Direct laser interference patterning and ultrafast laser-induced micro/nano structuring of current collectors for lithium-ion batteries

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ABSTRACT

Laser-assisted modification of metals, polymers or ceramics yields a precise adjustment of wettability, biocompatibility or tribological properties for a broad range of applications. Due to a specific change of surface topography on micro- and nanometer scale, new functional properties can be achieved. A rather new scientific and technical approach is the laser-assisted surface modification and structuring of metallic current collector foils for lithium-ion batteries. Prior to the thick film electrode coating processes, the formation of micro/nano-scaled surface topographies on current collectors can offer better interface adhesion, mechanical anchoring, electrical contact and reduced mechanical stress during cycling. These features in turn impact on the battery performance and the battery life-time. In order to generate the 3D surface architectures on metallic current collectors, two advanced laser processing structuring technologies: direct laser interference patterning (DLIP) and ultrafast laser-induced periodic surface structuring (LIPSS) were applied in this study. After laser structuring via DLIP and LIPSS, composite electrode materials were deposited by tape-casting on the modified current collectors. The electrode film adhesion was characterized by tensile strength measurements. The impact of various surface structures on the improvement of adhesive strength was discussed.

Keywords: Laser-induced periodic surface structuring, Direct laser interference patterning, femtosecond and picosecond laser processing, lithium-ion battery, Peel-off adhesion test, film adhesion, 3D battery.

1. INTRODUCTION

Within the last two decades, lithium-ion batteries (LIB) became certainly essential storage of electric energy applying in the domains of electrical vehicles, mobile electrical devices, energy storage for solar and wind power [1-4]. Current research for the next-generation high power LIBs focus on improving electrode materials, electrolytes, and new battery concepts. However, one important property of electrode materials is the film adhesion coating towards to the current collector. The coating has to withstand the mechanical demands including the ultrasonic welding during the cell assembly, mechanical stress during de-/insertion of lithium-ions during cell cycling. Lack of film adhesion can result in the delamination of electrode film from the current collector after coating and cycling which lead to an enhanced internal resistance, dramatic capacity loss and reduced battery life-time. Delamination becomes even more problematic with advanced high power silicon-based anode materials due to a volume change of about 400 % during battery cycling [5, 6]. Alternative current collectors with 3D surface architectures are required with respect to an improvement of film adhesion, mechanical anchoring, and electrical contact.

In a rather new approach it could be shown that laser generated blind holes (50-100 µm in diameter, aspect ratio 1) in copper plates can act as mechanical anchoring for silicon-based active coating leading to a significant improvement of battery cycle retention [5]. Unfortunately, this approach cannot be transferred to state-of-the-art battery designs with

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current collector foils with thicknesses of about 8-20 µm. Therefore, the laser-assisted mirco/nano-structuring of thin film current collector was developed. In this work, two advanced laser structuring technologies: Direct Laser Interference Patterning (DLIP) and ultrafast Laser-Induced Periodic Surface Structuring (LIPSS) are introduced. The formation of the periodic surface structures via DLIP and LIPSS was investigated on different metallic surfaces. Furthermore, composite electrode materials were deposited by tape-casting on modified current collectors. The electrode film adhesion was characterized by applying a 90° peel-off adhesion tester.
Apart from impact of surface structures, active materials practical size, polymer binder and the practical morphology influence strongly the adhesion strength [7]. Ongoing studies will focus on the design of the surface architectures for different electrode materials in order to achieve further improvement of film adhesion. The electrochemical performance of batteries assembled with laser modified current collectors will be investigated.

2. EXPERIMENTAL

2.1 Laser-structuring

Two advanced laser structuring technologies were applied: laser direct interference patterning and ultrafast laser-induced periodic surface structuring.

Direct Laser Interference Patterning (DLIP)

In DLIP, two, three or more laser beams are required in order to achieve an interference pattern on the sample surface. At laboratory scale, a coherent laser beam is split into two or more sub-beams by using a beam splitter which are later overlapped on the surface. The number of used laser beams permit to control the intensity distribution of the interference pattern [8]. A two-beam configuration enables to produce a line-like interference pattern as shown in figure 1 a) and b).

a) b) c)

