Materials Research Proceedings 57 (2025) 286-293 https://doi.org/10.21741/9781644903735-33

Laser texturing of 3D Copper current collector for ultrafast Zinc metal plating

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Keywords: Laser Processes, Texture, Anode-Free Batteries

Abstract. Anode-free metal batteries with increased energy density hold promise for next-generation energy storage systems. However, the development of unwanted metal dendrites limits their practical application as electrodes. Zinc-ion batteries are promising since zinc is low-cost and allows the use of non-flammable aqueous electrolytes. 3D electrodes can reduce the current density per unit area and thus the dendrite formation. Quick laser texturing can selectively enhance zincphilicity within the grooves on Cu current collectors, increasing the charging rate. In this study, laser textures with different depths are performed on 100 μm Cu sheets electrode. Then, zinc metal is electrolytically deposited on the substrates and characterized by morphological and chemical (SEM/EDS) analysis. The half-cells with these collectors are tested in their functionality using a potentiostat. The textured current collectors will be evaluated as electrodes in Zn-ion batteries to achieve high charging rates.

Introduction

Zinc has emerged as a promising material in the field of energy storage, particularly for use in rechargeable batteries such as zinc-ion and zinc-air batteries. Its abundant availability, low cost, and high energy density make it an attractive alternative to other metal-based systems. The use of aqueous electrolytes [1] makes Zn-ion batteries safer than Li-ion batteries, which require flammable liquid electrolytes (e.g., 1M LiPF6 in Ethylene Carbonate/Diethylene Carbonate) [2].

The operating voltage of Zn-ion batteries is lower than that of Li-ion batteries, specifically 2V for Zn-ion vs 4V for Li-ion. However, the performance of zinc-based batteries heavily relies on the efficiency of the Current Collectors (CCs), which play a critical role in facilitating electron flow between the electrodes and external circuits. The selection of appropriate current collectors is crucial for enhancing the overall performance, stability, and lifespan of these systems. Metallic zinc can plate onto copper, forming dendrites, especially at high current densities. Therefore, this reduces the specific power attainable.

To overcome this limit, 3D electrodes are designed in order to limit the formation of dendrites. These three-dimensional structures can be obtained with several methods [3]. Among these, the use of laser treatment to modify current collectors represents an innovation in the field of energy storage.

Laser-based processes are largely studied as promising technologies for producing battery materials, cells, and packs. Laser welding is nowadays a reliable joining process for elements, cells, and batteries [4] while advances in laser cutting, especially using ultrafast laser sources are opening perspectives to substitute mechanical cutting [5]. Focusing on electrode production, laser

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drying is an alternative method compared to hot air blowing for efficient and homogeneous removal of solvent from the slurry deposited on the current collectors [6].

The laser can moreover be a valuable tool for structuring the electrodes to increase and homogenize the diffusivity of charges, reduce overpotentials, favor ion migration, and increase the performance of thick electrodes, guaranteeing high capacity coupled with high current density. Direct structuring was first implemented through laser drilling of micro-holes [7] and by grooving [8] the material electrodes with appropriate designs. The use of ultrashort pulses can strongly increase the aspect ratio of the holes and reduce the size of the Heat Affected Zone (HAZ), limiting the alteration of the chemical composition in the surrounding material. The coupling of low energy per pulse and high repetition rate demonstrated the achieving of good results in a relatively short processing time [9]. Laser surface structuring can be of great benefit when applied to the metallic current collectors, usually thin foils of Cu for the negative anode, and Al for the positive cathode. The laser beam can easily operate at the micrometric scale patterning features with dimensions that are comparable to the thickness of modern CCs, as thin as 10 μm In [10] a dense matrix of craters obtained by ns processing was employed to increase the adhesion of the active material layer on both Cu and Al foils, the process effectiveness was evaluated by peel-off test according to ASTM D 3167 and correlated with the laser fluence. Similar Al foils are then used to prepare Lithium Iron Phosphate half-cell electrodes that demonstrated a long-life capacity 86% higher with respect to cells based on commercial Al CC foil [11].

