Ultrafast laser ablation of high-voltage cathodes using GHz burst mode operation

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ABSTRACT

A key for developing high-energy and high-power lithium-ion batteries is the implementation of optimized material configurations and electrode architectures. A promising approach is the use of cathodes containing the high-voltage spinel $LiNi_{0.5}Mn_{1.5}O_4$ (LNMO) as active material and enhance their electrochemical performance by implementing a three-dimensional (3D) electrode architecture created through laser ablation. A high throughput of precisely fabricated 3D electrode geometries can be realized by using ultrashort pulsed (USP) laser radiation in combination with burst mode operation. In this work, the ablation characteristics of a line structuring of high-voltage LNMO cathodes in single pulse mode and GHz burst mode are analyzed and compared to identify optimized laser structuring parameters.

Keywords: Ultrashort pulsed laser ablation, GHz burst mode, lithium-ion battery, 3D battery, laser structuring, LNMO

1. INTRODUCTION

The increasing electrification of the transport sector rises the demand for affordable, sustainable high-energy and high-power lithium-ion batteries. A crucial factor for developing such lithium-ion batteries is the optimization of material configurations and electrode designs. In terms of cathode active material, the cobalt-free high-voltage spinel $LiNi_{0.5}Mn_{1.5}O_4$ (LNMO) is due to its high and flat voltage plateau at 4.7 V vs. Li/Li^+ and reachable practical capacities of around 140 mAh g^{-1}, which results in energy densities of around 650 Wh kg^{-1} on material level, a very promising candidate to balance the needs for high performance and low costs [1]. Concerning the electrode design, an effective approach enhancing the electrochemical performance of a lithium-ion battery is the implementation of a three-dimensional (3D) surface topography in the electrode architecture, for example realized by locally ablate electrode material [2, 3]. Previous studies have demonstrated the effectiveness of such an 3D electrode design in improving electrochemical performance for a variety of cathode and anode materials [4-7]. For a successful integration of the laser structuring in the industrial electrode manufacturing process, it is necessary to realize a high throughput of precisely fabricated 3D electrode geometries. It has been reported that an effective way to improve the precision and efficiency of laser ablation, is the use of ultrashort pulsed (USP) laser radiation in combination with burst mode operation [8, 9].

In the presented work, the ablation characteristics of high-voltage spinel LNMO cathodes in single pulse and GHz burst mode operation were analyzed and compared. For this, a line structuring of the manufactured LNMO cathodes was realized by using either a laser source working in single pulse mode or a laser source working in burst mode. The influence of the two different operation modes as well as the impact of the burst length on the resulting characteristic quantities like ablation efficiency and aspect ratio were determined and compared to identify optimized laser structuring parameters.

2. EXPERIMENTAL

2.1 Electrode manufacturing

For the experiments, a LNMO cathode containing LNMO (Haldor Topsoe, Denmark) as active material (93 wt.%), carbon black (CB, C-NERGY C65, Imerys G&C, Belgium) as conducting agent (4 wt.%) and polyvinylidene fluoride (PVDF) (Solvay, Germany) as binder (3 wt.%) was fabricated. For the manufacturing process, in advance to the slurry fabrication, a PVDF solution was prepared by dissolving PVDF powder in N-methyl-2-pyrrolidone (NMP) (Merck, Germany) with a weight ratio of 1:10. The LNMO slurry was then made by mixing the LNMO powder and the conductive carbon black in the prepared PVDF solution using a SpeedMixer (DAC 150 SP, Hauschild, Germany). Afterwards, the LNMO slurry was coated with a universal applicator (ZUA 2000, Proceq, Switzerland) onto an aluminum foil via doctor blade and subsequently dried for two hours at 90 °C. Finally, the LNMO cathodes were calendered to a porosity of 35 % using an electric rolling presser (MSK-2150, MTI, Cooperation, USA).

2.2 Laser structuring

For the analysis of the ablation characteristics of the LNMO cathode, two different laser sources either working in single pulse (FX600, EdgeWave GmbH, Germany) or burst mode (PXpv, EdgeWave GmbH, Germany) operation implemented in a laser material processing system (MSV203 Laser Patterning Tool, M-Solv LTD, United Kingdom) were used. The first laser source operates at a wavelength of 1030 nm, has a pulse length of 600 fs, a maximum average laser power P_{avg} of 300 W at a repetition rate f of 1.5 MHz and can be applied in single pulse mode. The second laser source operates at a wavelength of 1064 nm, has a pulse length of 10 ps, a maximum average laser power P_{avg} of 450 W at a repetition rate f of 1 MHz and can be used in burst mode. The pulse repetition rate within the bursts was fixed to 1 GHz.

