

Laser sintering of ceramic-based solid-state battery materials

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ABSTRACT

Solid-state batteries (SSBs) are a promising technology for high travelling ranges and safety in future electromobility. In SSBs, separator and liquid electrolyte materials are combined in a solid-state electrolyte layer. Possible materials for SSBs are ceramic oxides, for example LiCoO_2 (LCO) as cathode material and $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) as electrolyte material.

By means of screen printing, a mixed cathode material (mixture of cathode and electrolyte material to have higher ionic conductivity in the cathode) is applied on a stainless steel current collector foil and after thermal processing, the electrolyte material is printed on top of the sintered mixed cathode to create a half-cell. Both layers are thermally post treated (dried and sintered) in consecutive steps to produce functional layers for SSBs.

Conventional heat treatment is done in an oven process. A main disadvantage is the diffusion of materials into adjacent layers due to long process times (range of minutes) at high temperatures. Furthermore, the battery half-cell cannot be treated at high temperatures due to incompatibilities in decomposition temperatures of LLZO and LCO.

Preservation of the crystal structure and a suitable temperature management during the sintering process are of enormous importance. By means of laser processing, short interaction times (range of seconds and below) are realized. High heating rates show potential for reducing diffusion processes and preserving the crystal structure of the materials.

In this work, the influence of different interaction times on crystal structure and adhesion are investigated for laser sintering of LLZO and LCO micro particle layers.

Keywords: solid-state battery; laser processing; laser sintering; electromobility; composite cathode, LLZO, LCO

1. INTRODUCTION

Electromobility is a climate-friendly mobility concept and is becoming increasingly important, also due to restrictions imposed by government regulations¹. Current research is focused on the development of novel battery systems that further improve the safety and performance compared to currently used battery systems. Ceramic solid-state batteries are possible candidates for the new generation of battery systems for electromobility. They have the potential to achieve higher energy and power densities than conventional lithium-ion batteries (LIB), while being safer due to the elimination of organic liquid electrolyte materials.

A possible layer structure of a ceramic solid-state battery cell consists of a metallic current collector, a ceramic cathode layer, a ceramic electrolyte layer and an anode layer made of lithium metal. The solid-state battery layer system considered in this study is shown in Figure 1. A thin metallic substrate made of steel with a layer thickness of approx. 100 μm is used as the current collector. The mixed cathode (100 μm) on top is intended to generate both ionic and electrical conductivity. It consists of a mixture of cathode active material (e. g. lithium cobalt oxide (LCO) or lithium nickel manganese cobalt oxide (NMC)) and electrolyte material (e. g. lithium lanthanum zirconate (LLZO)).

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On top there is the electrolyte layer (e. g. LLZO), which acts as a separating layer between the two electrodes. Solid electrolytes usually have lower ionic conductivities than conventional liquid electrolytes². To overcome this disadvantage, the layer is aimed to be a thin film with a thickness of 10 μm or less. The anode could be lithium metal due to the stability of lithium metal against LLZO³.

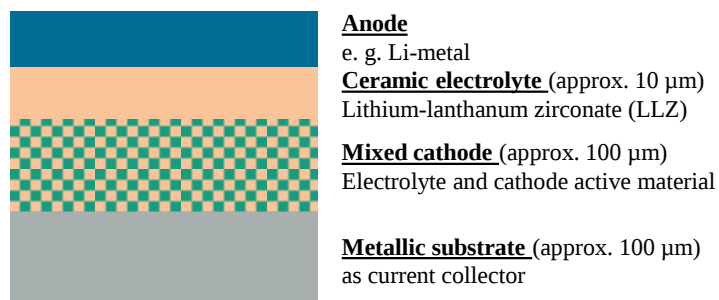


Figure 1. Exemplary structure of a ceramic solid-state battery cell

The multilayer system can be applied on the metallic substrate by screen printing of pastes, for example. These layers have to be thermally treated afterwards to evaporate the liquids and auxiliary materials needed for the printing process, and to sinter the remaining functional particles. Conventional oven processes are limited in the production of these multilayer systems. Oven sintering (Figure 2 left) is characterized by long interaction times (in the range of minutes), which lead to a homogeneous temperature distribution in the particles and in the entire sample (or multilayer system). Due to the long interaction times, element diffusion can occur between the materials. This can lead to a change in the crystal structure of the material, resulting in undesirable side phases with a reduced electrochemical performance. When building a multilayer system, there might be temperature incompatibilities between the sintering and degradation temperatures of the materials to be functionalized. Another possibility is rapid thermal processing (RTP). It is known as photonic sintering and means that the samples are heated by the light absorption in a quartz-lined furnace from all sides. This results in faster heating (in the range of seconds up to minutes) than oven sintering but not as fast as laser sintering (described below) and not as layer selective.