The bonding strength and the electrochemical contact between the CCs and the electrode material can be improved by ultrafast processing. Femtosecond pulses naturally induce hierarchical micro and nano-textures on the metallic foils increasing roughness and decreasing the wettability. Authors in [12] created a cross-hatched grid increasing the electrochemical performances, in particular, the long-life durability of both the half-cell electrodes based on Al cathode and Cu anode cells and the full batteries, compared to the counterparts assembled with commercial CCs.

Similar results are obtained in [13], by laser structuring CCs with a picosecond laser to generate a linear pattern. The linear pattern approach could in principle be more easily scaled up for mass production, authors moreover suggest that linear pattern can increase the recyclability of the materials thanks to the preferential orientation of the delamination cracks.

The peculiar characteristics of ultrashort pulses grant the possibility to operate exploiting different mechanisms: the generation of sub-micron Laser Induced Periodic Surface Structures (LIPSS), and the use of special optics to split the beam and produce Direct Laser Interference Patterns (DLIP) that, with enough available power can strongly increase the throughput of the texturing step. Both approaches were applied in [14] to process Silicon Carbide CC for next-generation Li-ion battery. DLIP appeared to appreciably increase the cycling stability of the electrodes, while LIPSS texturing appears marginally effective.

The objective of this work is to evaluate laser 3D structuring of current collectors for the reduction of local current density to minimize dendrite formation. The final aim is the future development of anode-less Zn-ion batteries.

Materials and Methods

Substrate preparation

The substrate material is a commercial 100 μm copper coil, generally used for electrodes. From this, samples in 60x40 mm^2 dimensions were obtained, and they were treated for 30 minutes in a 0.1 M $(NaPO_3)_6$ solution at 50 °C to remove any surface impurities and oxides.

They were then sonicated for 5 minutes, rinsed with water and acetone, and stored in acetone during the experimental campaign.

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Cu Laser texturing

The experimental laser set up includes an ultrashort-pulsed Ekspla Atlantic 50 laser source with a pulse duration of about 10 ps, equipped with three different wavelengths. To exploit the maximum power of the laser on copper, a wavelength of 1064 nm was employed. In addition, a Raylase Superscan V galvanometric scanning head precisely controls and directs the laser on the target and an F-theta lens provides a focused beam with a waist diameter at $1/e^2$ intensity of about 10 µm..

The 3D texturing chosen to ensure uniform deposition of zinc on copper is based on equispaced parallel lines with a pitch of 30 µm, to have about the same width of treated and untreated area, with three different depths: 5 µm (hereafter referred to as "5LT"), 10 µm ("10LT"), and 15 µm ("15LT"). The base material ("As is") shows the rolling direction signs.

The final laser parameters to ensure the design depths and good processing quality were: 500 kHz of repetition rate, 30 µm line spacing, 1000 mm/s of scan speed, 4-10-15 passes, 6 W of power, corresponding at 12 µJ energy per pulse and 15.3 J/cm^2 of fluence, see Table 1.

***Table 1**. Laser parameters employed in copper foils processing.*

	Fill spacing [µm]	Mark speed [mm/s]	Repetition Rate [kHz]	Passes	Power [W]	Energy per pulse [µJ]	Fluence [J/cm^2]
5 LT	**30**	**1000**	**500**	**4**	**6.0**	**12.0**	**15.3**
10 LT	**30**	**1000**	**500**	**10**	**6.0**	**12.0**	**15.3**
15 LT	**30**	**1000**	**500**	**15**	**6.0**	**12.0**	**15.3**

Zn metal electroplating

The zinc plating process was carried out using an electrochemical cell that was based on a glass container holding 40 mL of 0.5 M aqueous solution of $ZnSO_4$•7 H2O of electrolyte, see Fig. 1. The working electrode was connected to the copper sheet (10 × 20 mm^2), the counter electrode was connected to graphite (10 × 20 mm^2), and an Ag/AgCl electrode was used as the reference electrode. The immersed surface area of the copper (a) and graphite sheets (b) in the electrolyte solution (c) was consistently maintained at approximately 1 cm^2.

