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Process temperature measurement during nanosecond pulse laser micromachining of Li-Ion battery electrodes

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Abstract

Surface functionalization as well as the microstructure modification of electrodes by laser material processing has become increasingly important in recent years. Short and ultra-short pulsed lasers, which enable high-precision processing, are used for this purpose. However, the process mechanisms, such as the surface temperatures that emerge during the process are not fully understood yet. New infrared high-speed detectors and their application allow to close this gap. In the present study, the infrared emissions of the selective ablation process of Li-ion battery electrodes are investigated experimentally. The electrode consists of graphite active material embedded in a carbon/binder domain. Due to the compaction of high-energy electrodes, pore clogging occurs, which hinders its fast-charging capability and the electrolyte wettability. The selective ablation of the surface binder phase significantly improves these two properties. The investigation of pure graphite material results in lower heat accumulation values but comparable peak values in comparison to the compacted electrode.

Keywords: Infrared radiation; binder ablation; microstructure; lithium-ion battery

1. Introduction

Laser material processing is becoming increasingly important and is an integral part of the efficient series production of battery cells. A wide range of laser processes are already being used in the production of battery cells like welding or cutting of electrodes [1]. These laser processes offer enormous advantages compared to conventional processes in terms of process speed and precision. Another area of application for laser material processing in battery production is the laser structuring of electrodes in order to achieve various advantages. This includes, for example, the laser perforation and laser trenching to increase fast-charging capabilities [2,3]. Another approach is the surface modification by selective laser ablation. This demonstrated advantages in terms of fast-charging capability, but also electrolyte wettability [4,5]. For fast parameter determination, as well as for optimization of the laser processes, simulative approaches are carried out in which thermal laser processes are investigated [6]. In order to optimize simulative studies, in-situ measurements during the process are necessary. To obtain such data, measurement methods with very high resolutions (< ns) are necessary, such as IR radiometry. This method has already been used to analyse heat accumulation in ultrashort pulse laser processing [7].

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2. Experimental Setup

2.1. Material

For the investigations, the following three materials were used:

- Graphite anode
- Graphite compressed (powder)
- Graphite solid

The used graphite anode consists of 94 wt% graphite (SGL carbon, synthetic graphite, D10 = 6.8 µm, D50 = 18.4 µm, D90 = 42.9 µm), 2 wt% carbon black (Imerys, C-Nergy Super C65), 2 wt% CMC (Nippon, Sunrose MAC 800LC) and 2 wt% SBR (Zeon, BM-451B). With the addition of 52 % deionized water, the compound was mixed to a slurry. After coating a layer with a capacity of 3.0 mAh/cm^2 using the doctor blade method on an 11 µm copper foil and drying, the layer was compacted by a lab calander (MTI Corporation) to an active mass layer density of 1.6 g/cm^3.

The second sample that was used consisted of compressed graphite powder, for which the same material as for the anode manufacture was used. For this, 1 g of graphite was compressed with 1 t to a chip with a diameter of 16.5 mm. In the next step, these compacts were placed in a sample holder to avoid damage.

The third sample was an isotropic solid graphite (Nippon Techno-Carbon Co., Ltd IGS-844) with a density of 1.72 g/cm^3. The samples were cut to a size of 45 x 45 mm and had a thickness of 5 mm.

For all samples, care was taken to ensure that the surface was flat and that there were no superficial irregularities on the surface before processing. Since all the samples and materials are basically carbon with comparable surface properties, a comparable emissivity can be assumed.

2.2. Laser

The investigated laser process was carried out by using a TruMark 5020 from the company TRUMPF GmbH. This is a short-pulsed fiber laser with a wavelength of 1064 nm. The beam was placed on the workpiece surface using a scanner optic with a focal length of 160 mm. The focal diameter in the presented experiments was about 70 µm. The tests were always carried out on a single processing line with a length of 4 mm, whereby the measurement was aligned to the center of the processing line in order to avoid the influence of the scanner acceleration. After each machining, the sample was moved by 1.5 mm with the help of an axis in order to ensure a pristine surface for the following measurement. Each parameter combination was processed and analyzed three times. To evaluate the emitted radiation during the process, the laser power was varied from 0.62 – 6.9 W (compare. Table 1).