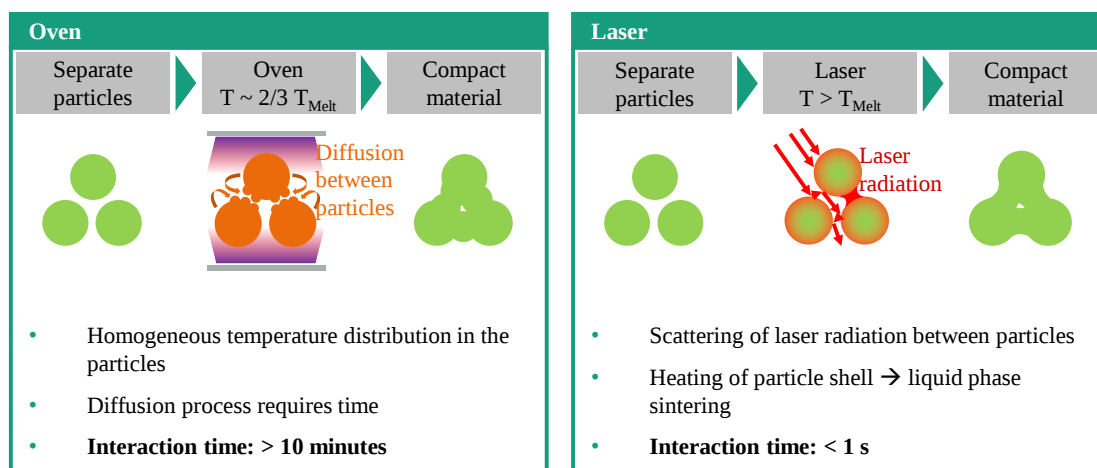


Figure 2. Comparison of oven sintering and laser sintering

The use of laser processes can be a solution to overcome these drawbacks. Laser sintering (Figure 2 right) is characterized by short interaction times in the sub-seconds range. The laser radiation is scattered between the particles and absorbed by them, resulting in heating, and melting of the particle shells. This process is therefore referred to as liquid phase sintering. Due to the shorter interaction times, diffusion is reduced, and the crystal structure of the material can be

preserved. In addition, laser sintering offers layer-selective heating, which allows temperature incompatibilities to be overcome.

In this work, the laser sintering process for a mixed cathode layer on a metallic current collector is presented. The challenge in laser sintering is to achieve complete sintering of the mixed cathode material over the layer thickness and achieve adhesion to the substrate while maintaining the crystal structure and thus its electrochemical properties such as ionic conductivity. Due to the high absorbance of the mixed cathode layer at the wavelength used, most of the optical energy is absorbed in the upper part of the layer, while heat dissipation into the lower part of the layer is based on thermal conduction. To investigate the influence of different interaction times, different process speeds are used. The mixed cathode layers are tested for adhesion, and the resulting crystal structure is analyzed and benchmarked to a sample sintered with rapid thermal processing (RTP). The experiment will give first insights into the feasibility of laser sintering in SSB production and the possibilities of process scalability.

