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Current status of laser electrode structuring for enhanced lithium-ion batteries

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Abstract

The trade-off between a high fast-charging capability and a high energy density is a central challenge for lithium-ion batteries. The conflict of objectives can be significantly alleviated by introducing microscopic channels into the electrode coatings facilitating lithium-ion diffusion through the porous electrode network. Short-pulsed and ultrashort-pulsed laser radiation are versatile tools to structure electrodes with micrometer precision at a low heat input. Hence, laser structuring of lithium-ion battery electrodes has seen widespread research attention recently. This publication examines current advances and challenges in the field through a comprehensive literature analysis. The state of research is clustered regarding processed electrode materials, created structure geometries, and laser material processing aspects, such as beam sources, process parameters, and process strategies. Further, laser structuring of graphite anodes is discussed in detail. Finally, future research directions are pointed out, especially regarding the industrialization of laser electrode structuring.

Keywords: Laser structuring; Electrode structuring; Lithium-ion batteries; Short-pulsed laser; Ultrashort-pulsed laser

1. Introduction to laser electrode structuring

Lithium-ion batteries currently dominate the energy storage sector due to their high energy density, long cycle life, and low self-discharge rate. They are increasingly important for various applications, including portable electronics, electric vehicles, and grid-scale energy storage (Blomgren 2017). However, multiple challenges need to be overcome to reduce the cost, enhance the safety, and improve the performance of lithium-ion batteries. Regarding the latter, the electrodes are the most critical components, as their properties

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strongly influence the overall performance of a lithium-ion battery. The electrodes consist of active materials such as graphite for anodes and metal oxides for cathodes on metallic current collector foils. Lithium-ions are stored in and released from these active materials during processes called intercalation and de-intercalation, respectively. In order to enhance the electrochemical performance of lithium-ion battery electrodes, researchers have been exploring various methods to modify their structure and composition. A promising approach is laser structuring, which uses pulsed laser radiation to selectively drill microscopic structures into the electrode coatings. These drillings facilitate the diffusion of lithium-ions through the electrolyte-filled electrode pore network by shortening the ion pathways. The directed pores enhance the fast-charging capability of lithium-ion batteries and reduce degradation effects, resulting in a prolonged lifetime. Furthermore, the wetting with electrolyte during lithium-ion battery production is accelerated, resulting in decreased production costs. Consequently, laser structuring of lithium-ion battery electrodes has gained increasing research attention in the last years (compare Fig. 1).

This publication reviews recent developments in laser structuring of battery electrodes. For reasons of scope and extent, potential applications of laser structuring in battery technologies other than lithium-ion batteries, e.g., vanadium redox flow batteries, solid-state batteries, and sodium-ion batteries, are not considered. Also, laser structuring of current collector foils, which enlarges the specific surface area and increases the wettability (Sun et al. 2023), is explicitly excluded in this literature review. Alternative electrode structuring approaches, e.g., by mechanical embossing (Bryntesen et al. 2023; Keilhofer et al. 2023; Sandherr et al. 2023), pore-forming agents (Jang et al. 2021), or freeze casting (Amin et al. 2018; Delattre et al. 2018), are not discussed either. After giving an overview of the literature on laser electrode structuring in Chapter 2, laser structuring of graphite anodes is discussed in detail based on selected publications in Chapter 3. At the end of this publication, future directions of academic research and industrial development in laser electrode structuring are elaborated.

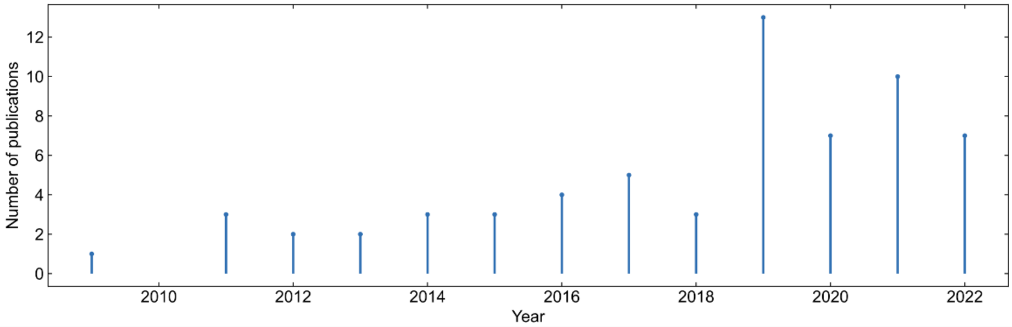

Fig. 1: Number of publications in the field of laser electrode structuring per calendar year analyzed in this literature review