To compare the ablation characteristics in the two operational modes, the repetition rate in single pulse mode and the burst repetition rate, so the inter-burst repetition rate, in burst mode were both set to 150 kHz. Combined with a scan speed of 2 m s^{-1}, this results in a pulse-to-pulse or burst-to-burst distance of 13.3 µm, leading to a line structuring of the LNMO cathode. For all experiments, three repetitions of the line structuring were applied. Furthermore, same values were chosen for the burst energy in burst mode and the pulse energy in single pulse mode. In case of burst mode, four different burst lengths (50 ns, 100 ns, 200 ns, and 500 ns) were used. To characterize the ablation behaviour, a cross-sectional profile was recorded with a digital microscope (VHX 7000, Keyence, Japan) and the resulting ablation depth d, width at full w_u and half maximum w_m, and area A of the generated grooves were measured. With these values, further characteristic quantities like the ablation efficiency ε and the aspect ratio AR were determined (see Equation (1) and (2)).

$$\varepsilon = \frac{A\,v}{n\,P_{avg}} \tag{1}$$

$$AR = \frac{d}{w_m} \tag{2}$$

For the comparison of the results in the two variants, the different analyzed parameters are shown either in dependence of the pulse peak fluence F_0 in case of single pulse mode or the burst fluence F_B in case of burst mode which is defined as the pulse peak fluence of a single pulse inside a burst multiplied with the number of pulses N_B inside a burst [10]. As the same energy was applied for single pulse mode and burst mode and the calculated focal radii were nearly identical, more or less same pulse peak fluences and burst fluences were the results.

3. RESULTS AND DISCUSSION

3.1 Comparison of single pulse mode and burst mode

The ablation characteristics of a line structuring of the LNMO cathode were studied by using either a laser source working in single pulse mode or a laser source working in burst mode. In Figure 1, the resulting ablation efficiencies are plotted over the fluence. It can be seen that in case of the burst mode, the resulting ablation efficiencies are higher than in case of the single pulse mode, especially for higher fluences. This corresponds very well to literature, where higher ablation efficiencies could be observed by using burst mode instead of single pulse mode for example for LFP and NMC cathodes [8]. However, the ablation efficiency is not a very well suitable characteristic quantity to identify a good set of laser parameters for the laser structuring of battery electrodes. Aim is here to create channels, which are deep, but narrow, so that for a well-defined and possibly low mass loss, the electrode material can be ablated completely down to the current collector by meanwhile realizing short channel distances reducing the transport pathways inside the porous electrode structure. Therefore, a better characteristic quantity for this kind of application is the aspect ratio, which is defined as the ablation depth divided by the full width at half maximum (Equation (2)). Nevertheless, the same trend as for the ablation efficiency can also be observed for the aspect ratio. For example, at a fluence of ε = 33 J cm^{-2}, the aspect ratio *AR* can be increased by a factor of two for bursts with 200 ns and 500 ns burst length.

Responsible for that are quite similar ablation widths at half maximum w_m for single pulse and burst mode, but significantly higher ablation depths *d* in case of burst mode. Therefore, using burst mode instead of single pulse operation mode seem to be an effective way in case of laser structuring of LNMO cathodes to reduce the number of repetitions that have to be applied for a line structuring to reach the current collector, resulting in a higher throughput.

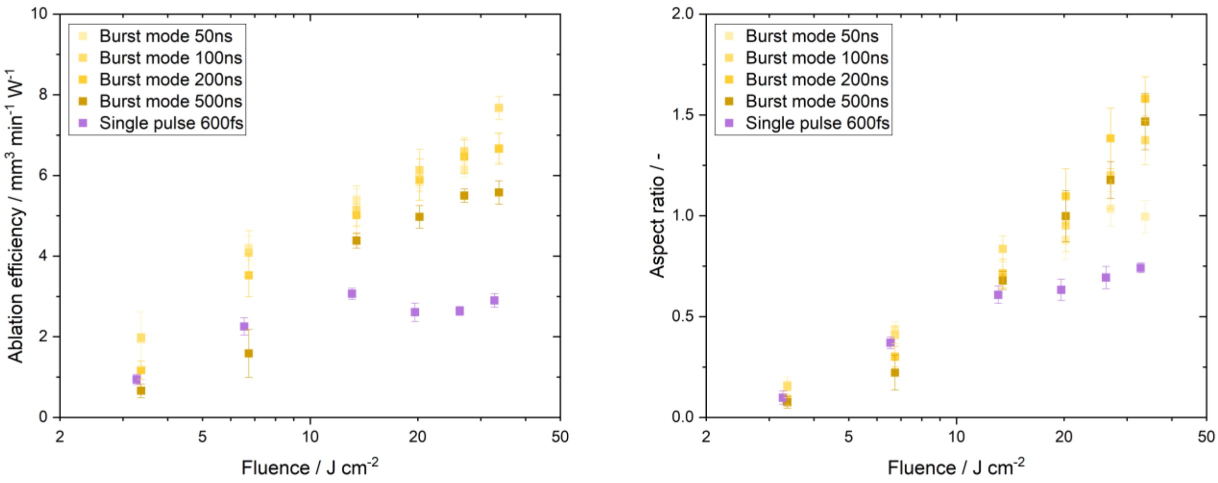

Figure 1. Ablation efficiency (left) and aspect ratio (right) of the line structuring of the LNMO cathode in dependence of the pulse peak fluence F_0 in case of single pulse mode or the burst fluence F_B in case of burst mode.

