

Femtosecond Laser Processing Structural Surfaces of Zinc anodes for rechargeable zinc-air battery

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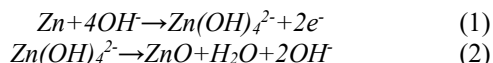
Abstract. Researches about renewable rechargeable battery have attracted the attention of many scholars, due to increasing demands of energy and global energy crisis. Zinc-air batteries are one of most promising energy sources, but the morphological changes and forming dendritic of zinc anodes greatly limit their cycle life during the charging-discharging process. In order to improve zinc-air batteries electrochemical performance and control dendritic growth, surface of zinc anodes is irradiated by femtosecond laser with different power. The electrochemical results indicate that zinc anodes of zinc-air batteries with different surface structures show different electrochemical properties. Due to the removing oxide layer on the surface of zinc anode, adding contact areas of zinc anodes and electrolytes, and restraining dendritic growth by femtosecond laser processing, first discharge time of zinc anodes with surface structures of zinc-air batteries is about 10 times than that of without processing. It is also found that more intense chemical reactions occur in the area treated by femtosecond laser.

1 Introduction

Ever-increasing demands in the energy and deteriorating environment have propelled researchers to develop renewable energies, except fossil and fuel. To solve the energy problems, secondary batteries are developed for several years. Zinc-air batteries have been become one of most promising batteries, due to the high theoretical energy density and free-free cathode from air [1-3]. Zinc-air batteries contain three parts, metal zinc anode, oxygen cathode, electrolyte. Work principle in the aqueous electrolytes is as below [4-6]:

Discharge process:

Anode:



Cathode:

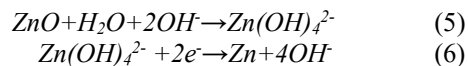


Overall reaction:

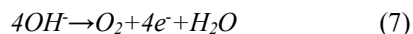


Charge process:

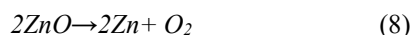
Anode:



Cathode:



Overall reaction:



Based on the chemical reaction, oxygen reaction is called oxygen reduction reaction (ORR) in the discharge cathodes, and hydroxyl releases electrons getting oxygen and diffuses into atmosphere called oxygen evolution reaction (OER) in the charge reaction. The reaction rate of a natural ORR and OER is sluggish, due to low kinetic energy of the reaction [7-9]. Hence, there is a strong need of high efficient catalysts to accelerate reactions of ORR and OER for zinc-air batteries. Many nanomaterials are employed as bifunctional catalysts, such as carbon-based composites [10-11], cobalt-based compounds [12]. Metal zinc, as the only active material, occurs randomly reversible process of dissolution-deposition, which causes severe changes of surface morphology, such as dendritic forming [13]. Dendritic growth at the zinc anode damages cyclic time and decreases zinc rate capacities, which is a big challenge for the application of zinc-air batteries. Chemical methods are used to hinder dendritic growth, such as organic compounds by chemical doping layers [14], and coating metal compounds [15] or additive [16] into zinc. Laser processing is a potential technology on this problem due to its superior capability of surface treatment.

Laser has a wide application in the manufacturing, such as welding, cutting, and micro-nano processing [17]. The researches of laser micro/nano-processing on the batteries has been reported on many publications.

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Jennifer [18] employed printing technology in 3D full printing electrodes of lithium-ion batteries, and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ worked as anodes and LiFeO_4 as cathodes active materials. Multilayers electrodes were tested electrochemical performance, and 8-layers full cell delivered 14.5 mAh cm^{-2} at the current density of 0.2 mA cm^{-2} . Yu [19] reported laser sintering of printing anodes of aluminum-air batteries. Aluminum powders and binders were printed on the PI sheets substrate at different layer mixtures. Electrochemical results indicted 3-layers cell discharged 239 mAh g^{-1} at the operation potential of 0.95 V . In addition, laser direct writing [20] in constructing electrochemical cells was flexible in the design of operating geometries.

