Geometric Accuracy Analysis of Porous Current Collectors for Lithium Ion Batteries Based on Nanosecond Laser

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Abstract. In order to overcome the disadvantages of foam copper, template method and dealloy method in processing porous current collectors for lithium ion batteries, a new method of processing porous current collectors by nanosecond laser is proposed. Microporous fabrication experiment was carried out on the electrodeposited copper foil. The effects of laser repetition frequency and processing speed on the entry diameter, exit diameter, taper and roundness of the micropores were investigated. It is found that the laser repetition frequency has a significant influence on the entry diameter and exit diameter of micropores, but has little effect on the taper and the roundness. Furthermore, it is concluded that high processing speed leads to large roundness but small taper of the micropores. In addition, the variation trend of the entry diameter and exit diameter is complex because of the plasma shielding effect.

1. Introduction

It is well-known that lithium ion batteries have excellent performance which secondary batteries is lack of. Besides, using conventional copper foil as current collector material, powdering, cracking and even severe plastic deformation of the negative electrode material may occur during charging and discharging of the battery, which could probably increase the irreversible capacity of the battery. Compared with the conventional copper foil, the porous copper foil has some obvious advantages. The porous copper foil not only retains good electrical conductivity, ductility as well as other mechanical and electrical properties of the conventional copper foil, but also has better contact performance with the negative active material due to its porosity [1-2]. In addition, the porous copper foil has a high specific surface area and better ability to carry the active material. Therefore, the initial capacity of the lithium ion battery can be significantly improved [3].

The preparation methods of the porous current collector material mainly include foam copper, template method and dealloying method. Li [4] used foam copper as the current collector material, and plated the negative electrode material Sn on the foam copper. It was found that foam copper can enhance the cycle performance of battery. Tan [5] used hydrogen template method to prepare the copper foil material with porous characteristics, which can adapt to the large volume change during charging and discharging process of the battery. It can also enhance the binding force between the copper foil and the active material. Yu [6] etched the Ag-Au alloy in a nitric acid solution. It made use of the potential difference between Ag and Au [7] to prepare a nano-porous material, which can improve battery cycle performance.
Nowadays laser surface texturing has become an important part of the surface modification technology. It has some obvious advantages such as good controllability, excellent processing precision and high processing efficiency [8].

This paper proposes a method for processing porous copper foil using the technology of laser surface texturing by nanosecond laser. The quality of micropores was characterized by the entry and exit diameters, the taper as well as the roundness of micropores. The effects of laser repetition frequency and processing speed on the quality of micropores were investigated.

2. Experimental method

The specimen is made of electrolytic copper foil which contains 99.9% copper with the thickness of 12 μm. The nanosecond laser is used to irradiate the surface of copper foil under different repetition frequencies and processing speeds. The processing schematic is shown in Fig. 1. The laser is Polar-355-20 nanosecond ultraviolet laser from China Huari Laser Co., Ltd. The parameters of the laser are shown in Table 1. The laser beam is focused by lens and irradiates on the surface of material. The center of the laser spot moves along the circumference of the designed micropores. The material melts and gasifies after absorbing laser energy. Finally, the micropore with the size of 40μm is formed.

![Figure 1](image1.png)

**Table 1** Nanosecond Laser system characteristics

| Characteristics                      | Symbols | Values | Units |
|-------------------------------------|---------|--------|-------|
| Wavelength                          | λ       | 355    | (nm)  |
| Average power                       | \(P_a\) | 0–20   | (W)   |
| Pulse frequency(This experiment)    | \(f\)   | 20-50  | (kHz) |
| Pulse duration                      | \(T_D\) | 50     | (ns)  |
| Focused spot diameter               | \(D\)   | ≈20    | (μm)  |
| Scan speed(This experiment)         | \(V\)   | 0–900  | (mm/s) |