2. MATERIALS AND METHODS

2.1 Material and sample preparation

As mixed cathode material a mixture of cathode active material and electrolyte material is used. The cathode active material is LiCoO_2 (LCO) with particle sizes of $d_{10} = 1.2 \mu\text{m}$, $d_{50} = 3.4 \mu\text{m}$, $d_{90} = 6.2 \mu\text{m}$. The electrolyte material is $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) with particle sizes of $d_{10} = 0.6 \mu\text{m}$, $d_{50} = 3.4 \mu\text{m}$, $d_{90} = 6.3 \mu\text{m}$, partially doped with tantalum and aluminum. The ratio of the two materials is 1:1 (mass fraction) and mixed with terpineol as solvent and ethyl cellulose as binder to obtain a screen printable paste. The resulting paste has a powder loading of 50 wt%. A screen printer is used to deposit the material on a 2 mm thick current collector made of stainless steel (EN 1.4301). After printing and prior to the laser sintering process, the samples are dried for 2 h at 35 °C in an oven to remove the solvent. They are then heated to 500 °C with a heating rate of 2 K/min and a dwell time of 30 minutes for binder removal. The dried and debindered mixed cathode layers have a layer thickness of $(15.66 \pm 1.05) \mu\text{m}$, measured with a laser scanning microscope.

The optical properties (transmittance T and reflectance R spectra) of the mixed cathode material printed on a glass substrate are measured with an UV/VIS/NIR spectrometer Lambda 1050 from PerkinElmer. The absorbance is calculated by $A = 100 - R - T$ to about 73 % at a wavelength of 1470 nm (Figure 3).

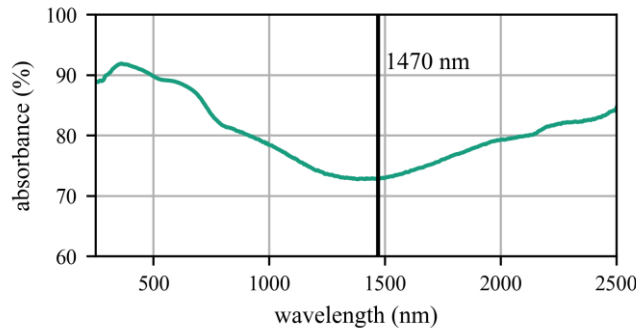


Figure 3. Absorbance spectra of a mixed cathode layer (about 15 μm thickness) printed on a glass substrate (after drying and binder removal)

The RTP sample, in contrast to the laser-sintered sample, is made using a 100 μm metallic current collector (EN1.4767). RTP sintering is conducted with a heating rate of 600 K/min up to 1000 °C (which adds up to a total interaction time of about 98 s (including a time period of 50 s above 500 °C which is taken into account for comparability to the laser sintering of 500°C preheated samples, which are explained in Chapter 2.2).

2.2 Experimental Setup

For laser sintering of the mixed cathode, a line-beam laser system from Limo GmbH with a wavelength of 1470 nm and a maximum laser power of 250 W is used. A line beam shape is relevant for industrial upscaling and a possible approach

for laser processing in roll-to-roll machines (R2R). The laser beam has a line shape of 6.3 mm x 0.084 mm (length and width). The experimental setup for laser sintering is shown in Figure 4. The sample is placed on a sample holder. In this case it is a hotplate which offers pre-heating during laser sintering to improve the adhesion between layer and substrate. The whole system is placed on a two-axis handling system which moves the sample under the laser beam with a certain feed velocity v_{feed} . For processing a complete sample, three lines are placed next to each other every 6.7 mm.