In this study, in order to improve zinc-air batteries electrochemical performance and control dendritic growth, femtosecond laser is used to process different surface structures by changing the incident laser power. The effects of surface morphology of zinc on the electrochemical performance of zinc-air batteries are also investigated by electrochemical test. Surface structures on zinc anodes fabricated by femtosecond laser strongly affect the charge-discharge performance of zinc-air batteries. Compared to the sample without laser processing, first discharge time of zinc anodes with surface structures of zinc-air batteries is about 10 times than that without processing. This phenomenon is due to removing oxide layer on the surface of zinc anode, adding contact areas of zinc anodes and electrolytes, and restraining dendritic growth by femtosecond laser processing. More intense chemical reactions occur in the area treated by the femtosecond laser. Hence, laser processing not only increases batteries performance but

also weakens dendritic forming during charge-discharge cycles.

2 Methods and Materials

Zinc sheets (0.3 mm-thickness) were washed by absolute ethyl alcohol at the ultrasonic cleaner, and then dried naturally. Micro surface structures of washed zinc sheets were fabricated by a femtosecond laser, as shown in Fig. 1(a). The Ti: sapphire laser (Spitfire Ace PA-100, Spectra-Physics, USA) produced femtosecond pulse at the repetition rate of 1 kHz with a wavelength of 800 nm and pulse duration of 100 fs . The moving speed of processing platform was 1 mm/s . The 10 mm beam diameter was focused by a Nikon lens, and the processing power was set at 0.25 W , 0.27 W , 0.30 W , respectively. A line-by-line method was used with a line interval of 0.5 mm . The scanning direction was perpendicular to the laser incidence direction. As shown in Fig. 1b, micro-stripes on the zinc surface at different laser powers were fabricated under the protection of ethanol. Surface morphology was characterized by scanning electron microscopes (SEM, SU3500). Zinc sheets with femtosecond laser processing were used as anodes of zinc-air battery, and mixtures of Pt/C ($20 \text{ wt\%}/70 \text{ wt\%}/10 \text{ wt\%}$ PVDF) were used as cathodic catalysts. Organic glass was employed as muld package zinc-air battery, and mix solution of $25 \text{ wt\%}$ 6 M KOH/ $75 \text{ wt\%}$ 0.2 M $\text{Zn}(\text{CH}_3\text{COO})_2$ was used as electrolytes, as shown in Fig. 1(c). The open circuit voltage (OCV) of zinc-air battery is about 1.369 V which is less than theoretically value (1.636 V), as shown in Fig. 1(d).

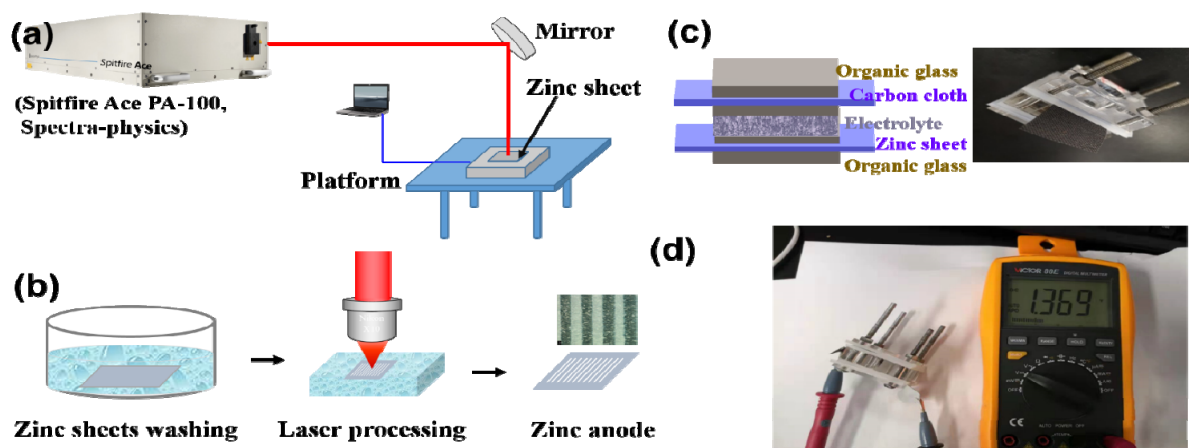


Fig. 1 Schematic diagrams of experimental process: (a) experimental setup, (b) process of femtosecond laser, (c) components of zinc-air battery and photo of package battery, (d) photo of battery open circuit voltage.

