Laser structuring and functionalization of nanoscaled battery materials

W. Pfleging*, A. Meyer, U.Rist, P. Smyrek, Y. Sterzl, Y. Zheng, P. Zhu

Karlsruhe Institute of Technology, IAM-AWP, P.O. Box 3640, 76021 Karlsruhe, Germany

ABSTRACT

Possible laser processes in battery manufacturing are quite diverse regarding the control of electrochemical characteristics: LIPSS on current collector surfaces are used to adjust the adhesion of composite electrodes to current collectors, laser surface patterning turns ceramic-coated separator materials into superwicking with regard to electrolyte wetting properties, and laser structuring of composite thick film electrodes is applied to generate 3D electrode architectures with shortened lithium-ion diffusion pathways. In the field of cathode thick film development, secondary particles with nanoscaled primary particles are used and ultrafast laser ablation is applied to pattern the composite electrodes to optimize the lithium-ion diffusion kinetics by enlarging the active material surface with a view to reducing cell polarization, which develops at high battery power. This enables high energy batteries to be upgraded for operation at high power. In the field of anode development for electromotive vehicles, efforts are being made to develop silicon anodes in order to significantly increase the energy density. In addition, the issue of fast charging, mainly influenced by the anode architecture, is a major topic in research and industrial development. Silicon nanoparticles are used and combined with graphite particles in a binder matrix. The large volume change as a result of the lithiation of silicon during battery operation requires laser structuring of the composite electrodes in order to counteract mechanical degradation. Analogous to cathode materials, the lithium diffusion kinetics for anodes are also significantly enhanced by the applied 3D battery concept. The impact of laser structuring and modification of battery materials on the electrochemical performance with respect to the nanoscale is of considerable relevance for future applications in battery manufacturing.

Keywords: ultrafast laser ablation, laser structuring, laser modification, electrode, lithium-ion battery, 3D battery

1. Introduction

Typically, diffusion and electrochemical processes in lithium-ion battery (LIB) materials are nanoscale in nature [1]. In case of a classical lithium-ion battery (LIB) concept, the respective composite electrode consists of active material particles of µm-scale, carbon black with a size in the lower 100 nm range and finally the binder material with a diameter at nm scale. The binder is for enabling mechanical stability of the layer and for improving adhesion to the current collector and the carbon black guarantees a sufficient electrical conductivity. In addition, within the composite electrode nanoscaled pores exist which need to be filled with liquid electrolyte and which give the electrode the ability to undergo volume changes of the active material during battery operation, typically 2-3% volume change for cathodes such as NMC (lithium-nickel-manganese-cobalt-oxide). In general, the pore distribution is of bi-modal type with dominant pore sizes in µm range and in the range of a few 100 nm [2]. The NMC active material consists of agglomerates. Those called secondary particles consists of primary particles which are typically of nano-scale size. The inner structure of such particles can be also quite complex and of porous nature [3]. But in general the primary particles are of cylindrical shape which are oriented towards the particle center [4]. On anode side the classical active material is consisting of microscaled particles such as flat, flake-like graphite. However, the next generation battery, the so-called “generation 3” [5], is using also silicon nanoparticles as active material which is mixed with graphite microparticles forming together with binder and carbon black a composite electrode with micro- and nano-sized porosity. Silicon is applied in order to boost the energy density. In the final electrode design, graphite particles of micrometer scale are surrounded by silicon nanoparticles as shown in [6]. During battery operation, the volume change of graphite is typically about 10 % while for silicon values of about 280 % can be reached.

* wilhelm.pfleging@kit.edu; phone +49 721 608 22889; http://www.iam.kit.edu/awp/165.php

A main task in research and development is the evaluation of impact of laser processing to influence the functional properties of nanoscaled battery materials. Laser technology in battery manufacturing is quite various: laser welding of so-called bus bars for module fabrication is already very well established in battery production. Well established is also laser cutting of electrodes instead of using conventional mechanical punching. Hereby, laser cutting using ultrafast lasers delivers the best cutting edge quality [7]. Another approach is using diode lasers for the electrode drying process. About 50 % of energy consumption during drying can be saved by using laser instead of a classical oven technology [8]. With regard to high energy and high power batteries, the structuring of thick film composite electrodes is at the threshold of becoming a relevant technology for next generation battery manufacturing. All in all, laser technologies are completing technical approaches for optimizing electrode architectures on different scale levels, on nm, µm, and on macro-scale. For improvement of the electrochemical performance, the electrode architecture must designed according to the application scenario. Main elements of the electrode architecture are: film thickness (mass loading), particle size and distribution, multilayer coating, active surface area, and capillary and pores design for optimized electrolyte wetting behavior. An overview about recent progress in laser structuring of battery materials is given in [9,10].