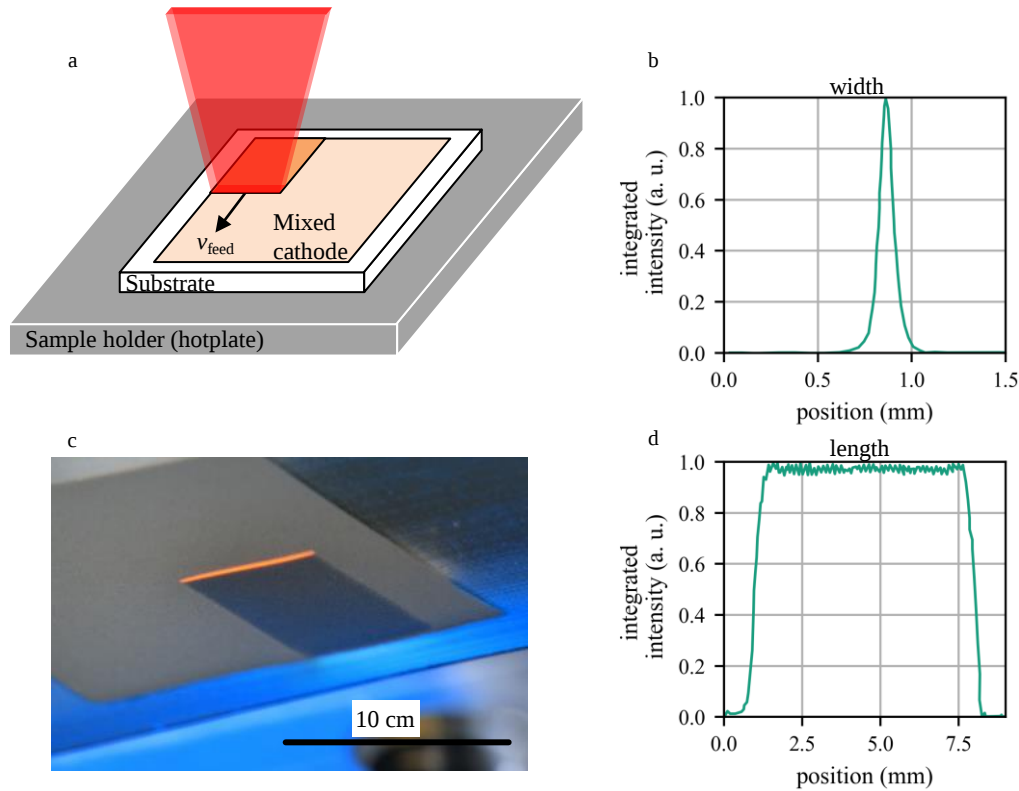


Figure 4. Experimental setup for laser sintering (a), laser line profile (b, d) and a photo of the laser process (c)

Three different feed velocities are investigated. Beginning from 1 mm/s the velocity is multiplied by four for each progression, resulting in 4 mm/s and 16 mm/s. All experiments are conducted with a preheating temperature of 500 °C (hot-plate). In relation to that, the expected sinter temperature is between 1000 °C and 1100 °C which is known from previous experiments. Several experimental series with increasing laser power at fixed feed velocities (1, 4, and 16 mm²/s) are conducted to identify parameter sets which are suitable to obtain sufficient layer adhesion to the substrate. Adhesion is verified by tape tests. A layer is seen as sufficiently adhesive if no particles (visible to the eye) get stuck on the tape. The results are listed in Table 1.

Table 1. Parameters used (feed velocity and laser power needed for adhesion), calculated energy per area and interaction time.

<u>Feed velocity (mm/s)</u>	<u>Laser power (W)</u>	Process parameters		
		<u>energy per area (J/mm²)</u>	<u>interaction time (ms)</u>	<u>intensity (W/mm²)</u>
1	34.5	5.48	84.0	65.2
4	42.7	1.69	21.0	80.7
16	53.5	0.53	5.3	101.1

For each parameter set, energy per area and interaction time are calculated. The laser power and related energy per area do not scale linearly with feed velocity. A reason might be a change in thermal conductivity from a particulate to a mol-

ten state within the upper layer (which appears to be different between the samples made with different parameter sets) or drain of thermal energy from the sample to the sample holder etc. during longer process times.

The sintering degree is investigated with a scanning electron microscope (SEM) Leo 1455 EP by Carl Zeiss AG. The sample surfaces are sputtered with gold to avoid charge effects. The crystal structure is measured in Theta-2Theta geometry between 15° and 60° with a Bruker Advance D8 X-Ray diffractometer having a Cu X-ray tube ($\lambda = 1.45059 \text{ \AA}$). Electrochemical impedance spectroscopy (EIS) was performed for selected parameters to determine the ionic conductivity of the laser-sintered mixed cathode layers. Measurements were conducted with Autolab M204 device from Deutsche METROHM GmbH & Co. KG in combination with ECC-Ref test cell from EL-Cell in frequency range from 0.01 Hz to 10^6 Hz. For EIS measurements, samples with 17 mm diameter were laser sintered and sputtered with gold in the middle of the surface resulting in a measuring area of 1.13 cm^2 .

3. RESULTS

Figure 5 shows SEM images of the surfaces of laser-sintered mixed cathode layers at different feed velocities (and different related laser power values). All surfaces show a sintering behavior with different surface porosities. Some parts seem to be melted. But due to the dewetting behavior at the surface the sintering degree cannot be quantified or compared by surface SEM pictures. Cross-sectional SEM pictures are not yet available due to difficulties at preparing the cross-sections but will give more information about the sintering behavior in the future, especially depth selective.