3 Results and discussions

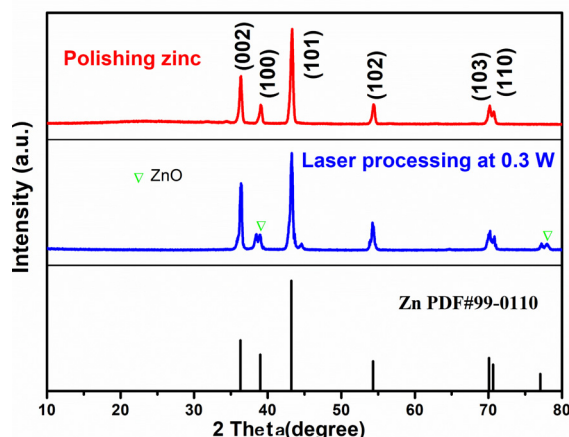


Fig. 2 XRD curve of zinc anode with 0.3 W laser processing.

Metal zinc is an actively chemical material, this research employs absolute ethyl alcohol layer above zinc sheets during processing to avoid oxide reaction. Referring to standard PDF card of zinc (No. 99-0110), polishing zinc anodes were pure metal zinc. At the 2 theta of 36.289°, 38.993°, and 43.220°, diffraction peaks corresponding to metal zinc planes of (002), (100), (101), even 2 theta up to 70.073°, 70.630°, 77.046° crystals were pure zinc. Comparing to polishing processing, fs laser processing changed a little, as Fig. 2 shown, the 2 theta of 39.328°, 78.046° and 77.046° diffraction peaks corresponding to zinc oxide. Zinc anodes kept pure metal after polishing and laser processing induced little zinc oxide, which proved that fs laser processing with thermal effect. Although the pulse of fs laser is short, high energy may affect oxide reaction during long time processing. Fs laser processing made variously structural surfaces of zinc anodes, improved surface area and electrochemical

performance, so that oxide was ignored and results were at the below analysis.

In order to investigate the effects of surface morphology of zinc on the electrochemical performance of batteries, different structures on the surface of zinc are obtained by femtosecond laser processing. SEM images of zinc after femtosecond laser processing are shown in Fig. 3(a-h). Zinc sheet without laser processing keeps almost flat surface with a little defect (shown in Fig. 3(a-b)). Under the protection of ethanol, the oxide layer on the zinc surface is firstly removed and special patterns are induced at different laser powers. Compared to zinc sheets without laser processing (shown in Fig. 3(a-b)), regular and obvious stripes on the zinc after laser processing are observed, (shown in Fig. 3(c-g)). The stripes widths are about 106.5 μm , 155.5 μm , and 182.1 μm at the laser powers of 0.25 W, 0.27 W, and 0.3 W, respectively. The ablation area of zinc becomes larger with the increase of laser power. Due to the intensity distribution of Gaussian beam, the central parts of the ablation lines are with a rougher surface. Also, laser power has a strong influence on the surface structure of zinc, and the surface micro-structures of zinc after laser processing are more intricate and irregular with the increase of processing power. At the processing power of 0.25 W, irregular micro-grooves (yellow circles as shown in Fig. 3(d)) and micro-clusters (red circles as shown in Fig. 3(d)) are observed on the surface of zinc. When processing power is fixed at 0.27 W, micro-grooves direction are almost coincident and micro-clusters are more and more concentrated on the surfaces of zinc (as shown in Fig. 3(f)). As the laser power increasing to 0.30 W, micro-grooves are at the same direction and the micro-clusters are at semblable shapes and sizes (as shown in Fig. 3(h)). The main reason is persistent bubbles adhering around zinc resulting laser inefficient incidence [21].

