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Laser sintering of ceramic-based solid-state battery materials

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Abstract

Solid-state batteries (SSB) can increase gravimetric energy density and safety compared to conventional lithium ion batteries. Possible materials for SSB are ceramic oxides, for example $LiCoO_2$ (LCO) as cathode material and $Li_7La_3Zr_2O_{12}$ (LLZ) as electrolyte material. Due to the low ionic conductivity of the cathode material it is necessary to mix the cathode material with the electrolyte to generate a mixed cathode with higher ionic conductivity. Microparticle layers of cathode and electrolyte materials must be sintered to reach a functional and dense layer. A laser sintering process enables short interaction times at elevated temperatures. Therefore, diffusion processes and side phases could be reduced. In this work, mixed cathode layers consisting of LCO and LLZ were screen printed on steel substrates generating a direct contact to the current collector and afterwards laser sintered. Crystallographic investigations by x-ray diffraction revealed the existence of the desired phases (LLZ and LCO), while the densification was successfully observed by scanning electron microscopy. The adhesion of the layer to the substrate was proven by tape tests. A pyrometry based control of the laser power is implemented and different process temperatures are compared. Additionally, a thermal pre-heating on a hotplate was applied leading to an improved layer-substrate adhesion.

Keywords: solid-state battery; laser processing; laser sintering; electromobility;

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1. Motivation

In recent years, electromobility has become increasingly important as a climate-friendly mobility concept (Nat. Plattform Elektromobilität, 2014). Appropriate battery systems are required to achieve high ranges and meet high safety standards. For this reason, research on alternative battery systems is currently being conducted, whereby new material combinations can be used to generate higher energy and power densities than achieved with conventional lithium-ion batteries (LIB). One alternative battery system is the ceramic solid-state battery.

The functionalisation of ceramic solid-state battery materials by means of laser radiation offers, on the one hand, the reduction of diffusion processes and thus the preservation of electrochemical properties at high process temperatures due to short interaction times. On the other hand, applying laser radiation offers layer selective heating so that, compared to a furnace process, individual materials can be built up in a layer system to form a battery cell despite temperature incompatibilities. A possible ceramic solid-state battery cell consists of a metallic current collector, a ceramic cathode layer, a ceramic electrolyte layer and an anode layer consisting of Li metal or a Li-Si alloy.

In this work, the laser sintering process of a mixed cathode layer on a metallic current collector is presented. Mixed cathode means a mixture of particles of ceramic cathode active material (lithium cobalt oxide, LCO) for the storage of Li ions, and ceramic electrolyte material (lithium lanthanum zirconate, LLZ) to increase the ionic conductivity. The challenge in laser sintering is primarily a suitable temperature management to achieve complete sintering over the layer thickness, on the one hand. On the other hand, the process temperature is limited during the process so that the materials keep their crystal structure and thus their electrochemical properties such as ionic conductivity. As a result of the high absorption coefficient of the mixed cathode layer at the wavelength used, most of the optical energy is absorbed in the upper part of the layer while the heat dissipation into the lower part of the layer is based on heat conduction. To improve the particle connection at lower temperatures than sintering temperature, a sinter additive with a lower melting point than the ceramic particles can be used. A pre-heating of the sample during the process can increase the interface temperature between layer and substrate and therefore lead to better adhesion.

2. Materials and Methods

2.1. Material System 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 D10 = 1.2 µm, D50 = 3.4 µm, D90 = 6.2 µm, the electrolyte material is $Li_7La_3Zr_2O_{12}$ (LLZ) partially substituted with Niob (Nb) with particle sizes D10 = 0.6 µm, D50 = 3.4 µm, D90 = 6.3 µm. The ratio of the two materials is 1:1 (mass fraction). Additionally, Li_3BO_3 (LBO) is mixed in as a sinter additive with a melting point around 700 °C (Shoji et al., 2016). The layers were produced by screen-printing, where the particles were processed as a paste with terpineol as solvent and ethyl cellulose as binder. The resulting paste has a powder loading of 45 wt% and of this, 8 wt% are LBO. A screen printer is used to deposit the material on a 2 mm thick current collector made of stainless steel (VDM 1.4301). Prior to the laser sintering process, the samples are dried for 3 h at 40 °C in an oven to remove the solvent and then heated up from 20 °C to 550 °C with a heating rate of 2 K/min for binder removal. Between the drying and binder removal, the samples are pressed at 130 °C with a force of 50 kN for two minutes.