As already shown in past studies [5], the ablation threshold for the used graphite material is around 2 J/m. The decomposition threshold for the binder phase, on the other hand, is only at about 0.8 J/m. The laser powers used in the presented study results in energy per unit length from 0.41 J/m to 4.6 J/m, which covers the whole range from "no ablation" to "complete ablation".

Table 1. Used laser parameters.

Parameter	Unit	Value
wavelength	nm	1064
focal diameter	µm	70
pulse duration	ns	9
laser power	W	0.62 – 6.9
repetition rate	kHz	200
scan velocity	m/s	1.5

2.3. Method of IR emission analysis

A picture of the experimental set-up for the investigation of IR-radiation from the surface can be seen in Fig. 1.

With the help of a parabolic mirror, the emitting IR radiation from the surface was captured during laser processing. The collimated radiation beam from the mirror is further guided through a germanium window, which acts as a filter for the laser radiation. Another parabolic mirror focuses the radiation into a liquid nitrogen cooled HgCdTe photovoltaic IR detector manufactured by InfraRed Associates, Inc. (MCT-11.76-0.5 PV). The signal from the detector was amplified by an external amplifier and recorded with an oscilloscope. The measurement setup has already been described in detail in the literature [7]. The visible point of view for the detector is about 700 x 700 µm. A micro-positioning Z-axis was used for fine adjustment of the sample height.

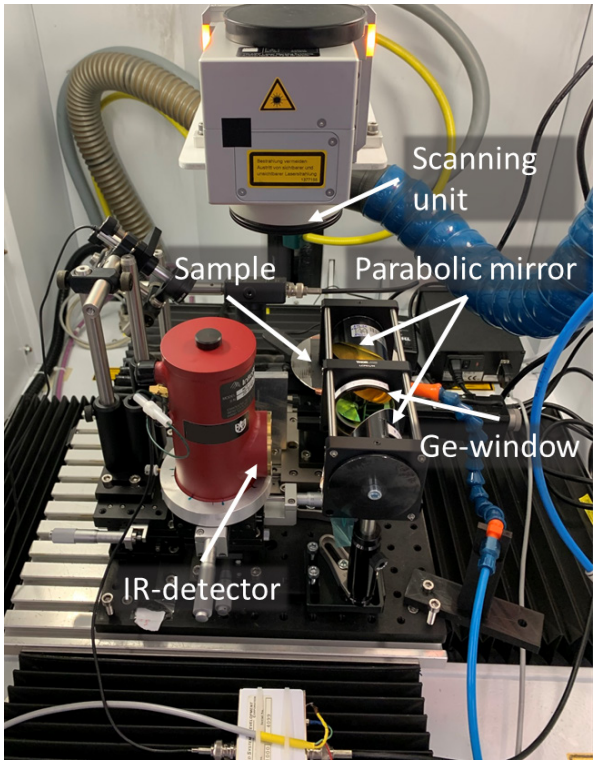

Fig. 1. Experimental setup of the IR-detector system inside the TruMark 5020

2.4. Analysis of the data

To analyze the data, an evaluation algorithm was used to determine the various measured values. As shown in Fig. 2, ground level, accumulation level and peak level are detected.

The ground level refers to the base voltage of the detector and was determined for each measurement separately in order to avoid possible temperature variations during the measurement. This basic voltage was determined on the basis of the plane areas before and after the processing phase. Furthermore, the accumulation level was determined by the highest signal right before the next pulse arrives. This signal describes the IR radiation emitted from the surface due to an increased surface temperature. Another value that was evaluated is the peak level, which was analyzed by the emission peaks. In this case, the maximum was also used as the peak level for further analysis.

Finally, the value between accumulation level and peak level was calculated by the difference of the two values to get an information about the peak height (from accumulation to peak).