2. Structuring of current collectors

Current collectors are quite thin metallic foils made of copper (Cu) or aluminum (Al). Cu can be about 6 µm in thickness only. However, the challenge one faces is that the adhesion of the active material to the current collector can be critical, e.g., after coating of thick film electrodes the composite electrode can lift-off from the current collector foil. And secondly, during electrochemical cycling the material undergoes a periodical volume change which can decrease the cell lifetime due to a restricted adhesion of the composite layer to the current collector. Therefore, the effort of structuring the current collector seems to be justified. However, structuring should be quite gentle due to the small thickness of the metallic foils. Another question is about the scale of structuring, should it be on nm scale or on the µm-scale? Microscaled dimples were generated via laser ablation in aluminum capturing the size of NMC agglomerates as shown in Figure 1 a.

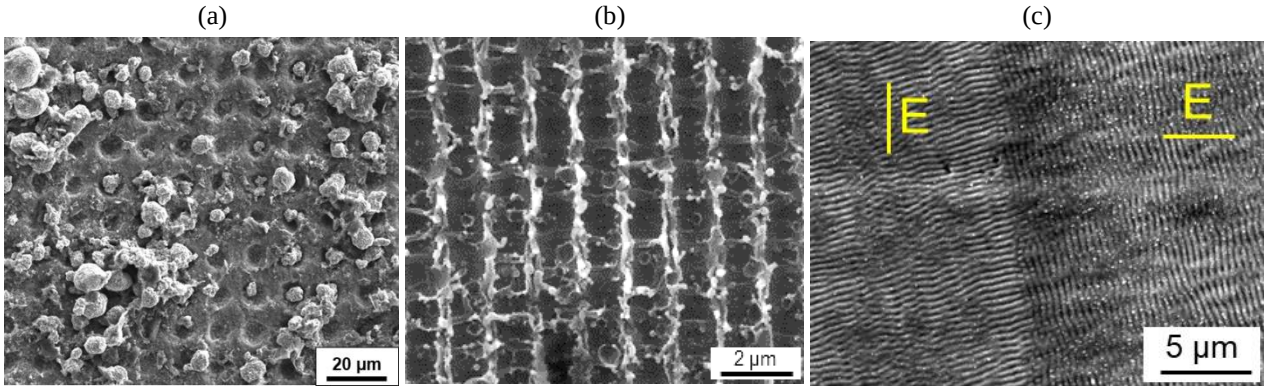

Figure 1:Scanning electron microscopy (SEM) images of laser structured copper current collector foils: (a) laser-generated dimple structures with diameter of about 6 µm and NMC particles attached to the surface after peel-off adhesion test, (b) DLIP line pattern with a periodicity of 1.3 µm and (c) LIPSS pattern with a line period of about 400 nm.

However, those surface patterns delivered a significant reduced film adhesion in comparison to unstructured Al foils. Since the nanoscaled binder is mainly responsible for adhesion properties, a further reduction in structure size was evaluated. For this purpose DLIP (Direct Laser interference Patterning), Figure 1 b, and LIPSS (Laser-induced Periodic Surface Structuring), Figure 1 c, were established to cover a structure range from about 400 nm up to the micron scale. It could be proven that the NMC film adhesion is improved with decreasing pattern periodicity. Electrochemical performance such as lifetime and cell impedance are expected to scale with film adhesion [11].

3. Structuring of ceramic coated separator materials

The ultra-fast laser structuring of ceramic-coated separator material is established with a line periodicity of 50 µm and a line width of 7 µm each (Figure 2 a, b). The thin ceramic coating already enables a good electrolyte wettability of about 20 ° contact angle in comparison to 80° of the uncoated PP separators.