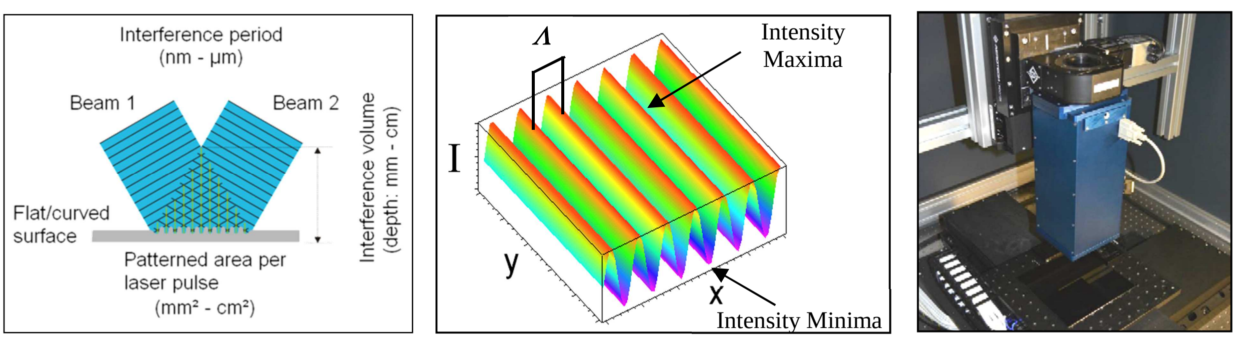

Figure 1. a) Principle of two-beam-interference; b) line-like interference patterns by using two laser beams; c) compact DLIP optical head integrated into 500 mm x 500 mm translation stages.

The periodicity Λ of line-like structures can be adjusted by varying the angle α between two sub-beams as well as the wavelength λ:

$$\Lambda = \frac{\lambda}{2 \cdot \sin(\alpha/2)} \tag{1}$$

DLIP technology is a very efficient method for fabrication of large scale periodic surface structures by using a single laser pulse. Recently surface structuring speeds up to 0.7 m²/min could be reached using a 180W IR laser [8]. In this study, the DLIP structuring process was performed for all experiments applying a laser wavelength of 1064 nm and a pulse duration of 10 ps.

Laser-Induced Periodic Surface Structuring (LIPSS)

Ultrafast laser-induced periodic surface structures (LIPSS, so-called nano-ripples) are currently under intense investigation. LIPSS are nano-scaled periodic wave-like structures with a periodicity close to the laser wavelength. Within many studies it was found that LIPSS with different morphology can also be formed, e.g. by femtosecond laser processing on semiconductors [9, 10], metals [11-13], and polymers [14]. At KIT, we focus our study on fabrication of LIPSS and micro/nano-surface structures on metallic surface with enhanced surface adhesion and friction.
LIPSS were generated by direct femtosecond laser processing. A femtosecond laser source (Tangerine, Amplitude Systèmes, France) with a maximum average laser power of 20 W and a maximum laser pulse energy of 100 µJ at a central wavelength of 1030 nm was utilized for the experiments. Laser radiation is linear polarized with a tunable pulse duration from 350 fs up to 10 ps and a variable repetition rate of up to 2 MHz. Moreover, the laser system can also operate at a wavelength of 515 nm and 343 nm by means of second harmonic generation (SHG) and third harmonic generation (THG), respectively.

The structuring process was performed for all experiments applying a laser wavelength of 515 nm, a repetition rate of 200 kHz, and a pulse duration of 350 fs in ambient air as well as under normal incidence of the laser beam. Furthermore, the laser beam was focused using a beam expander and a F-Theta objective lens with a focal-length of 100 mm. The focused laser beam had a spot size on the sample surface of about 20 µm.

The formation of LIPPS was investigated on copper current collector surfaces as function of laser fluence, laser pulses and scanning speed. Subsequently, the morphologies of laser generated surface structures were analyzed by means of a scanning electron microscope (Philips, FEI XL/30-S FEG). In order to study surface properties of LIPSS, atomic force microscopy (AFM, Bruker Dimension Icon) was applied.

2.2 Tape-casting of electrode materials on aluminum and copper current collectors

The cathode/ anode composited electrode materials were prepared and coated by using a tape-casting film coater (Model: MSK-AFA-L800-H, MTI Corporation, USA). The cathode material is constituted of NMC (BASF, Germany), polyvinylidene fluoride (PVDF) binder (MTI Corporation, USA), conductive agent (Timcal Super C65, MTI Corporation, USA) and N-Methyl-2-pyrrolidone (NMP) (BASF, Germany) as solvent. The anode slurry consisted of graphite (Targray technology, USA), PVDF binder (MTI Corporation, USA), conductive agent (Timcal Super C65, MTI Corporation, USA), and NMP (BASF, Germany) as solvent. The cathode and anode slurries were deposited onto the 15 µm thick aluminum substrate and the 12 µm thick copper substrate (Targray technology, USA), respectively. The coated electrodes were dried up by using a heating lid at ~ 60 °C in ambient air for 2 hours. All the films were calendered using a compact hot rolling press (Precision 4” Hot Rolling Press/Calender, MTI Corporation, USA). After calendaring, the film thickness was adjusted in the range of 80-95 µm.