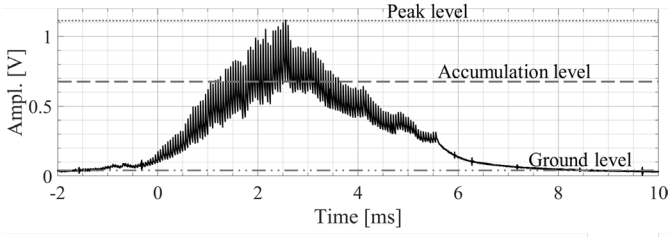

Fig. 2. Exemplary representation of the determination of peak level, accumulation level and ground level

3. Results and discussion

3.1. Comparison of emission accumulation level

Fig. 3 shows the accumulated emission against the energy per unit length for the anode and for the compressed graphite. The graph of both measuring series is described in the following.

In the lower range of the energy per unit length, which is up to 1.34 J/m, an almost equal trend can be seen. In this area, the accumulated emission and thus the surface temperature of the two materials also increases with increasing energy per unit length. This progression can be described by comparable processes at the material surface. The selective laser ablation for graphite anodes has already been described in [5], where the ablation threshold for the binder phase is about 0.8 J/m. The ablation threshold for the graphite phase was found to be about 2 J/m. Thus, the first region described here is below the ablation threshold for graphite, which means that no significant energy loss due to material removal is expected. The binder phase at the anode, which is removed in this range, plays a subordinate role due to the low volume percentage of 6 wt%. It can therefore be assumed that the incoming pulses heat the surfaces of both samples comparably during processing. Leading to comparable emitted radiation.

Above an energy per unit length of 1.61 J/m, the curves of the measured data show a different gradient. From this energy per unit length, the measured data of the compressed graphite shows a higher slope than the measured data of the anode. The different slopes of the accumulated emission suggest that the surface of the compressed graphite heats up more than the surface of the anode. Several aspects are playing a role during heat transportation of these two materials. At first glance, the curve shown is not what we expected. The compressed graphite, as a single material with low porosity, is expected to have a good thermal conductivity, which should be beneficial for the transport of heat. However, the results are exactly the opposite. This can be described by different aspects related to the microstructure of the samples and the process itself. Starting with the process, it can be assumed that for both materials an ablation of graphite takes place above 2 J/m, which leads to the dissipation of energy and thus heat. This reduces the surface temperature. Nevertheless, the ablation is to be rated higher in case of the anode. The binder removal, which already starts at approx. 0.8 J/m, causes a removal into deeper regions even at higher energy per unit length by the heated particles which decompose the binder matrix. As a result, particles are also removed below the ablation threshold of the graphite as the accumulated temperature rises above the decomposition threshold of the binder phase.

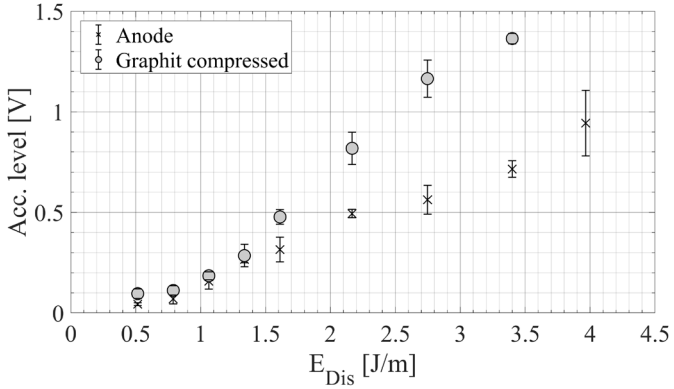

Fig. 3. Emission measurement: Heat accumulation level of Graphite anode and Graphite (powder) compressed for different Energy per unit length values

Another reason for the higher accumulated emission can be described in terms of the graphite particle boundary surfaces of the compressed graphite. By compressing the particles, the graphite flakes are pressed together. Since the compression does not result in a complete closure between the particles, it must be assumed that a very small porosity between the particles is present in the sample, which massively impedes heat conduction. However, in the anode, which has a significantly higher porosity, carbon black is added into the binder phase as a conductive additive for electrical conductivity. According to the Wiedemann-Franz-Lorenz law, there is a correlation between electrical conductivity and thermal conductivity for metals. Due to the comparable electrical conduction processes in graphite and metallic materials, this law can also be transferred to the present material. The use of carbon black to increase the electrical conductivity increases the thermal conductivity to the same extent, which leads to a preferential heat conduction into deeper layers during processing and thus to a lower surface temperature, as can be seen in Fig. 3 above 1.34 J/m.