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 70 % at a wavelength of 980 nm (Fig.1).

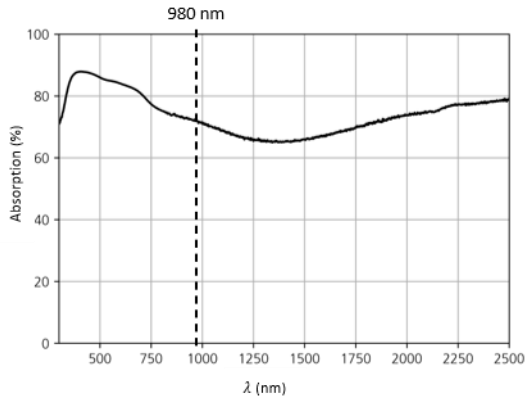

Fig. 1. Absorption spectra of mixed cathode material (about 25 µm) printed on a glass substrate (after drying and binder removal)

2.2. Experimental Setup

The experimental setup for the laser sintering process is shown in Fig. 2 (left). The main components are the laser source and a pyrometer. The sample is placed on a hotplate on a two-axes handling system and is moved in a meandric way by the handling system. The laser system used is a Dilas Compact Evolution diode laser with a maximum output power of 450 W (continuous wave, λ = 980 nm). The laser beam has quadratic top-hat profile with 1.85 mm edge length (Fig. 2 right). During the process, the heat radiation of a 1 mm diameter spot within the laser spot is detected by a pyrometer. For the pyrometry-based control of the laser power, a two-colour pyrometer (λ = 1.65 µm – 2 µm) is used.

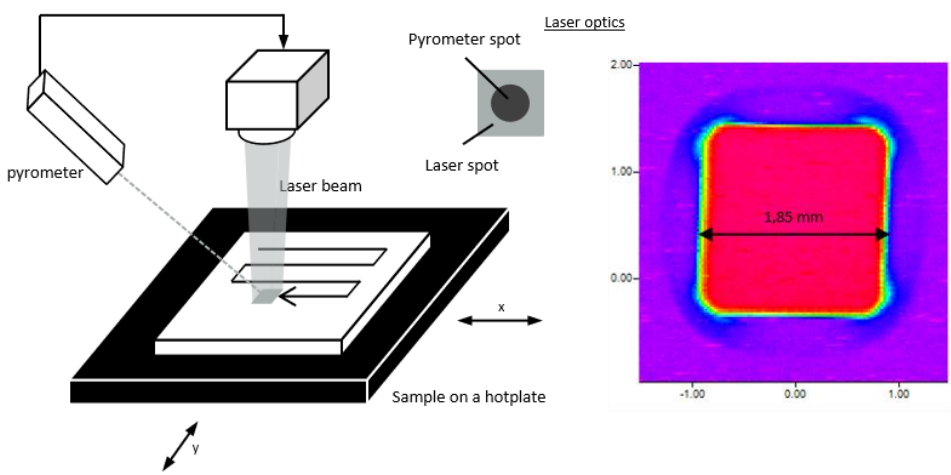

Fig. 2. Experimental setup for laser sintering (left) and laser intensity distribution (right)

To obtain absolute temperatures during the laser sintering process, the pyrometer is calibrated. For pyrometer calibration an unprocessed sample is placed on a hotplate and heated up between 500 °C and

800 °C in 50 °C steps. At each step the temperature is measured with a contact temperature sensor and the pyrometer. The linear relation between the two temperatures is extrapolated to the process temperature range.

Different laser sinter process temperatures from 900 °C to 1200 °C are investigated using different pre-heating hotplate temperatures (room temperature (RT), 300 °C, 500 °C) at substrate movement speeds of 1 mm/s, resulting in an interaction time (of laser radiation and material) of 1,85 s. The spacing between the meandric lines is 1 mm.