2.3 90° Peel-off adhesion test

Peel tests are a standard method in industry for evaluating bonding of adhesive materials to surfaces. In order to investigate the electrode film adhesion, a 90° Peel-off adhesion tester in the universal testing machine (10 T, UTS, Germany) was applied. As shown in figure 2, the electrode materials were stuck to the adhesive tape on the substrate. Using a mechanical clamp, the end of the electrode film was fixed to a mechanical testing machine load cell. Tensile force is perpendicular to the peeled electrode films in 90 degree (figure 2).

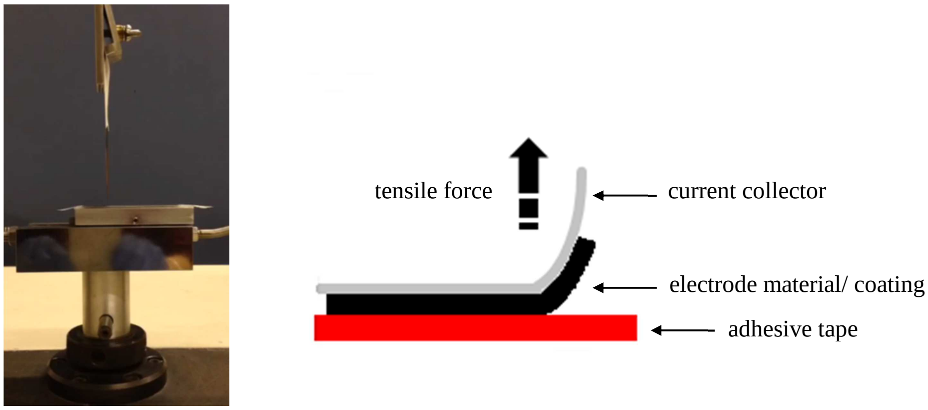

Figure 2. left: measurement setup of the 90° peel-off tester in the universal testing machine UTS; right: basic principle of the 90° peel-off testing mechanism.

During the measurement, the substrate was moving with a testing speed of 600 mm/min. The force needed to separate the electrode materials from the current collector was measured. The tensile strength γ is calculated from the measured tensile force F related to the width of sample d, which is equal to the equation (2):

$$\gamma = F/d \tag{2}$$

3. RESULTS AND DISCUSSION

3.1 Formation of laser-assisted surface structures

Direct laser interference patterning

In this study, the line-like periodic surface structures were successfully fabricated by applying a picosecond laser source operating at a wavelength of 1064 nm. Figure 3 shows the surface structures formed on aluminum and copper surfaces with defined periodicity of 1.3 µm and 3 µm, using laser fluence in the range of 250 – 300 mJ/cm². AFM-measurements on aluminum surface permitted to determine a spatial period between 1.3 µm and 1.5 µm with an average roughness R_a of 109 nm (not shown).

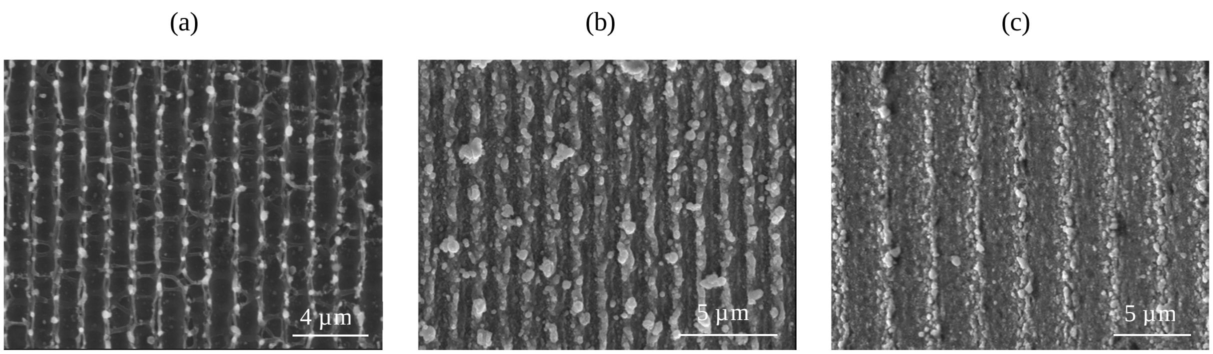

Figure 3. SEM images of line-like surface structures: a) aluminum, Λ = 1.3 µm, b) copper, Λ = 1.3 µm, c) copper, Λ = 3µm.