3.2. Comparison of peak-emission height

In the following, the peak height is considered, based on the accumulated level, whereby the absolute peak heights are not considered. These show a comparable behavior, which is only changed by the ablation and the amount of energy consumed in the pulse peak. The following investigations of the peak height were carried out on all three presented materials.

It can be seen that the measurement curves for all three materials show a similar progression (Fig. 4). At the beginning of the measurement sequence, the progression rises almost constantly up to a tipping point, from which the slope decreases significantly or the value remains constant. This tipping point varies slightly for the three materials examined in the range of 1.5 - 2.0 J/m. Thus, it is again in the range where the ablation threshold for graphite is reached, what explains this tipping point. From that point on, graphite is significantly ablated, which means that the peak temperature is no longer reached when the pulse arrives.

Nevertheless, the highest curve and thus the highest peaks based on the accumulated emission can be seen for the solid graphite. This distinguishes by a homogeneous microstructure and thus by an optimal thermal conductivity. This means that until the ablation threshold is reached, the deposited energy is conducted directly through the crystal structure. The accumulated emission is thus comparatively low and the incoming pulses cause an increasing amplitude in the measurements with increasing energy per unit length. From the point of reaching the decomposition threshold, the increasing energy per unit length mainly affects a rising ablation, which takes the peak energy out of the system again. However, the ratio between accumulated emission and peak emission remains almost constant.

The second material discussed in the following is the compressed graphite. Compared to the solid, this shows a significantly lower curve. This means that the peak height, starting from the accumulation level, is not that pronounced. Fig. 3 already shows the high accumulation level. The assumptions described above regarding the negative effect of the thermal conductivity due to the edge-to-edge graphite particles can be confirmed once again by this curve. This results in a high accumulation level and a low peak height.

Looking at the measured data for the anode material, in Fig. 4, it can be seen that it is between the values of compressed graphite and the solid graphite. The tipping point is also located approximately at the energy per unit length of the ablation threshold of the graphite. This again strengthens the assumption that the thermal conductivity can be significantly improved by adding carbon black. For the anode, it also shows that above the graphite ablation threshold, an increasing energy per unit length has no significant influence on the peak height. Only the surface temperature increases, which indicates an improved material removal. Due to the fact, that also the ablation plasma could impact the measured signal significantly this has to be investigated in the future in detail.

Since the focus of this work was on the analysis of the process mechanisms within the process of selective ablation of anodes by the help of IR radiation, the ablation depths are not discussed in detail here.

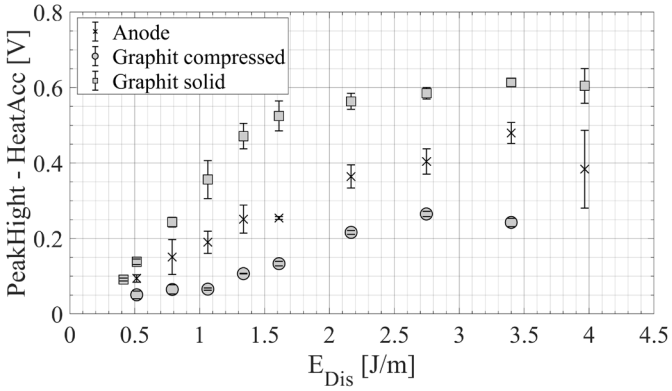

Fig. 4. Emission measurement: Peak level – Accumulation level for Anode, Graphite compressed and Graphite solid for different Energy per unit length

4. Conclusion

In the presented study, we investigated the thermal emission during the selective laser ablation processing of Li-Ion battery graphite anodes. Therefore, the accumulation level and the peak level – acc. level of the emission was analyzed. It was found that the specific microstructure and material composition is decisive for the understanding of thermal processes. In particular, it has been shown that the small amount of 2 % conductive carbon already has a significant influence on the measurement results.

Acknowledgements

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