

Preparation of current collector with blind holes and enhanced cycle performance of silicon-based anode

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Abstract: To enhance the electrochemical performance of silicon-based anode, a Cu current collector with blind holes (CCBH) was fabricated by laser machining. The electrodes were composed of CCBH and smooth current collector, and cells assembled with electrodes were tested by charge-discharge cycling. In comparison with smooth current collector, the CCBH exhibits performance superiority. The curves of voltage—capacity indicate that CCBH can keep electrode structure to offer low contact resistance. The results show that CCBH can improve the cycle performance and coulomb efficiency of silicon-based anode.

Key words: lithium ion battery; current collector; silicon; cycle performance

1 Introduction

Lithium ion battery (LIB) is regarded as an attractive power source, which can be used for portable electronic devices, power tools, electric vehicles and medical devices. The next generation LIB with higher energy capacity and longer cycle life requires advanced anode materials, because the theoretical capacity of conventional graphite materials is 372 mA·h/g. Silicon has been deemed as a promising anode material to replace the carbon-based materials because of its higher theoretical capacity of 4200 mA·h/g, more than 10 times higher than that of carbon-based materials. But the silicon-based materials are limited in practice, because silicon exhibits severe volume change during insertion and extraction, about 400% that of lithium, which leads to capacity fading and breakage of active materials [1,2]. In the view of current literatures, many approaches, silicon carbon composites [3–5], silicon thin film [6–8], silicon nanowires [9–11] and nano-size silicon [12,13], have been applied in LIB to realize better cycle performances.

However, the structure stability of silicon-based electrode has not been completely solved due to the

detachment between active materials and Cu current collector. This is attributed to huge volume changes during charge-discharge (C-D) cycling. The adhesion of anode materials to Cu current collector should be enhanced. The surface-roughened current collector [14] and three-dimensional substrate (such as carbon paper, Cu foam and nickel foam) [15–18] have been fabricated to elongate the lifetime of LIB. These current collectors offer better interface adhesion and conductive environment. Meanwhile, they relieve the stress caused by the volume changes of the electrodes. However, these current collectors prepared by multiple steps electro-deposition [19,20] and chemical etching [21] have low processing efficiency. The processing methods are harm to environment and cannot get uniform surface morphology to guarantee reliable performance of current collector.

In the present work, the electrode instability during lithium insertion and removal to further improve the cycle performance of silicon-based electrode was studied. A novel surface structure was proposed, blind holes and an environmental friendly approach were adopted to manufacture Cu sample as current collector. The cycle performances of silicon-based anode slurry-coated onto smooth Cu current collector and CCBH were evaluated.

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2 Experimental

2.1 Laser machining

The laser beam (power density of $8.42 \times 10^5 \text{ W/cm}^2$) was focused on the surface of the copper sample (thickness of $150 \mu\text{m}$). The surface temperature of copper exceeded the boiling point immediately, and generated copper vapor to remove materials. Subsequently, the laser pulses deepened the blind holes. Simultaneously, the copper vapor exhausted from the hole inside splashed and cooled on the surface of copper workpiece. The blind holes have the same diameter and depth (50 and $100 \mu\text{m}$, respectively) and the surface appearance of current collector with blind holes is shown in Fig. 1.

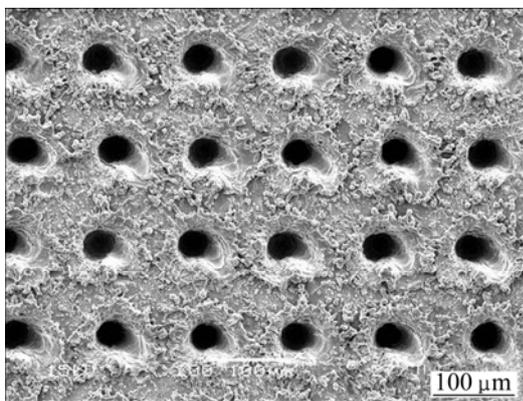


Fig. 1 SEM image of CCBH by laser machining

2.2 Preparation of silicon-based anodes

Silicon powders (average particle size of 300 nm) and carbon black (C) were blended with poly(vinylidene fluoride) (PVDF) and dissolved in N-methyl-2-pyrrolidinone (NMP) solution. Anodes slurry (silicon, C and PVDF, at a mass ratio of 70:20:10, milled for 4 h) was coated on CCBH (see Fig. 1) and smooth Cu current collector (see Fig. 2). The active area of the electrodes was 1 cm^2 ($1 \text{ cm} \times 1 \text{ cm}$). Ultrasonic vibration was used to fill the blind holes with slurry. The slurry-coated electrodes were dried in vacuum oven at $120 \text{ }^\circ\text{C}$ for 8 h prior to use and compressed under pressure of 8 MPa in order to increase the adhesion between copper current collector and electrode layer. Then the silicon-based working electrodes were assembled and packaged (2016 type coin cells) in an argon-filled glove box, using lithium foil as the counter and reference electrodes, Celgard2400 as separator, 1 mol/L LiPF_6 in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) (at a volume ratio of 1:1) as electrolyte.