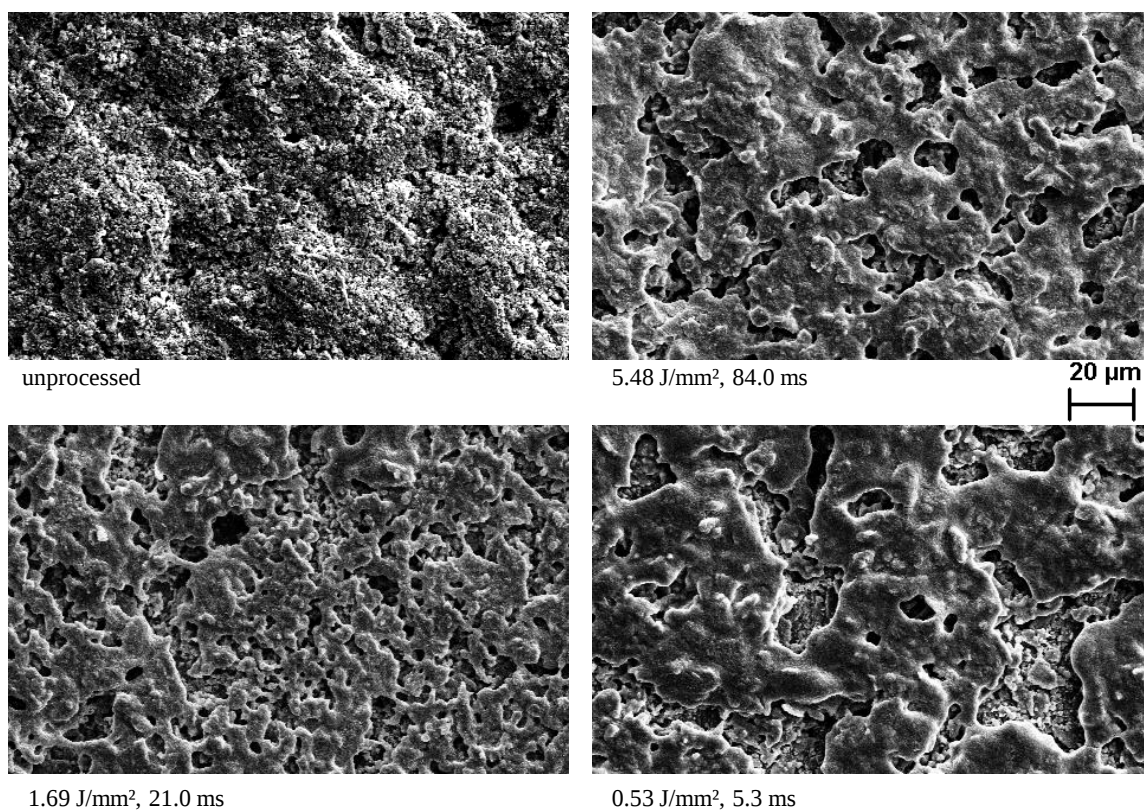


Figure 5. SEM images of the surfaces of laser-sintered mixed cathode layers with different interaction times (and laser power). Melted areas at the surface seem to be dewetted.

The desired crystal phases are LLZO and LCO and their preservation is important for obtaining sufficient electrochemical properties. Figure 6 shows the diffractograms of dried but unprocessed, laser processed and conventionally processed (RTP) samples. The adhesion of the mixed cathode layer to the substrate is given for all processed samples.