By using a Potentiostat Biologic VMP, two types of studies have been conducted: a first test lasting 10 minutes with an applied current of 20 mA/cm^2. and a second test lasting 20 minutes with an applied current of 10 mA/cm^2 between the graphite and copper electrodes.

Copper samples with deposited zinc were stored in Argon atmosphere before subsequent analysis.

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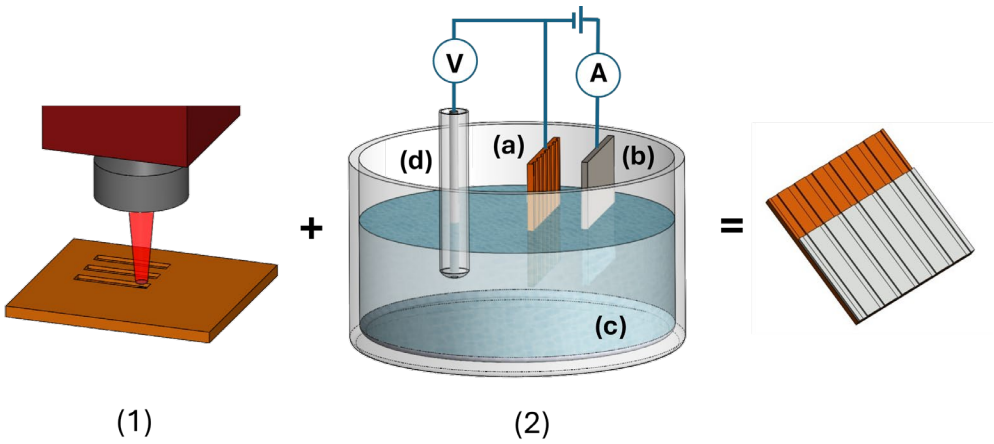


Fig. 1. *Scheme of fabricating samples: (1) Cu sheet laser processing, (2) electrochemical zinc deposition where (a) copper working electrode, (b) graphite counter electrode, (c) solution with electrolyte, (d) Ag/AgCl reference electrode.*

Morphological and chemical characterization

Firstly, an optical microscope was used to assess the depth of laser treatment by focusing on the lower surface of the treated region and on the upper surface of the untreated material and measuring the height difference.

Then, the specimen surface morphology was examined at various magnifications using a scanning electron microscope, the Nova NanoSEM 450 (Fei Company), and the surface composition was examined using EDS analysis (X-EDS Oxford INCA-350).

Point spectra were obtained every 30 seconds, and elemental maps were acquired after 6 minutes for untreated and laser-treated samples. The percentage of zinc, copper, and oxygen was evaluated quantitatively.

Results and Discussion

The processing time with the chosen parameters for patterning a 10 x 20 mm^2 5LT, 10LT, and 15LT area on the copper foils is 40 seconds, 1:40 minutes, and 2:30 minutes respectively.

The morphology of the untreated and 5LT laser-treated material without any deposition can be seen in the SEM images of Fig. 2 (a) and (b) respectively. Untreated foils show the striations caused by the rolling process while the grooves obtained by laser processing are quite regular with a depth of 5, 10, and 15 µm, a width of about 12 µm, and a taper angle of the vertical wall of about 20 degrees. The bottom of the processed grooves is filled with LIPPS with a pitch slightly less than 1 µm. The direction of the grooves is perpendicular to the rolling direction, while the orientation of the polarization plane was chosen parallel to the direction of the grooves, so the LIPSS are oriented perpendicular to the grooves with the final aim of generating a more pronounced hierarchical structure.

The other two images, Fig. 2 c) and d) show examples of the surface state after deposition at the very high current of 20 mA/cm^2 per 10 minutes. It is seen that the untreated foils in Fig. 2 (c) are very uneven, large portions of the material surface present free oxidation, which looks darker, the oxidation is caused by the dendritic aspect of the deposited zinc with a large surface exposed to the electrolyte. Zinc deposition on the patterned foils looks like in Fig. 2 (d), the linear grooves allow zinc to follow the morphology of the substrate and distribute uniformly over the surface, so the patterning promotes orderly zinc growth, preventing zinc oxidation.