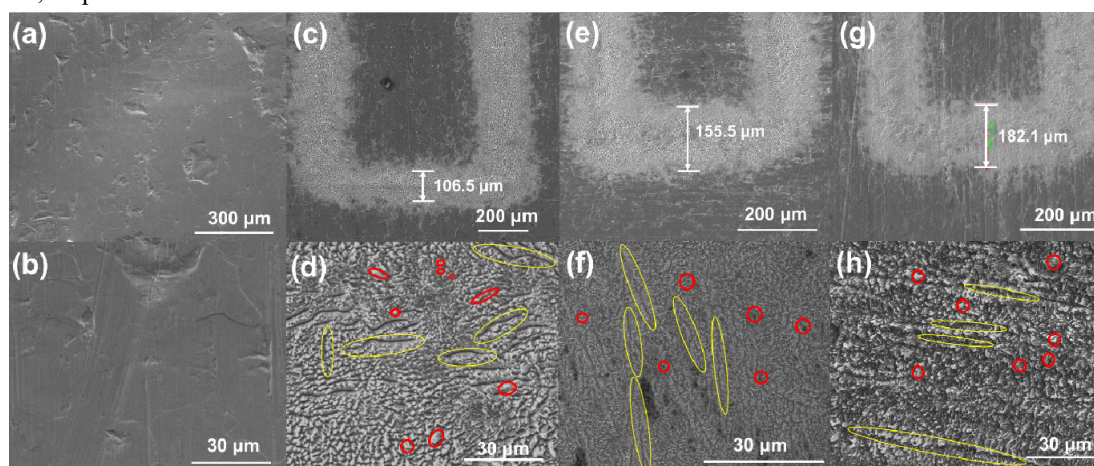


Fig. 3 SEM images of zinc after femtosecond laser processing, (a-b) 0 W, (c-d) 0.25 W, (e-f) 0.27 W (g-h), 0.30 W

The electrochemical properties of zinc-air batteries with anodes of zinc processed by femtosecond laser are studied by charge-discharge curves and cycle life, as shown in Fig. 4. In our experiments, the constant current density is about 3 mA/cm² and potential window is about 0.8-2.0 V. According to the chemistry reaction (equations

(4) and (8)) of zinc anodes, the theoretical working potential is about 1.65 V. Working potentials for batteries after laser processing is about 1.2 V, while working potential is low than 1.2 V for battery without laser processing. Without laser processing, zinc with oxide layer increases interface resistance of battery inner. The

oxide layers on the zinc surfaces can be easily removed by femtosecond laser, which leads to the improvement of working potential of battery. Also, surface treatment by femtosecond laser has great influence on charge-discharge performance of zinc-air batteries. At the first discharge process, battery without laser processing discharges time is only 2.05 h, and other batteries are 27.1 h, 19.9 h, and 25.3 h, after laser processing with laser powers of 0.3 W, 0.27 W, and 0.25 W, respectively. As shown in Fig. 3(c-h), zinc irradiated by different laser powers has various surface topography and line widths. After 0.3 W femtosecond laser irradiation, wider stripes are observed on the surface of zinc, which means more contact area of zinc anodes and electrolytes. Micro-

stripes and micro-clusters increase discharge performance by adding rate surface area and active parts. Charge performance is another important parameter to evaluate battery overall reaction reversibility and batteries actual application for rechargeable batteries. Zinc-air batteries with anodes of zinc processing by femtosecond laser at the processing power of 0 W, 0.25 W, 0.27 W, and 0.3 W deliver first charge for 0.1 h, 0.15 h, 0.59 h, and 0.55 h, respectively, as shown in Fig. 3. Zinc-air batteries with anodes of zinc processed by 0.27 W has better charge properties than that of 0.30 W, maybe cathodic catalysts are more active at the zinc-air battery.