The entry diameter and the exit diameter of micropores are observed by KH-7700 digital three-dimensional video microscope of HIROX. The taper and the roundness of the micropores are calculated. The diameter measurement method is as shown in Fig. 2, four sets of diameters were measured in the circumferential direction and the average diameter was calculated at last.
Figure 2 The schematic diagram of diameter measurement

Define the taper (HT) as:

\[ \text{HT}(°) = \arctan \left( \frac{d_i - d_o}{2t} \right) \times \frac{180}{\pi} \]  

(1)

Where \( d_i \) is the entry diameter, \( d_o \) is the exit diameter and \( t \) is the thickness of copper foil. In order to characterize the edge smoothness of the micropores, the roundness is introduced. The entry roundness and the exit roundness of the micropore are expressed as follows.

\[ C_i = \frac{d_{\text{min}}}{d_{\text{max}}} \quad C_o = \frac{d'_{\text{min}}}{d'_{\text{max}}} \]  

(2)

Where \( C_i \) is the micropore entry roundness, \( d_{\text{max}} \) is the maximum entry diameter, \( d_{\text{min}} \) is the minimum entry diameter, \( C_o \) is the micropore exit roundness, \( d'_{\text{max}} \) is the maximum exit diameter, and \( d'_{\text{min}} \) is the minimum exit diameter.

3. Results and Discussion

3.1. Influence of laser repetition frequency

The processing speed is 500mm/s, the laser repetition frequency is 20 kHz, 30 kHz, 40 kHz and 50 kHz respectively. The typical processing morphology is shown in Fig. 3.

Figure 3 The typical micropore morphology by laser with \( f = 20 \text{ kHz}, \nu = 500\text{mm/s} \) ((a) entry diameter, (b) exit diameter)

The variations of entry and exit diameters with laser repetition frequency are shown in Fig 4. It is found that the entry diameter as well as the exit diameter decreases with the increase of laser repetition
frequency. Moreover, the attenuation rate of entry diameter increases with the repetition frequency, while the attenuation rate of exit diameter is less sensitive to the repetition frequency.

![Figure 4](image.png)

**Figure 4** The variations of the entry diameter and the exit diameter with laser repetition frequencies

The taper and roundness of micropores at different repetition frequencies are shown in Table 2. As the laser repetition frequency increases, the taper decreases. The taper at the repetition frequency of 50 kHz is much smaller than those at the repetition frequencies of 20 kHz, 30 kHz and 40 kHz. The results show that the consistency of entry and exit diameters increases with laser repetition frequency. Moreover, comparing against the effect of repetition frequency on the exit roundness, it was found that the entry roundness is less sensitive to the repetition frequency.

| Repetition frequency/kHz | HT/° | $C_i$ | $C_o$ |
|--------------------------|------|-------|-------|
| 20                       | 29.34| 0.90  | 0.81  |
| 30                       | 25.48| 0.91  | 0.85  |
| 40                       | 23.34| 0.93  | 0.88  |
| 50                       | 8.47 | 0.94  | 0.92  |

The relationship between the laser single pulse peak energy density $I_p$ and the laser repetition frequency $f$ is:

$$I_p = \frac{P}{\pi D^2 f} \tag{3}$$

Where $D$ is the effective diameter of laser spot, and $f$ is the laser repetition frequency. The relationship between the peak energy density of single laser pulse and the laser repetition frequency could be expressed as:

$$E_p = \frac{P}{f} \tag{4}$$

Where $E_p$ is the peak energy density of single laser pulse. Because the laser average power is constant (20W) in this study, the peak energy density of single laser pulse decreases with the increase of laser frequency.
repetition frequency. The laser energy abides by Gaussian distribution, and its energy field could be expressed as:

\[ \varphi(s) = \frac{2E_0}{\pi\omega_0^2} \exp\left(-\frac{2r^2}{\omega_0^2}\right) \]  

(5)

Where \( r \) is the distance from the center of laser beam, and \( \omega_0 \) is the radius of laser beam waist.