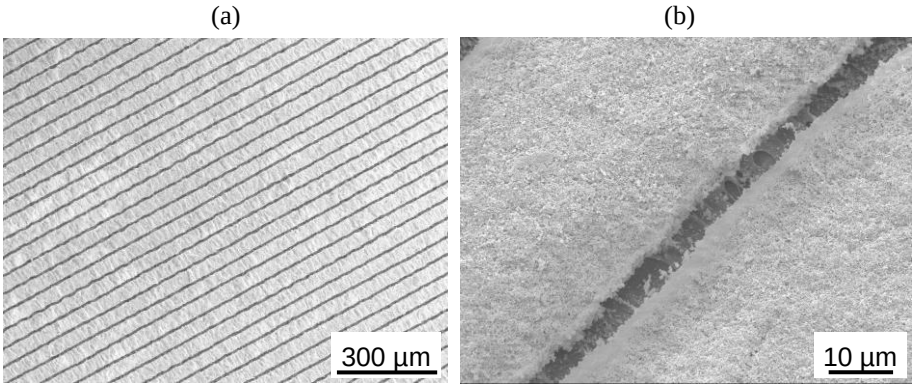

Figure 2: SEM of fs-laser structured ceramic coated separator foil (PP separator (thickness 15 µm) coated with Al_2O_3 (thickness 2 µm)): (a) overview and (b) detail view (line periodicity 50 µm).

However, introducing a laser patterning as shown in Figure 2 a further improvement of wetting properties, namely a contact angle of 0°, is achieved. Electrochemical studies show that the capacity retention is significantly enhanced by using structured separator materials. This research is quite at the beginning because structuring of separator materials can have also impact on safety issues and laser generated defects leading to an electrical shortcut should be strongly avoided.

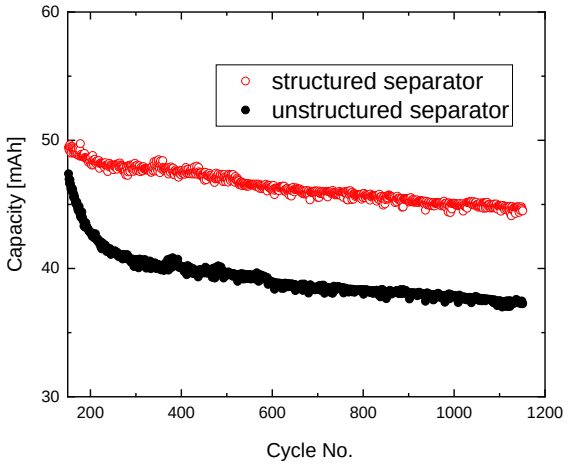

Figure 3: Lifetime cycling performance of NMC battery in pouch cell design (Charging C/5; discharging 1 C) with structured and unstructured ceramic coated separator (see Figure 2).

4. Structuring of composite electrodes

Laser structuring of electrode materials is quite a new research field which was initiated by KIT in 2008 [10,12]. At the beginning laser micro- and nano-structuring of compact thin film electrodes were studied to increase the active surface area [13], and diode laser annealing was established to adjust the crystalline phase and grain size [14]. A few years later, first studies were carried out for patterning of composite electrodes [15,16]. Finally it took a few years until more research institutions became aware of the new research field as documented in [10]. To understand the impact of laser radiation on micro- and nano-scale, a closer look on laser structured electrode materials is necessary. Ultrafast laser ablation of composite NMC electrodes leads to cut through of active particles (a) while ns laser ablation is a thermally driven process leading to selective evaporation of binder material without affecting the active material particles (b). However, due to the thermal nature of ns laser ablation the highest achievable aspect ratio is in the range of one or less. Additionally, ns laser ablation can lead to partial surface melting of active material particles or even to material decomposition [17], especially along the sidewalls of generated cavities but also at the laser scanning turning points where heat accumulation occurs. In comparison to ns laser ablation, ultrafast laser ablation of composite electrodes can reach much higher aspect ratios while

maintaining the electrochemical phase of active materials [18]. For line patterning, hole drilling, and cutting of electrode materials one can recognize almost similar ablation characteristics.