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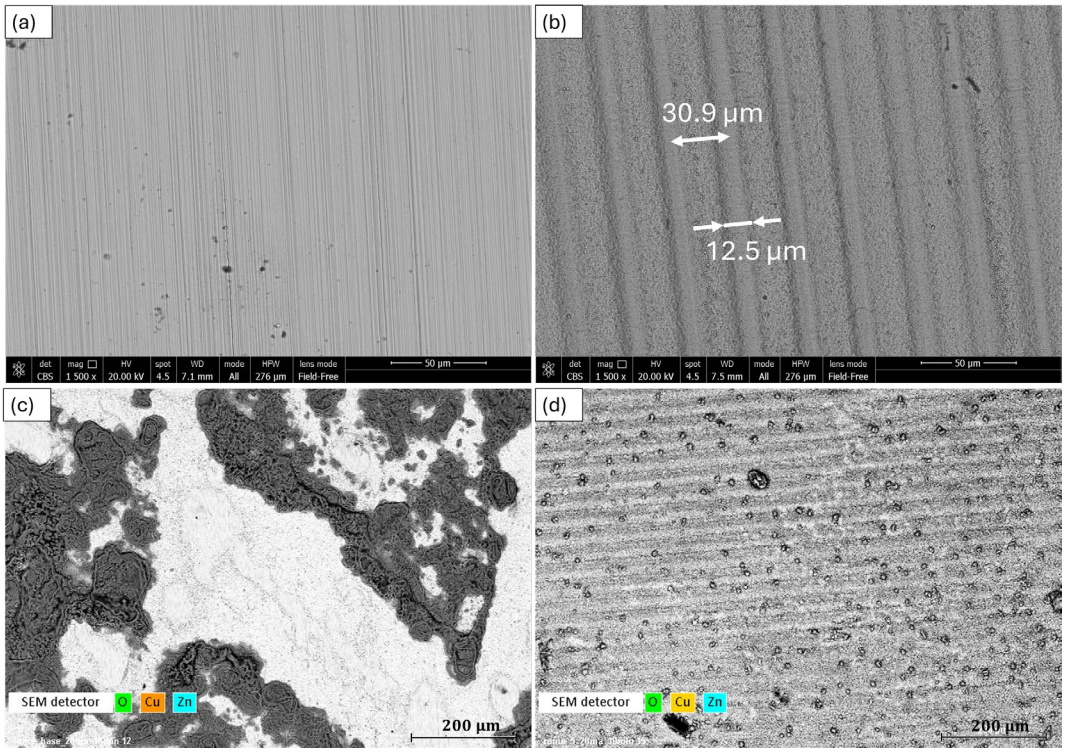


***Fig. 2**. SEM morphology of the (a) untreated and the (b) 5 µm groove laser treated material (LT5) without any zinc deposition; (c) untreated material and (d) LT5 with zinc deposition at 20mA for 10 minutes.*

Fig. 3 shows the voltage profile of the different samples of the copper foils during zinc electrodeposition. The two graphs illustrate the potential behavior during zinc electrodeposition on copper at current densities of 10mA/cm^2 and 20 mA/cm^2. In the first case, the potential is more negative for the "10LT" substrate compared to "5LT" and the "As is" indicating higher deposition overpotential on the substrate with a more complex microstructure. A similar trend in the potential hierarchy is observed in the second case, with more negative values across all curves compared to the 10 mA/cm^2 condition. The differences between the substrates become more pronounced, suggesting that microstructure significantly affects the deposition kinetics at higher current densities.