In summary, the laser energy decreases with the increase of distance from the spot center within the laser spot. As the laser repetition frequency increases, the single pulse peak energy density decreases, resulting in the energy reduction at the edge of laser spot. When the energy at the edge of laser spot is lower than the ablation threshold of copper foil, the effective diameter of laser spot is reduced, and the ability to remove material is weakened, therefore the entry and exit diameters are decreased. In addition, it is found that when the laser repetition frequency increases, the entry roundness as well as the exit roundness increases while the taper decreases.

3.2. Influence of laser processing speed

The laser repetition frequency is 50 kHz, the processing speed is 300mm/s, 500mm/s, 700mm/s, 900mm/s respectively, and the aperture is 40 \( \mu \)m. The typical morphology of the micropore is shown in Fig 5.

![Figure 5](image)

**Figure. 5** The typical micropore morphology by laser with \( f = 50 \) kHz, \( v = 900 \) mm/s ((a) entry diameter, (b) exit diameter)

Figure 6 shows the variations of entry and exit diameters of micropores with laser processing speed. It can be clearly seen that when the processing speed is between 300mm/s and 500 mm/s, the entry diameter as well as the exit diameter decreases with the increase of processing speed. When the processing speed is between 500mm/s and 900mm/s, however, the entry exit diameters first increase, and then decrease.
The variations of the entry and exit diameters of micropores with laser processing speed

The taper and the roundness of micropores at different processing speeds are listed in Table 3. It is found that when the processing speed increases, the taper decreases while both of the entry and exit roundness increase. When the processing speed increases from 300mm/s to 500mm/s, the taper decreases sharply from 33.99° to 8.47°. When the processing speed is in the range from 500mm/s to 900mm/s, the entry and exit roundness keep stable around 0.94 and 0.92, respectively.

Table 3 Taper and roundness of micropores at different processing speeds

| Processing speed/mm s⁻¹ | HT/°  | Ci   | Co   |
|--------------------------|-------|------|------|
| 300                      | 33.99 | 0.84 | 0.77 |
| 500                      | 8.47  | 0.94 | 0.92 |
| 700                      | 7.48  | 0.94 | 0.91 |
| 900                      | 4.95  | 0.94 | 0.92 |

The relationship between the laser spot overlap ratio and the laser processing speed could be expressed as:

$$\mu = 1 - \frac{\pi R v}{f}$$

Where $\mu$ is the laser spot overlap ratio, $v$ is the laser processing speed and $R$ is the diameter of processed micropore. For processing the same specification of micropores on the same material, since the laser repetition frequency is constant, the laser spot overlap ratio will be changed with the processing speed. According to Eq. (6), high laser processing speed leads to low laser spot overlap rate and low material removal rate. As a result, both of the entry and exit diameters are reduced. On the contrary, small laser processing speed results in large overlap rate of laser spot, high accumulating amount of absorbed laser energy. In this case, it’s difficult for plasma dissipation and the melt accumulation is serious, so the entry and exit diameters are large with high taper and bad roundness. It’s worth noting that when the processing speed is changed from 500mm/s to 700mm/s, both of the entry and exit diameters are not decreased but increased. The probable reason is that when the processing speed is 700mm/s, the plasma shielding effect gets weakened, leading to large material removal rate [9].

4. Conclusion
(1) It is feasible to fabricate micropores on copper foil by nanosecond laser.
(2) Large laser repetition frequency leads to small laser single pulse peak energy density, low material removal rate and therefore small entry and exit diameter of micropores. In addition, under the low peak energy density of single laser pulse, the micropores show good roundness and the difference between the entry and exit diameters is small.

(3) The effects of laser processing speed on the entry and exit diameters of micropores are complicated. When the processing speed is 300mm/s, the entry and exit diameters are large due to high laser spot overlap rate. When the processing speed is further increased, laser spot overlap rate is reduced, and therefore resulting in low material removal rate but weak plasma shielding effect. As a result, the entry and exit diameters are small at the processing speed of 500mm/s and 900mm/s, but relatively high at the processing speed of 700mm/s.

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