Laser-induced periodic surface structuring

This section is focused on the laser-based modification of the copper surface by applying ultrafast laser processing. The formation of LIPSS was investigated as function of laser fluence, pulse number and scanning speed.

As shown in Fig. 4, a copper surface was exposed to the laser beam at a fluence of 10.35 J/cm². During the first laser pulse, randomly distributed nano-pores and nano-pillars are formed on the laser irradiated surface. With a further increase in laser pulse number, the nano-sized ripples in the range of 400 nm could be achieved in the periphery of the laser irradiated surface. These experimental results depict that the ripples can be formed at low laser fluence and with increased pulse number. For surface functionalization, it is of great interest to form nano-sized ripples on large surface areas. For this purpose, the laser process has to be performed in scanning mode. As shown in Figure 4, well defined ripples were observed after applying the optimized laser parameter: laser fluence of 0.16 J/cm² and scanning speed of 50 mm/s. This corresponds to a laser pulse overlap of 80 laser pulses per irradiated area. An average roughness R_a of 181 nm and a maximum depth of LIPSS of 500 nm could be realized.

In our experiments it was determined that the LIPSS on copper can be generated with a laser fluence close to the ablation threshold of 0.41 J/cm². However, by using an appropriate combination of laser fluence and scanning speed, the micro-scaled line structures combined with nano- ripples can be formed (Fig. 5). Line and grid patterns with a pitch distance of 50 µm were fabricated on the copper current collectors.

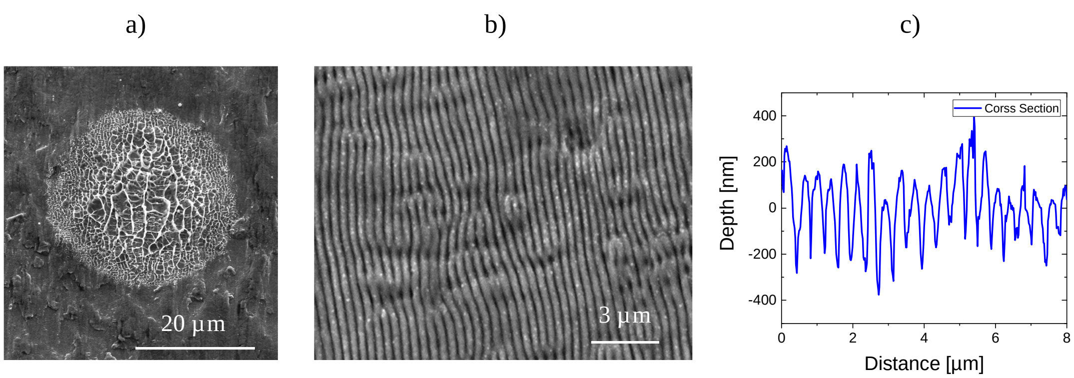

Figure 4. SEM image of laser pulse induced nano-structures (a), well defined LIPSS on copper surface by using laser fluence of 0.16 J/cm² und scanning speed of 50 mm/s (b) and the corresponding cross sectional surface profile by applying AFM.

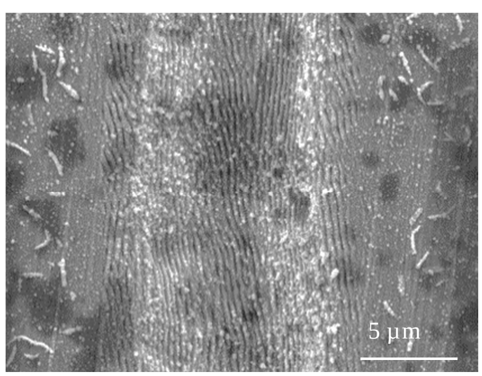

Figure 5. SEM image of micro-scaled line structure combined with nano-ripples (Laser fluence: 0.14 J/cm², scanning speed: 10 mm/s).