3.2 Impact of burst length

As a second part, the impact of the burst length on the resulting ablation characteristics was analyzed. By comparing the ablation efficiencies of the different burst lengths (see Figure 2), it can be seen that for lower burst energies, an increase in burst length leads to a decrease in ablation efficiency. In case of higher burst energies, the ablation efficiency could be increased by going from a burst length of 50 ns to a burst length of 100 ns, reaching a maximum there, followed by a decrease of the ablation efficiency by further increasing the burst length to 200 ns and 500 ns. However, as mentioned in the previous section, a better characteristic quantity for laser structuring of battery electrodes to look at is the aspect ratio. In the corresponding diagram in Figure 2, it can be observed that for low burst energies, the aspect ratio decreases with increasing burst length whereas it increases with increasing burst length for higher burst energies, reaching a maximum at a burst length of 200 ns.

Responsible for that are different effects. At higher burst energies, the highest ablation depths are achieved for 100 ns and 200 ns, and a decreasing ablation width at half maximum with increasing burst length is observed. At low burst energies, a decreasing ablation depth with increasing burst length can be found, whereas the ablation width is more or less identical for the different burst lengths. With these results, it can be concluded that for laser structuring of LNMO cathodes, it would be attractive to use a high burst energy in combination with a burst length of 200 ns to receive with less repetitions very deep and still quite narrow channels.

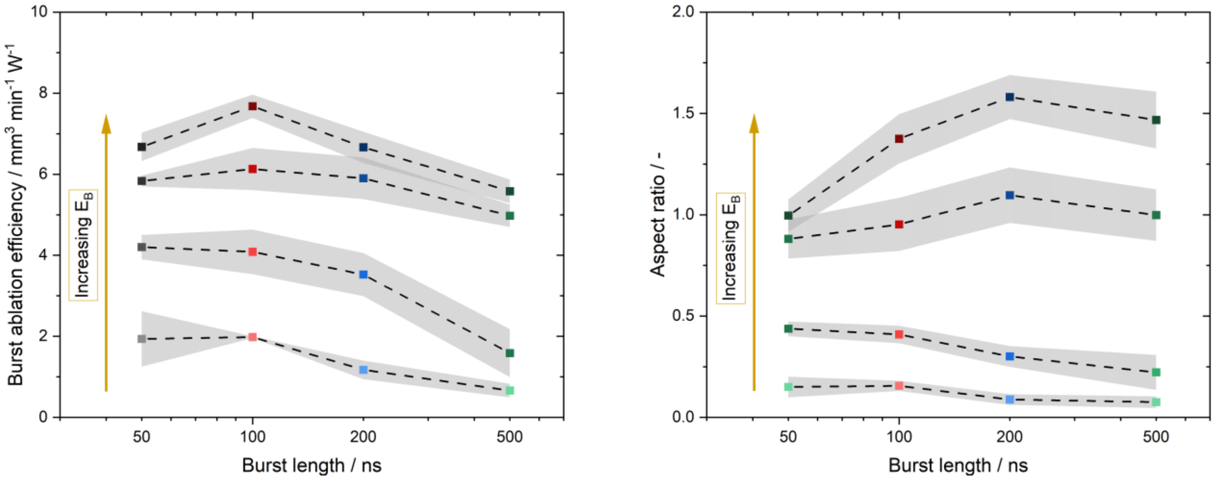

Figure 2. Ablation efficiency (left) and aspect ratio (right) of the line structuring of the LNMO cathode in dependence of the burst length.

4. CONCLUSION

Aim of the presented work was to analyze and compare the ablation characteristics of LNMO cathodes in single pulse and GHz burst mode operation. A comparison of both variants showed, that in burst mode, the ablation efficiency as well as the aspect ratio, which is a better characteristic quantity for laser structuring of battery electrodes then the ablation efficiency, could be increased. Reason for an improved aspect ratio was the increase in ablation depth while maintaining a nearly comparable ablation width as for the single pulse mode. By analyzing the influence of the applied burst lengths, different effects could be observed for low and high burst energies. In case of low burst energies, an increase of the burst length led to a decrease of ablation efficiency, aspect ratio and ablation depth, while the ablation width nearly stayed constant. In case of high burst energies, an increase of the burst length led at to an increase of the ablation efficiency, the aspect ratio, and the ablation depth, reaching a maximum either at 100 ns or 200 ns, followed then by a decrease by using longer bursts whereas the ablation width became constantly smaller with longer bursts. All in all, from the results of this study, it can be concluded that for line structuring of LNMO cathodes, it would be most favorable to use a GHz burst mode with a high burst energy in combination with a burst length of 200 ns to receive, with fewer repetitions, quite narrow channels with dimensions expanding all the way down to the current collector.

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