3. Results

In the experiments, a pre-heating with different hotplate temperatures is investigated to reach a higher interface temperature between steel surface and layer and thus improve the adhesion. Without pre-heating (at room temperature), the mixed cathode layers with laser-induced process temperatures between 900 °C and 1200 °C are not adhering to the substrate, especially at 1100 °C and 1200 °C the mixed cathode layer detaches from the substrate during the process (Fig. 3 left). Using pre-heating temperatures of 300 °C and 500 °C the layers do not detach from the substrate. Adhesion is verified by a tape test. The tape is pressed on the mixed cathode layer and then quickly removed. A layer is called adhesive if no particles (visible to the naked eye) get stuck on the tape. At 300 °C pre-heating the layers processed from 1100 °C upwards are adhesive, for 500 °C hotplate temperature the layer processed from 900 °C upwards are adhesive. This result shows that a higher hotplate temperature leads to better adhesion.

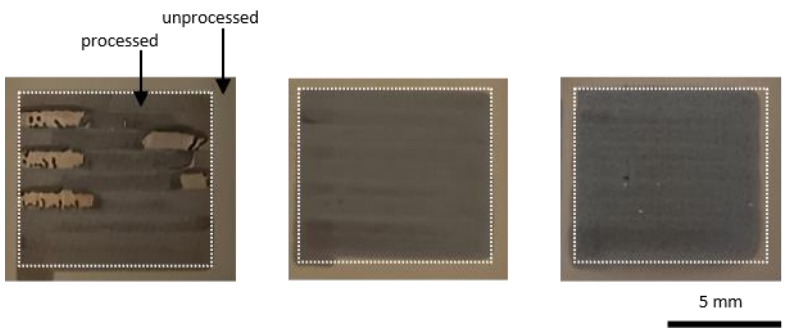

Fig. 3. Microscopic pictures (top view) of mixed cathode layers laser-sintered at 1200 °C without pre-heating (left), 300 °C pre-heating (middle), 500 °C pre-heating (right)

The sintering degree is investigated with a scanning electron microscope (SEM) Leo 1455 EP by Carl Zeiss AG. Fig. 4 shows SEM images of the surfaces of laser-sintered mixed cathode layers at different process temperatures (900 °C to 1200 °C) and two different pre-heating temperatures (300 °C and 500 °C). The higher the process temperature, the more the particles are sintered and form bigger particles. By means of laser sintering, the particle shells are melted but the particle form is nearly preserved, this is called liquid-phase sintering. The formation of big particles is a result of an anisotropic shrinkage and sinter process. The aim is the highest possible density for good electrical conduction in battery process. A difference between the degree of sintering with different hotplate temperatures cannot be seen from the SEM surface images. Only a difference in structure can be seen, for a hotplate temperature of 500 °C, the big particles are rounder.