2. Overview of laser electrode structuring

As shown in Fig. 1, laser structuring of electrodes has gained increasing attention in the academic community in the last decade. Research groups that are active in the area of laser electrode structuring typically combine expertise in lithium-ion battery production and laser material processing. A geographical concentration of research activities can be found in Germany, where significant contributions to the field were made at the *Karlsruhe Institute of Technology*, at the *Technical University of Munich*, and at the *Aalen University of Applied Sciences* (compare Fig. 2 top right). Further, various publications in the field of laser electrode structuring originate from the United States of America, Japan, and South Korea.

Fig. 2: The 63 publications analyzed in this literature review clustered by the first authors (left) and affiliation of the first authors (right), wherein the *Karlsruhe Institute of Technology* (KIT), the *Technical University of Munich* (TUM), and the *Aalen University of Applied Sciences* (AUAS) are highlighted

In lithium-ion batteries, graphite anodes dominate the market due to their high specific energy of 372 mAh/g, whereas shares of silicon (3579 mAh/g) can be implemented to further boost the electrode's energy storage capability (Chae et al. 2020). The material costs of anodes are lower than for most cathode active materials (Kwade et al. 2018). Graphite-based materials possess a high thermal conductivity, electrical conductivity, and mechanical flexibility (Li and Kaner 2008). For lithium-ion battery cathodes, a wide variety of active materials is used ranging from lithium cobalt oxide (LCO) over lithium iron phosphate (LFP) and lithium nickel cobalt aluminum oxide (NCA) to lithium nickel manganese cobalt oxide (NMC) (Nitta et al. 2015). The latter is a popular choice for electric vehicles as it offers a balance of high energy density and good cycle life (Jung et al. 2021). An approximately equal number of studies considered in this review investigated laser structuring of anodes and cathodes, respectively (compare Fig. 3 top left).

Regarding the created microstructures (compare Fig. 3 top right), most approaches have created lines, either aligned parallelly to each other or crossing each other, forming a grid in the electrode coatings. Since straight line trajectories can be scanned with high feed rates by scanning systems, they are attractive regarding process scaling. However, a higher mass portion of the electrode coating is typically ablated compared to hexagonally or quadratically arranged holes drilled into the material. Further, self-organized microstructures (SOMs) and the selective ablation of additive residues on the electrode surfaces ("Surface" in Fig. 3 top right) are options for patterning of battery electrode surfaces, which yet both represent a niche in laser electrode structuring.

Fig. 3 (bottom left) shows that pitch distances of 100 µm to 200 µm between the microstructures were typically chosen. For industrially established electrode loadings (e.g. 4 mAh/cm^2), these values increase electrochemical performance at a bearable material loss.

In most studies, laser sources emitting pulsed radiation at an infrared wavelength (> 1000 nm) were used for laser structuring of electrodes. These laser sources offer the most attractive combination of average power, beam quality, and procurement costs. Laser radiation in the visible wavelength regime, which in theory allows for smaller focal beam diameters, becomes increasingly attractive due to technical advances at falling prices for beam sources.