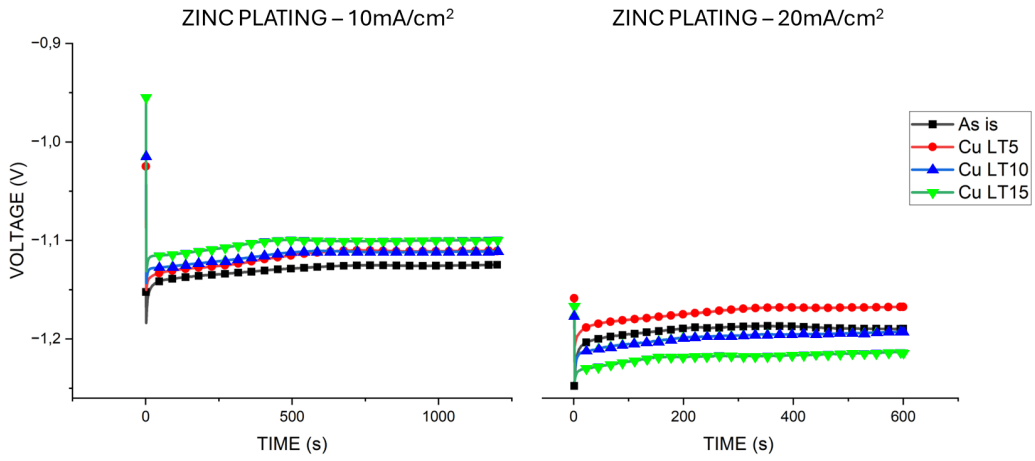


***Fig. 3.** Voltage profiles of Zinc deposition at 10 and 20 mA/cm^2.*

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Following zinc deposition, the samples are evaluated by X-EDS for a semi-quantitative comparison of the elemental balance and the uniformity of zinc on the surface.

The results of the quantitative mass percentages of oxygen, copper, and zinc are shown in the histograms in Fig. 4 for the untreated and laser treated materials. The histograms were obtained investigating areas of 0.75 mm^2, and the error bars represent 1σ error.

Regardless of the deposition strategy, laser treatment mostly increases the percentage of local zinc deposited. By depositing at a higher current, on average, an increase in the presence of oxygen is observed as expected. With a high charging current, the effectiveness of the laser patterning is obtained with the 10 µm deep grooves.

X-EDS map results for bare Cu foils and 10LT at 20 mA/cm^2 are presented in Fig. 5a) and b) respectively. In the images, Zn is highlighted in light blue on the right part of the images and Cu in orange on the left one.

It is evident from the results that laser structuring in Fig. 5b makes Zn deposition more homogeneous. Several large areas of exposed Cu are found in the bare copper, Fig. 5a) where Zn is missing altogether.

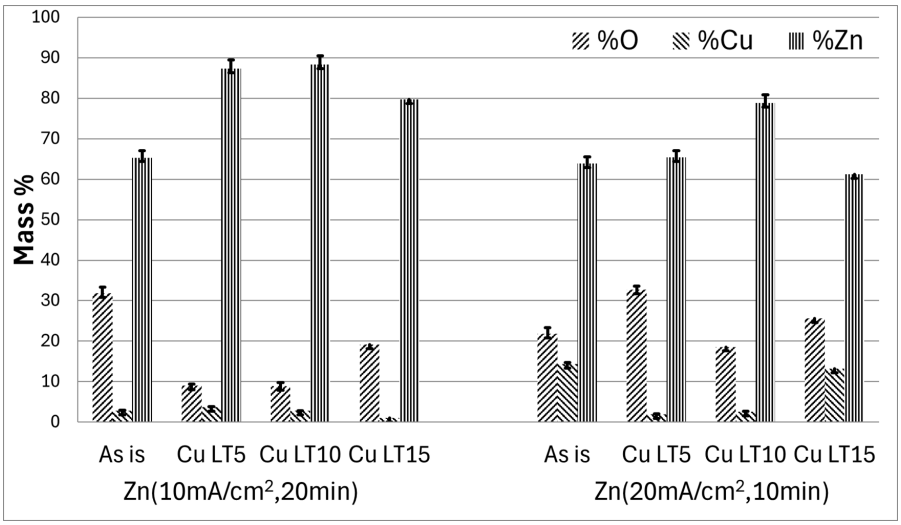


Fig. 4. *Quantitative mass percentages of Oxygen, Copper and Zinc, for the untreated material (As is), and laser treated material (CuLT5, CuLT10 and CuLT15) after the two different zinc deposition strategies. The bar error is calculated at 1σ.*