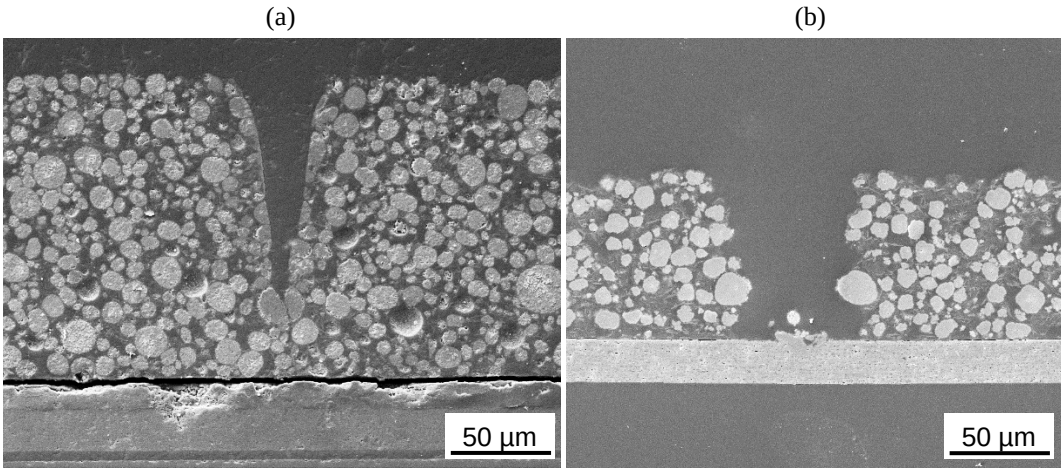

Figure 4: SEM of laser structured NMC cathodes in cross-sectional view: (a) fs laser structuring (pulse length 600 fs); (b) ns laser structuring (pulse length 200ns).

The thick film concept is an important tool to increase energy density on cell level by a value of 30 % [9]. Increasing the film thickness of an electrode means that ratio of active mass to inactive mass in a battery is increased. Less amount of current collector foils and separator material is used. The main benefit is achieved for electrode thicknesses in the range of 150 µm to 200 µm. However, increasing electrode thickness also induces some drawbacks, especially for high power operation. Due to the high diffusion overpotential for thick film electrodes as a result of battery operation, the resulting lithium concentration in composite electrodes strongly varies from top of the electrode down to the current collector. Finally, this will lead to a drop in overall capacity. The thick film concept is suitable for the realization of high energy batteries. However, to make those batteries also suitable for high power operation, the thick film concept needs to be flanked by the establishment of 3D electrode architectures. The so-called 3D battery concept is very well known from micro-battery applications [12]. Hereby the diffusion kinetics and impedance properties are enhanced. Furthermore, especially of interest for silicon anode materials, the avoidance of mechanical tensions becomes possible due to 3D electrode structuring. Different structure types are possible such as holes, lines, or grid patterns. While state of the art commercial thin film electrodes do not really need a 3D pattern due to an already good lithium diffusion kinetics, the thick film electrodes require a 3D structure to suppress cell polarization which mainly arises from long lithium diffusion pathways.

5. Outlook

Laser processing of battery materials is a versatile tool to enhance electrochemical performance in a controlled manner. In most cases the use of ultrafast laser radiation for structuring of battery material is superior to ns laser ablation. The structuring of composite electrode materials seems to be the most promising approach to be introduced for next generation batteries. The process upscaling issue is currently the main challenge for introducing this laser technology into battery manufacturing. However, process upscaling to a TRL of 6 was already realized at KIT by applying roll-to-roll multibeam laser processing. The results were outstanding and revealed a boost in electrochemical performances even for advanced high nickel NMC electrode materials. It was shown, that structuring of both electrode types, anode and cathode, provides the best electrochemical performance data. Recently and for the very first time, the 3D battery concept was transferred to a large footprint and high capacity (20 Ah) cell with a battery lifetime that is more than twice as long as that of an unstructured cell.

6. Acknowledgements

We are grateful for the help of our colleagues A. Reif, H. Besser, and M. Kapitz for their scientifically and technically support and assistance in laser processing, material characterization, and battery analyses. This research was funded by the Federal Ministry of Education and Research (BMBF), project NextGen-3DBat, project No. 03XP01798F.