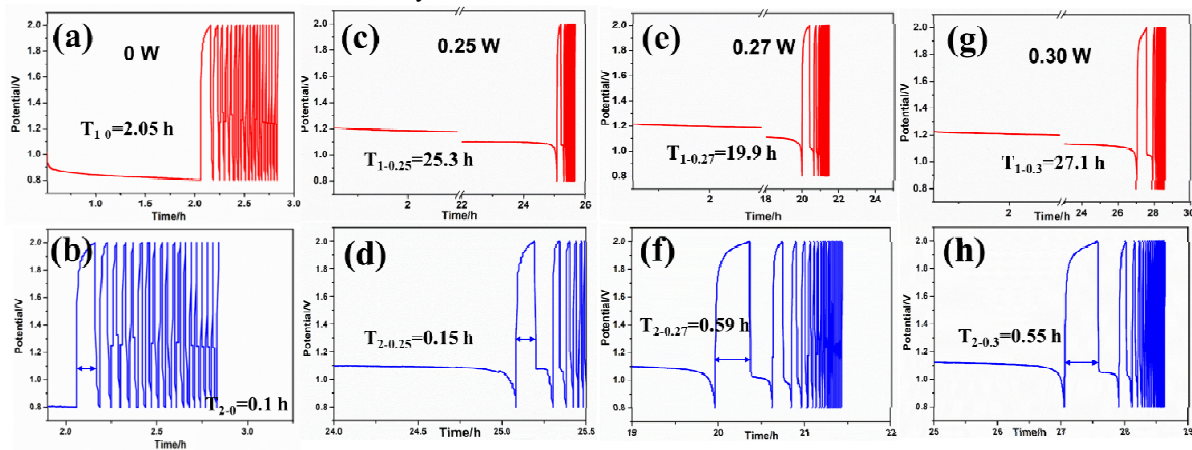


Fig. 4 Zinc-air batteries charge-discharge curves of anodes with femtosecond laser processing at the processing powers of (a-b) 0 W, (c-d) 0.25 W, (e-f) 0.27 W, (g-h) 0.3 W. T1 represents for discharge time and T2 represents for charge time

SEM images of zinc anodes of zinc-air batteries after charge-discharge test are shown in Fig. 5. It can be easily found that more intense chemical reactions occur in the area treated by the femtosecond laser, as shown in Fig. 5(a). Moreover, particles appear after charge-discharge at the reaction stripes. A relatively mild chemical reaction occurs on the whole zinc surface when the zinc anodes is without laser processing, as shown in Fig. 5(b). Without femtosecond laser processing, many particles are dispersive on the whole zinc surface. Continuous morphological changes appears on the whole battery cycle, such as dendritic forming. Besides, laser processing not only increases batteries performance but also weakens dendritic forming during charge-discharge cycles.

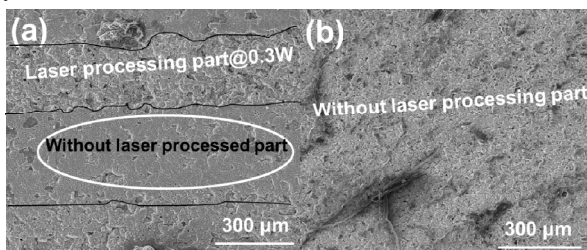


Fig. 5 SEM images of zinc anodes after charge-discharge test (a) with 0.3 W femtosecond laser processing and (b) without femtosecond laser processing.

4 Conclusion

With the increasing demands of energy, zinc-air batteries become one of most promising renewable energy due to the high energy density and free-free cathode from air. Zinc-air batteries suffer the morphological changes and dendritic of zinc anodes, which greatly limits the cycle life of zinc-air batteries. In this study, in order to investigate the effects of surface morphology of zinc on the electrochemical performance of zinc-air batteries, different structures on the surface of zinc are obtained by femtosecond laser processing. Laser power has strong effects on the surface morphology. Hence, the power of incident laser is about 0.25 W, 0.27 W and 0.3W. The experimental results show that: 1) zinc anodes with surface treatment by femtosecond laser has great influence on charge-discharge performance of zinc-air batteries. 2) First discharge time of zinc anodes with surface structures of zinc-air batteries is about 10 times than that of without processing. 3) Wider micro-stripes and micro-clusters are induced by 0.3 W femtosecond laser irradiation increase discharge performance by adding rate surface area and active parts. 4) More intense chemical reactions occur in the area treated by the femtosecond laser. 5) Laser processing not only increases batteries performance and also weakens dendritic forming during charge-discharge cycles.

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