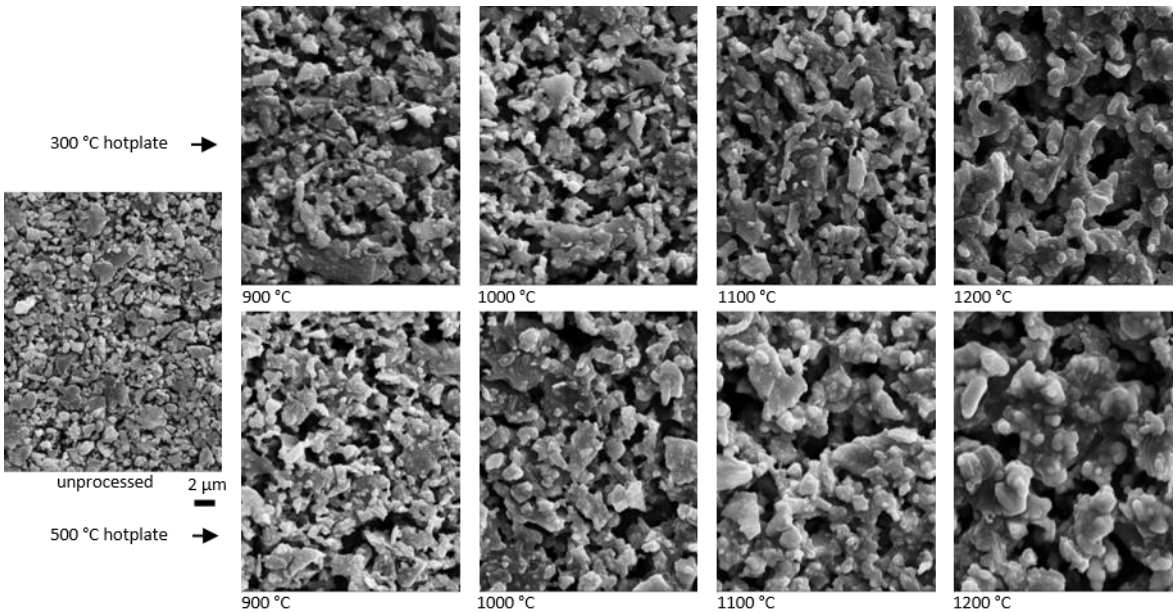

Fig. 4. SEM images of the surfaces of laser-sintered mixed cathode layers at different process temperatures and two different pre-heating temperatures

The crystal structure is measured in Bragg-Brentano geometry between 15 ° and 60° with a Bruker Advance D8 X-Ray diffractometer having a Cu X-ray tube (λ = 1.45059 Å). A requirement for the laser sinter process is the preservation of the crystal structures of LLZ and LCO and therefore preservation of electrochemical properties. This means a prevention of Lithium loss which is usually correlated with high process temperatures and a reduction of diffusion processes which are usually seen at long interaction times by side reactions.

The x-ray diffraction pattern (Fig. 5) of the debindered but non-sintered mixed cathode layer shows intensity peaks at the respective angles of the LLZ and LCO crystal structure. Additionally, small peaks around 22° show the existence of lithium carbonate (Li_2CO_3) and around 28° the existence of lanthanum zirconate ($La_2Zr_2O_7$). Both crystal phases worsen the electrochemical properties. The comparison of the two non-sintered but pre-heated layers shows no significant influence of the pre-treatment on the crystal structure.

After laser sintering at 900 °C, no more lithium carbonate is detected in the layer. With increasing process temperature, the amount of lanthanum zirconate phase also decreases. At 1000 °C no more lanthanum zirconate is detected in the layer. A possible chemical reaction at high temperatures is

$$La_2O_3 + 2\ La_2Zr_2O_7 + 7\ Li_2CO_3 \rightarrow 2\ Li_7La_3Zr_2O_{12} + 7\ CO_2. \quad (1)$$

This means the laser sinter process can rebuild the main crystal phases. For all sintering temperatures the main phases, LLZ and LCO, are measured.

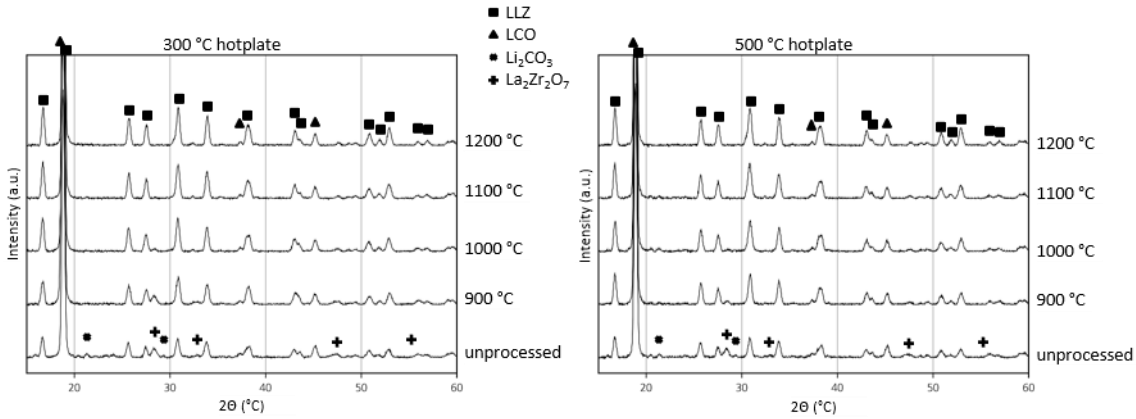

Fig. 5. XRD-pattern of mixed cathode layers, laser sintered at different process temperatures with 300 °C (left) and 500 °C pre-heating temperatures (right). Different crystal structures are marked, expected is LLZ and LCO.

