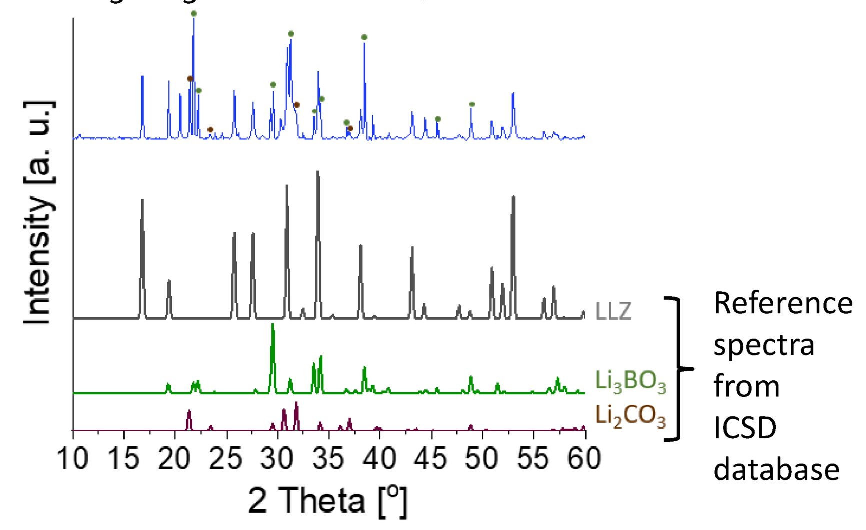
Spin-coating on planar pellet substrates yield model systems, which guide the development of powder coatings.

Applying the additive in powder form at low concentrations (1 wt%, 5 wt%) yielded the highest conductivity.
The coating composition depends on the precursor ratio (Li:B) and calcination temperature.

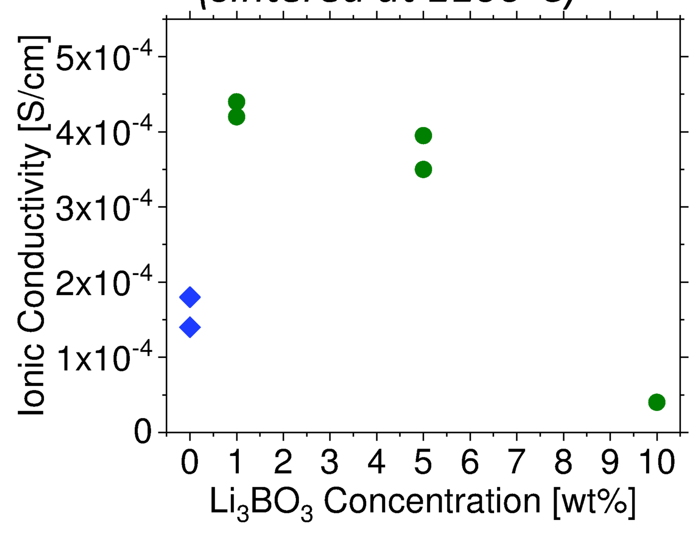




X-ray diffractogram of Li_3BO_3 coated LLZ pellet



Conductivity as a function of sintering additive concentration (sintered at 1100°C)



Summary

- LATP can be modified using sol-gel precursors leading to acceptable ionic conductivities at lower temperatures
- Key factors to further optimize the relative density and the sintering are control of particle size, elimination of agglomeration
- The application of lithium borate powder as a sintering additive yields improved ionic conductivity
- Wet chemical processing enables the application of lithium borate coatings on planar substrates and powders. The desired structure and stoichiometry can be achieved by controlling the precursor composition and calcination temperature

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