3.2 Measurement of adhesion strength between structured current collectors and electrode materials

Various surface structures via LIPSS and DLIP were formed on the metallic current collectors. Subsequently, NMC-based as well as graphite-based composite materials were deposited by tape-casting on current collectors for the following adhesion measurements.

Figure 6 depicts enhanced tensile strength of films deposited on structured aluminum and copper surfaces in comparison to the reference samples which were not modified by laser radiation. A tremendous increase of film adhesion could be achieved with a value of about 250 N/m on laser structured aluminum surface by applying DLIP (reference: γ = 140 N/m). After the adhesion measurements, SEM images exhibit that NMC-particles and binder were tightly stuck on the modified aluminum surface. Meanwhile the coating on the reference samples was completely separated from the current collector (not shown).

It was shown that the adhesion strength of graphite thick films on copper surfaces was significantly lower than the measured values of NMC on aluminum surfaces (figure 6). This might be due to different particle sizes and shapes of graphite and NMC particles. However, structured copper surfaces reveal improved tensile strengths and lower standard deviation (figure 6b). The major impact of different surface structures on graphite anode film adhesion can be attributed to the enhanced contact area between the particles, basically here graphite, and binder and to the structured current collectors. It is obvious that various designs of surface structures influence the film adhesion. The best result achieved on copper surfaces was by applying hierarchical surface structures containing line/grid-patterns and nano-ripples. SEM studies reveal that graphite particles and binder were anchored inside of line/grid structures randomly due to an appropriately increased contact area for the graphite particles. This could explain why the surface with micro/nano-scaled line/grid structures reached a larger adhesion strength compared to those with nano-scaled surface structures.

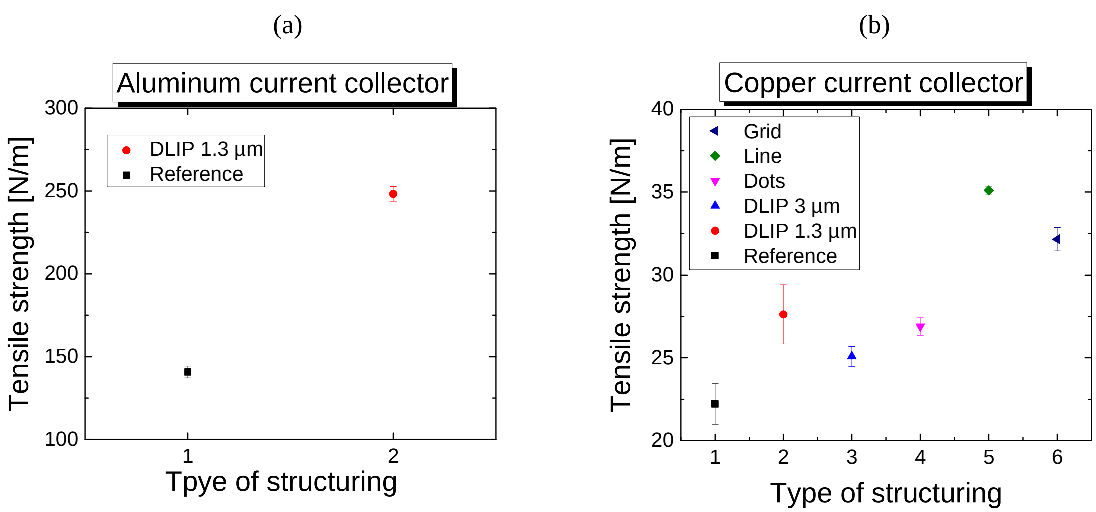

Figure 6. Tensile strength of NMC (a) and graphite film (b) on laser modified current collectors as function of surface structures.

4. CONCLUSIONS

In our study, the formation of periodic surface structures via LIPSS and DLIP was investigated as function of laser parameters. Line-like surface structures with different periodicity were formed on aluminum and copper current collectors by applying DLIP. A huge improvement of adhesion strength was obtained for modified aluminum current collectors. Well-defined nano-ripples (LIPSS) and hierarchical surface structures (LIPPS combined with line or patterns) could be successfully generated on copper surfaces by using ultrafast laser materials processing. Ultrafast laser processing technology enables the fabrication of various surface patterns, such as dots, lines or grids. For copper, hierarchical surface structures with line patterns delivered the best results regarding graphite anode film adhesion.

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