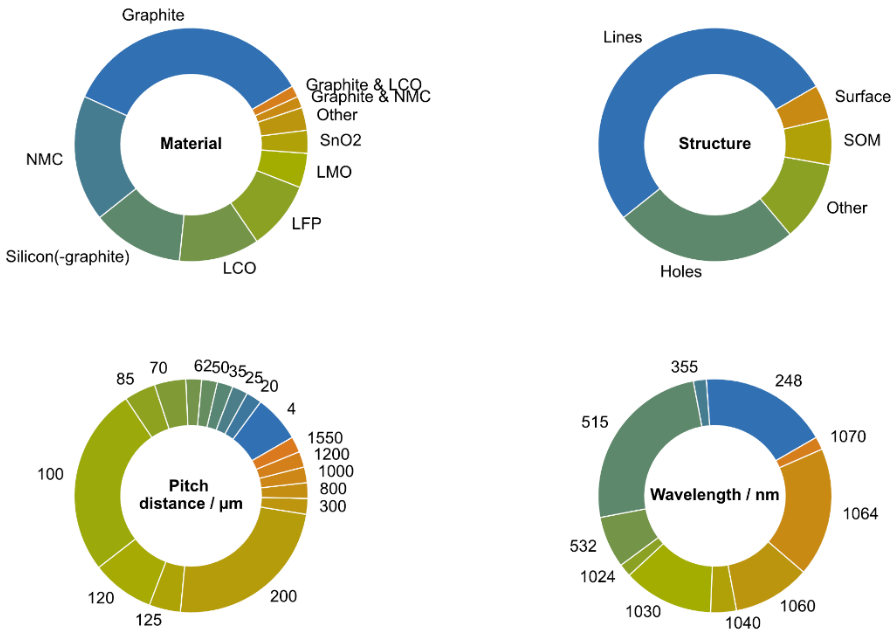

Fig. 3: Processed electrode materials (top left), structure types (top right), chosen pitch distances (bottom left), and applied wavelengths (bottom right) in the 63 publications analyzed in this literature review; used abbreviations: NMC = Lithium nickel manganese cobalt oxide; LCO = Lithium cobalt oxide; LFP = Lithium iron phosphate; LMO = Lithium manganese oxide; SnO2 = Tin(IV) oxide; SOM = Self-organized microstructures

3. Insights into laser structuring of graphite anodes

3.1. Electrochemical benefits

The concept of three-dimensional battery electrode architectures was initially realized for graphite anodes by Habedank et al. (2018) and Kim et al. (2018). Both authors observed an increased capacity by anode structuring in discharge rate tests of lithium-ion batteries. The results of Kim et al. (2018) suggested that an improved charge rate acceptance through laser structuring can be achieved by mitigating the effects of concentration polarization in graphite anodes with a high energy density. Habedank et al. (2018b) developed a three-dimensional electrochemical model calibrated using experimental data to simulate voltage responses and discharged capacity under varying C-rates. A restricted C-rate window that can be positively affected by electrode structuring was identified, with the highest increase in relative capacity retention at 3 C. The modeling was further developed by Kraft et al. (2020), showing that modifying the pore morphology with laser structuring reduces lithium-ion concentration gradients and improves the charge and discharge rate capability while also increasing safety by reducing the risk of lithium plating during fast charging. Habedank et al. (2019a) experimentally demonstrated an enhancement of the fast-charging capability and reduced lithium plating in lithium-ion batteries with laser-structured anodes using electrochemical impedance spectroscopy. Lower impedances of cells with laser-structured anodes than their conventional counterparts were further evidence of the success of laser structuring. Although lithium plating could not be entirely avoided at low temperatures, the data showed that laser structuring improved the fast-charging capability of lithium-ion batteries, especially under demanding operating conditions, such as low temperatures. Shorter charging times were achieved with laser-structured electrodes and the upper cut-off voltage was reached at a higher state-of-charge. Zheng et al. (2019) used laser-induced breakdown spectroscopy to quantitatively study lithium concentration profiles in structured and unstructured graphite electrodes to prove that structured electrodes had less lithium-ion content in de-lithiated state than unstructured electrodes. The 3D architecture accelerated the lithium-ion extraction process and reduced inactive parts of the electrodes during electrochemical cycling.

3.2. Interdependencies with material properties

Hille et al. (2021) compared laser structuring of graphite anodes and NMC cathodes regarding their respective impact on the electrode properties and lithium-ion battery performance. In accordance with results by Park et al. (2021) it was concluded that laser structuring offers a particular potential to overcome the diffusion-limiting characteristics of the graphite anodes resulting in a distinct tortuosity decrease and rate capability improvement of lithium-ion batteries through laser-structured graphite anodes. Furthermore, studies on the interdependencies of laser electrode structuring and electrode calendering by Hille et al. (2022) revealed that despite an increase in thickness and porosity, laser-structured graphite anodes exhibited a higher volumetric energy density at high current rates than unstructured electrodes. The results underlined the potential of laser electrode structuring for highly compressed graphite anodes and agreed with data published by Dubey et al. (2021), who showed an improved rate capability and enhanced volumetric capacity of lithium-ion batteries by laser structuring of graphite electrodes with a low porosity and high mass loading.