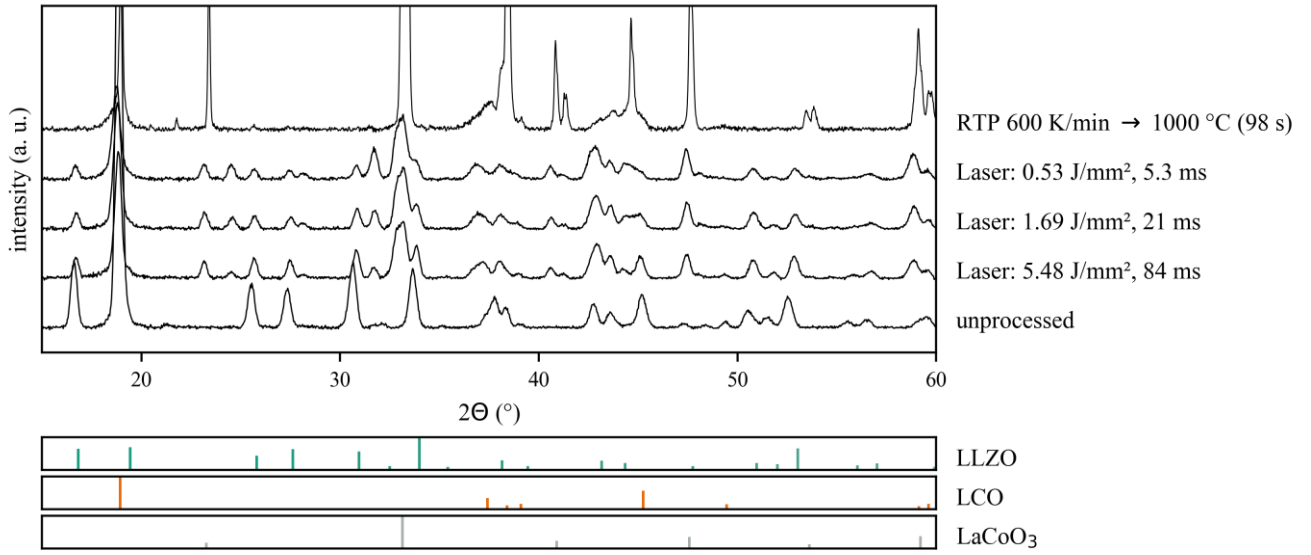


Figure 6. XRD measurements of unprocessed, laser sintered and RTP sintered, mixed cathode layers.

Alle processed samples show an increase of side phases and a decrease in LCO and LLZO main phases compared to the unprocessed sample. With decreasing interaction time in laser processing (combined with increasing laser radiation intensity), the amount of the side phase lanthanum cobalt oxide (LaCoO_3) increases, while the amount of the desired main phase LLZO decreases. LaCoO_3 is a reaction product of LLZO and LCO. The LCO peak intensities decrease and show a shift to smaller angles. The shift could be due to a small loss of lithium from the LCO. Additionally, the LCO peaks widen which indicates a change in crystallinity. Compared to the laser sintered samples, the RTP sample shows a higher intensity of the side phase LaCoO_3 . At the same time, the desired phase LLZO, which is relevant for ionic conductivity is less present than in the laser-sintered samples. The differences in the XRD diffractograms of the RTP and the laser sintered samples can be attributed to two main aspects: The first is the interaction time, which is in the ms regime for the laser process, and can preserve the crystal structure and suppress diffusion as well as loss of lithium. The second aspect is the location-specific energy absorption of the sample. Laser sintering offers layer-selective heating at short interaction times, which leads to a colder substrate and less material interaction at the interface.

EIS measurements results are shown as Nyquist-Plots in Figure 7. The real part of the resistance is much lower for the laser-sintered sample as for the RTP sintered sample. For the laser-sintered sample, the ionic conductivity is calculated with the relation

$$\sigma = \frac{1}{R} \cdot \frac{A}{d} \quad (1)$$

from the real part of the resistance to $2.3 \cdot 10^{-4} \text{ S/cm}$, assuming a layer thickness of $15 \text{ }\mu\text{m}$. The ionic conductivity is lower compared to conventionally sintered LLZO disks with almost full density⁴ ($1 \cdot 10^{-3} \text{ S/cm}$). The reason for this could be the more porous morphology of the laser-sintered layer and a not yet perfect contact between the remaining grains due to the short interaction times. Also, it must be considered that the measured sample is a composite cathode and not a pure LLZO sample.