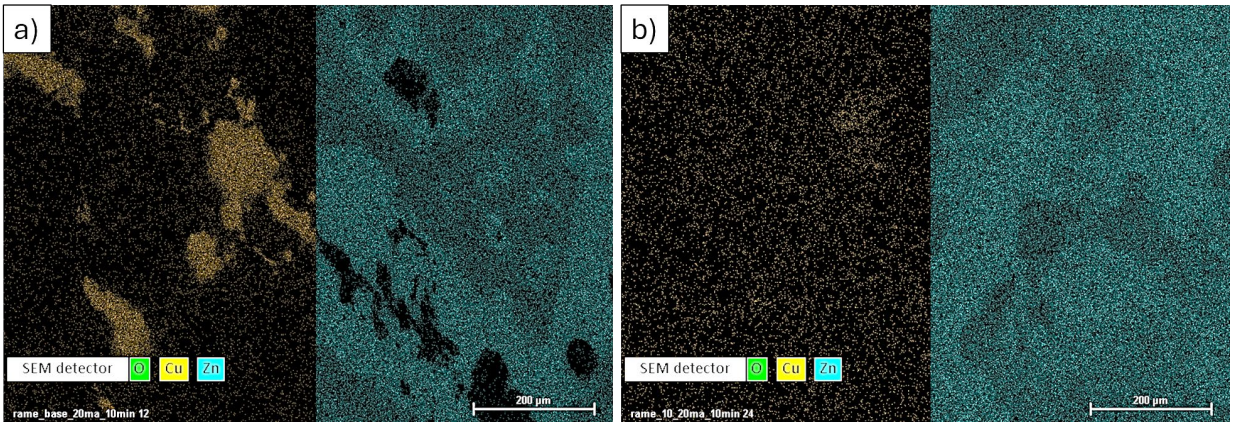


Fig. 5*. X-EDS map results for As is Cu (a) and 10LT (b) after zinc deposition at 20 mA for 10 minutes: copper is in orange on the left, zinc is in light blue on the right.*

Conclusions

In the field of energy storage, zinc has shown great promise, especially for usage in rechargeable batteries like zinc-ion and zinc-air batteries. It is a desirable substitute for other metal-based systems due to its high energy density, affordability, and wide availability.

However, to increase the overall performance, stability, and longevity of these systems, the right current collectors must be used. Particularly, metallic zinc can generate dendrites by depositing on copper. In this context, laser-structured 3D current collectors can be used for high current densities.

A regular parallel-line texture with 30 μm pitch was tested in this study, in three versions at different depths, 5, 10, and 15 μm. Zinc was electrolytically deposited on the textured copper according to two different deposition strategies, one at 10 mA/cm^2 for 20 minutes and the other at 20 mA/cm^2 for 10 minutes.

From the morphological analyses highlighting the percentage mass elemental components, it is found that the structuring makes the zinc deposition on the copper much more uniform. On the untreated copper, there are whole areas where zinc is missing.

Quantitative analysis shows that the percentage of zinc on treated copper increases regardless of the deposition strategy and with little influence on the depth of treatment between 5 and 10 μm with a saturation effect for more aggressive patterning 15 μm in depth. This demonstrates the validity of the proposed solution.

Further analysis should test the electrode in a high-current density battery. Our results have significant potential implications: using a 3D structure, we demonstrated the possibility of depositing Zn at high current densities more homogeneously compared to a 2D current collector. The currents used in this work (20 mA/cm²) are much higher than those typically reported in the literature for Zn-ion batteries (4-5 mA/cm²) and Li-ion batteries (1-2 mA/cm²). This study lays the groundwork for future applications such as Li-ion and Na-ion batteries.

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