7. References

1 Jung, S.-K., Hwang, I., Chang, D., Park, K.-Y., Kim, S.J., Seong, W.M., et al., *Nanoscale phenomena in lithium-ion batteries*, Chemical reviews, 120(14) (2019) 6684-6737

2 Meyer, C., Bockholt, H., Haselrieder, W., Kwade, A., *Characterization of the calendering process for compaction of electrodes for lithium-ion batteries*, Journal of Materials Processing Technology, 249 (2017) 172-178

3 Müller, M., Schneider, L., Bohn, N., Binder, J.R., Bauer, W., *Effect of Nanostructured and Open-Porous Particle Morphology on Electrode Processing and Electrochemical Performance of Li-Ion Batteries*, ACS Applied Energy Materials, 4(2) (2021) 1993-2003

4 Pimenta, V., Sathiya, M., Batuk, D., Abakumov, A.M., Giaume, D., Cassaignon, S., et al., *Synthesis of Li-rich NMC: a comprehensive study*, Chemistry of Materials, 29(23) (2017) 9923-9936

5 Bracklo, C., Bratz, K., Echtermeyer, R., *Fortschrittsbericht 2018 – Markthochlaufphase*. 2018, Berlin: Nationale Plattform Elektromobilität (NPE)

6 Meyer, A., Ball, F., Pfleging, W., *The Effect of Silicon Grade and Electrode Architecture on the Performance of Advanced Anodes for Next Generation Lithium-Ion Cells*, Nanomaterials, 11(12) (2021) 3448

7 Pfleging, W., Zheng, Y., Mangang, M., Bruns, M., Smyrek, P. *Laser processes and analytics for high power 3D battery materials*. in *Frontiers in Ultrafast Optics: Biomedical, Scientific, and Industrial Applications XVI*. 2016. SPIE

8 Neb, D., Kim, S., Clever, H., Dorn, B., Kampker, A., *Current advances on laser drying of electrodes for lithium-ion battery cells*, Procedia CIRP, 107 (2022) 1577-1587

9 Pfleging, W., *Recent progress in laser texturing of battery materials: A review of tuning electrochemical performances, related material development, and prospects for large-scale manufacturing*, International Journal of Extreme Manufacturing, 3(1) (2021) 012002

10 Li, Z., Wei, X., Yang, Z., *Pulsed Laser 3D-Micro/Nanostructuring of Materials for Electrochemical Energy Storage and Conversion*, Progress in Materials Science, (2022) 101052

11 Zhang, N., Zheng, Y., Trifonova, A., Pfleging, W., *Laser structured Cu foil for high-performance lithium-ion battery anodes*, Journal of Applied Electrochemistry, 47 (2017) 829-837

12 Pfleging, W., *A review of laser electrode processing for development and manufacturing of lithium-ion batteries*, Nanophotonics, 7(3) (2018) 549-573

13 Ketterer, B., Vasilchina, H., Seemann, K., Ulrich, S., Besser, H., Pfleging, W., et al., *Development of high power density cathode materials for Li-ion batteries*, International Journal of Materials Research, 99(10) (2008) 1171-1176

14 Pröll, J., Kohler, R., Mangang, A., Ulrich, S., Bruns, M., Seifert, H., et al., *Diode laser heat treatment of lithium manganese oxide films*, Applied Surface Science, 258(12) (2012) 5146-5152

15 Wollersheim, O., Pfleging, W., *Optimized Logistics of Manufacture Novel Electrolyte Filling Process for Lithium-ion Cells*, ATZelektronik worldwide, 7(1) (2012) 38-41

16 Pfleging, W., Proell, J., Kohler, R., Seifert, H. *Laser processing and functionalization of battery materials*. in *Laser and Tera-Hertz Science and Technology*. 2012. Optica Publishing Group

17 Mangang, M., Seifert, H., Pfleging, W., *Influence of laser pulse duration on the electrochemical performance of laser structured LiFePO4 composite electrodes*, Journal of Power Sources, 304 (2016) 24-32

18 Zhu, P., Seifert, H.J., Pfleging, W., *The ultrafast laser ablation of Li (Ni0. 6Mn0. 2Co0. 2) O2 electrodes with high mass loading*, Applied Sciences, 9(19) (2019) 4067