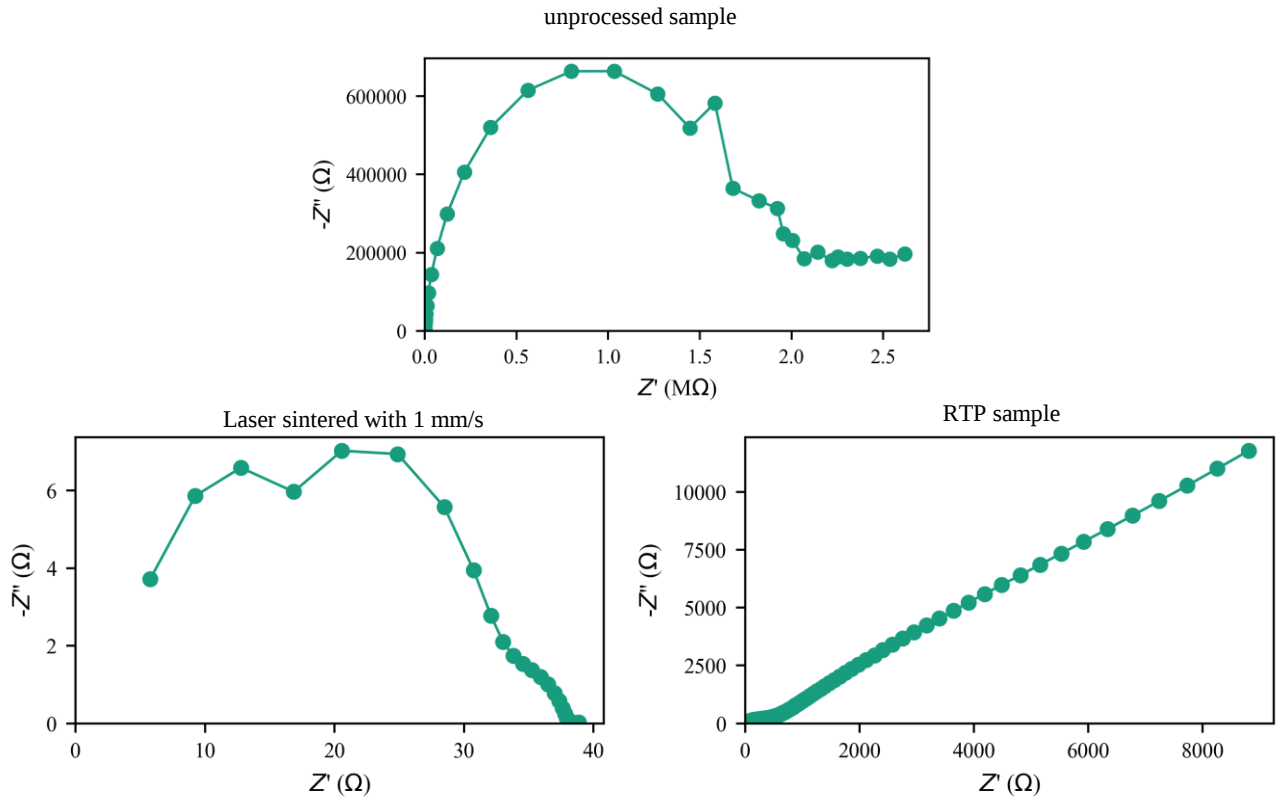


Figure 7. Nyquist-Plots from electrochemical impedance spectroscopy measurements of unprocessed (top), laser-sintered (bottom left) and RTP sintered (bottom right) mixed cathode layers.

4. CONCLUSION AND OUTLOOK

A laser sintering process of ceramic mixed cathode layers for thin-film solid-state batteries was presented. Laser sintering with different interaction times is compared to RTP sintering with interaction times two orders of magnitude higher. XRD measurements from laser sintered samples show a higher amount of desired phases LLZO and LCO compared to RTP sintered samples. This results in a lower resistance of the laser-sintered layer. The best ionic conductivity of a laser-sintered mixed cathode is $2.3 \cdot 10^{-4}$ S/cm.

The next step is to investigate the dependence of the electrochemical properties on the laser process parameters, especially the interaction time. Additionally, battery half-cells will be made using laser sintering. For this purpose, electrolyte material is applied to a laser-sintered mixed cathode and laser-sintered. The electrochemical properties must not be destroyed by excessive heat input. Both steps are to be examined for upscaling. In addition, process monitoring, for example by means of pyrometry, will be integrated.

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