3.3. Enhanced electrolyte wetting

Besides the electrochemical benefits of laser electrode structuring, Habedank et al. (2019b) reported an accelerated electrolyte wetting of lithium-ion batteries containing laser-structured electrodes using in-situ neutron radiography of multi-layer pouch cells. The experiments revealed that laser structuring accelerated the wetting process by at least one order of magnitude, proving that the liquid was quickly absorbed into the capillary grid structures and effectively distributed into the center of the electrode stack. The results were substantiated by Dunlap et al. (2022) and Kleefoot et al. (2022a) for graphite anodes and analogously observed for LMO cathodes by Pfleging et al. (2014), for LFP cathodes by Berhe and Lee (2021), and NMC cathodes by Dunlap et al. (2022).

3.4. Ablation characteristics

Using femtosecond laser structuring Habedank et al. (2018) systematically explored the ablation characteristics of electrode structuring under different laser processing parameters, such as fluence or pulse repetition rate. Further, an influence of the electrode composition on the ablation behavior was shown by varying the binder content. Kleefoot et al. (2022b) examined the parameter dependency in graphite anode laser structuring with picosecond-pulsed laser radiation over a large parameter set and reported a high impact of the laser fluence on the obtained hole depths.

3.5. Transfer to industrial battery production

Laser structuring of graphite anodes was transferred from small-scale coin cells to large-format lithium-ion batteries by Chen et al. (2020) and Kriegler et al. (2021). Chen et al. (2020) demonstrated over 97 % and 93 % capacity retention after 100 cycles of 4 C and 6 C fast charging, respectively, compared to 69 % and 59 % for unstructured electrodes. Additionally, the design allowed cells to access over 90 % of the total cell capacity during fast charging, providing a pathway toward safe fast charging of high-energy-density batteries. In accordance, Kriegler et al. (2021) showed a superior rate capability of large-format lithium-ion batteries containing laser-structured graphite anodes at temperatures of -10 °C, 0 °C, and 25 °C at discharge rates of up to 8 C and charge rates of up to 6 C. Higher capacity retention of cells containing structured anodes was observed in an aging study with 500 charge and discharge cycles, and a reduction of lithium plating by laser structuring was concluded based on incremental capacity analyses as well as post-mortem scanning electron microscopy and energy-dispersive X-ray spectroscopy analyses of the anodes. In a study on different integration options for laser structuring into the electrode manufacturing process chain for lithium-ion batteries by Hille et al. (2023), different ablation behaviors were suspected when structuring graphite anodes with and without residual moisture. As a result, diverse geometrical, mechanical, and electrochemical characteristics of anodes laser-structured at different positions in the process chain were reported.

3.6. Alternative structuring approaches

In addition to the wide-spread structuring of graphite anodes with line, grid, or hole patterns, Bolsinger et al. (2020) and Enderle et al. (2020) proposed an alternative approach for laser processing of battery electrodes. The selective laser ablation of additives, especially the binder, at the electrode surfaces enhanced the ion accessibility into the microporous structure of the electrodes, resulting in reduced cell overpotentials and an increased rate capability of the anodes (Sandherr et al. 2022).

4. Outlook on the industrial application of laser electrode structuring

Laser electrode structuring allows enhancing the electrochemical performance of lithium-ion batteries remarkably. However, the process has not progressed beyond the laboratory scale due to several production-related challenges. Besides issues regarding its implementation into the process chain of industrial electrode manufacture (Hille et al. 2023), laser structuring needs to be scaled to industrial processing speeds. Patterning large surface areas in short intervals poses high challenges to beam deflection, requiring novel system technology solutions, such as polygon scanning units (Habedank et al. 2020). Recently, innovative machine concepts were proposed for laser structuring of electrodes compatible with industrial-style, continuous roll-to-roll processes at high web speeds (Yamada et al. 2023). Alternatively, direct laser interference patterning represents an attractive option for increasing the throughput of laser electrode structuring (Zwahr et al. 2023). Sufficient product quality must be ensured in all approaches, i.e., high aspect ratios of the created structures at a low heat input and a low removal of active material. Conclusively, further academic and industrial research on laser structuring of battery electrodes is necessary to transfer the technology from the laboratory to industrial lithium-ion battery production.

Acknowledgments

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