SEM images of cross-sections of laser-sintered mixed cathode layers are shown in Fig. 6. The unprocessed layer (left) has a thickness of 21 µm. The laser-sintered layer (processed at a sintering temperature of 1200 °C and a pre-heating temperature of 300 °C, right) has a reduced thickness of 16 µm. Therefore, the layer is compressed during the sintering process, but the porosity is still high, shown by the SEM pictures of the surfaces.

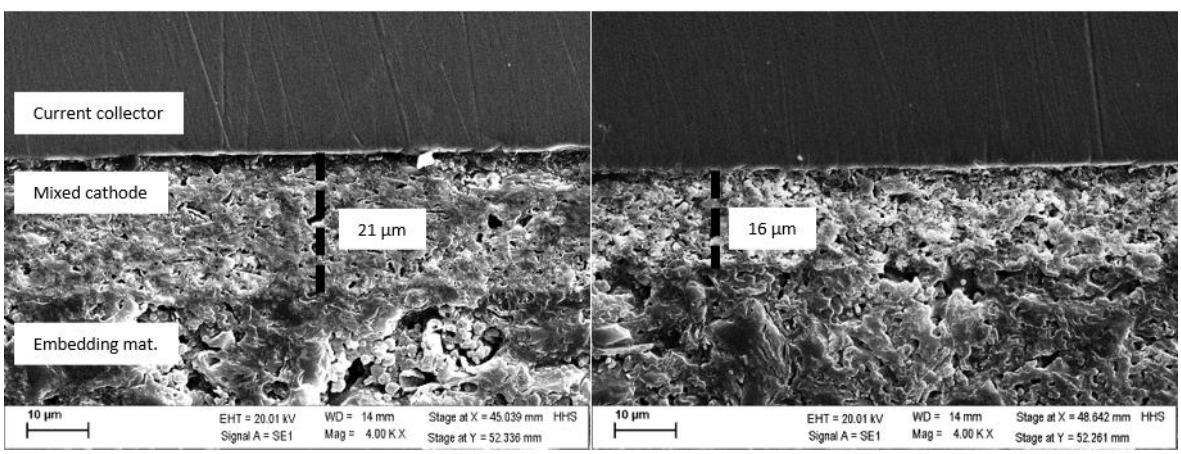

Fig. 6. SEM images of cross-sections of laser-sintered mixed cathode layers. The unprocessed layer (left) has a thickness of 21 µm. The laser-sintered layer at 300 °C pre-heating and 1200 °C process temperature (right) has a reduced thickness of 16 µm.

Electrochemical impedance spectroscopy was performed on selected samples to determine the ionic conductivity of the layer. The highest ionic conductivity was measured for the layers sintered at 1100 °C with 300 °C hotplate temperature with $5{,}54 \cdot 10^{-7}$ S/cm. The ionic conductivity is lower compared to pure conventionally sintered LLZ discs with almost full density ($1 \cdot 10^{-3}$ S/cm) (Tsai et al., 2016). The authors attribute this to the significantly more porous morphology of the laser-sintered layer, and a not yet perfect contact between the grains due to the extremely short heat treatment time.

4. Conclusion and Outlook

A laser sintering process of a ceramic mixed cathode layer for thin film solid-state batteries was presented. By means of laser sintering, an adhesive and sintered mixed cathode layer made of LLZ and LCO with preserved crystal structure can be produced. A pre-heating of the coated substrate during laser sintering improves the layer adhesion to the steel current collector. Further process development is needed to improve the density of the sintered layer and therefore the electrochemical properties. As a further step the process should be adapted to thinner current collectors.

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