The cells were charged at a constant current density of 0.2 mA/cm^2 until the cutoff voltage of 1.5 V (vs Li^+/Li)

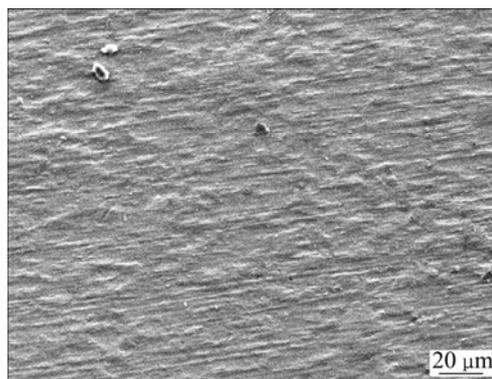


Fig. 2 SEM image of smooth current collector

and discharged at the same current at lower potential of 0.02 V (vs Li^+/Li) using LAND-CT2001A. After reaching the up and down cut-off voltage, the cells were relaxed for 10 min to get equilibrium. The test was conducted at room temperature.

3 Results and discussion

Figure 3 shows the cycling performance and coulomb efficiency of electrodes prepared with smooth

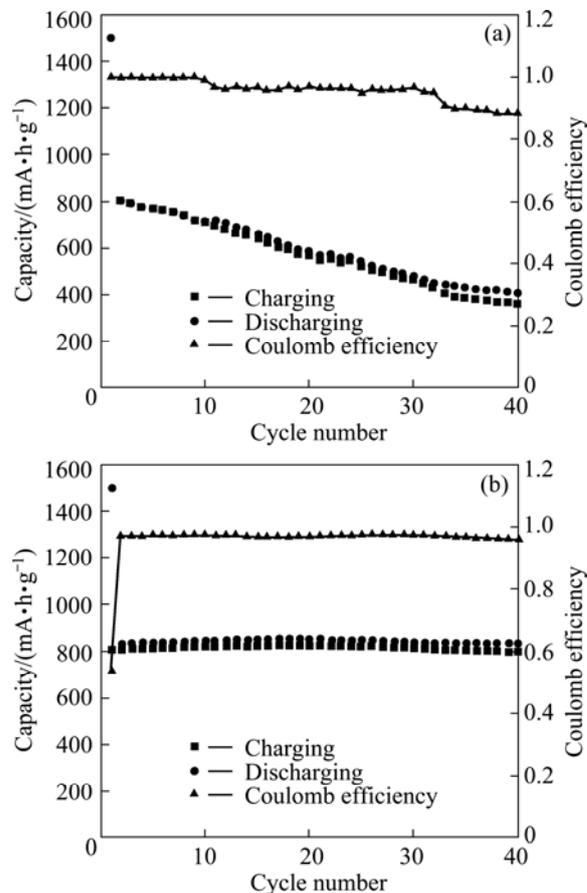


Fig. 3 Cyclic performance and coulomb efficiency of smooth current collector (a) and CCBH silicon-based anodes (b)

current collector and CCBH by C-D test. The discharge capacity of two electrodes is 1500 mA·h/g in the first cycle, and the discharge capacity is about 800 mA·h/g for the following cycles. In Fig. 3(a), the electrode with smooth current collector shows a high coulomb efficiency of 98% in the initial cycle approximately, and higher than 85% in the following cycles. But its reversible capacity sharply decreases from 800 to 400 mA·h/g. This result is associated with volume change of the electrode, which leads to the fading in reversible capacity. In contrast, the silicon-based electrode with CCBH exhibits better cycle performance and coulomb efficiency, as shown in Fig. 3(b). No evident fading of charge capacity is observed in the whole C-D test process. At the 40th cycle, the electrode with CCBH shows much higher capacity retention of about 780 mA·h/g. The coulomb efficiency stays a high rate of 97% approximately. This remarkable performance of CCBH electrode should be attributed to the blind holes in the copper current collector, which means that there is good contact between the electrode layer and CCBH. Meanwhile, materials splashed on the surface of CCBH, as shown in Fig. 1, should be able to reinforce the bonding force and keep good contact between the active materials and copper substrate.

Figures 4(a) and (b) show the smooth surface morphology of slurry-coated smooth current collector and CCBH before cycling. Figures 4(c) and (d) show the surface morphology after 40 cycles. After 40 C-D cycles, the surface morphologies of the two electrodes show distinct differences. It can be observed that the electrode

with smooth current collector exhibits pulverization and the electrode layer is mostly detached from the current collector and the surface morphology of the electrode cannot be observed clearly. It can be seen that the electrode structure is damaged. On the contrary, this phenomenon is scarcely found for the electrode with CCBH. It is evident that most parts of the electrode with CCBH show a better surface appearance. This is determined by the good adhesion between electrode layer and CCBH.

In Figs. 4(c) and (d), cracks can be observed on the electrodes with smooth current collector and CCBH. It can be noted that lots of macro-cracks are generated in the electrode with smooth current collector which is severely deformed. Few micro-cracks are formed in the electrode with CCBH and the electrode structure is integral. The results indicate that the volume changes of electrodes with two kinds of current collectors have happened during C-D test, and the electrode with CCBH is good at accommodating expansion, because the concaves of blind holes offer reasonable restraint for expansion. From the results mentioned above, it is concluded that the longer cycle life of the electrode with CCBH may be ascribed to the structural integrity and electric contact between electrode layer and CCBH.

Figure 5 shows the voltage—capacity curves of two different Cu substrates in cells during charging (lithium extraction) and discharging (lithium insertion) processes for the 2nd, 20th and 40th cycle. Figure 5(a) reveals the lithium insertion plateau at significantly lower voltages than the electrode with CCBH. This suggests that a

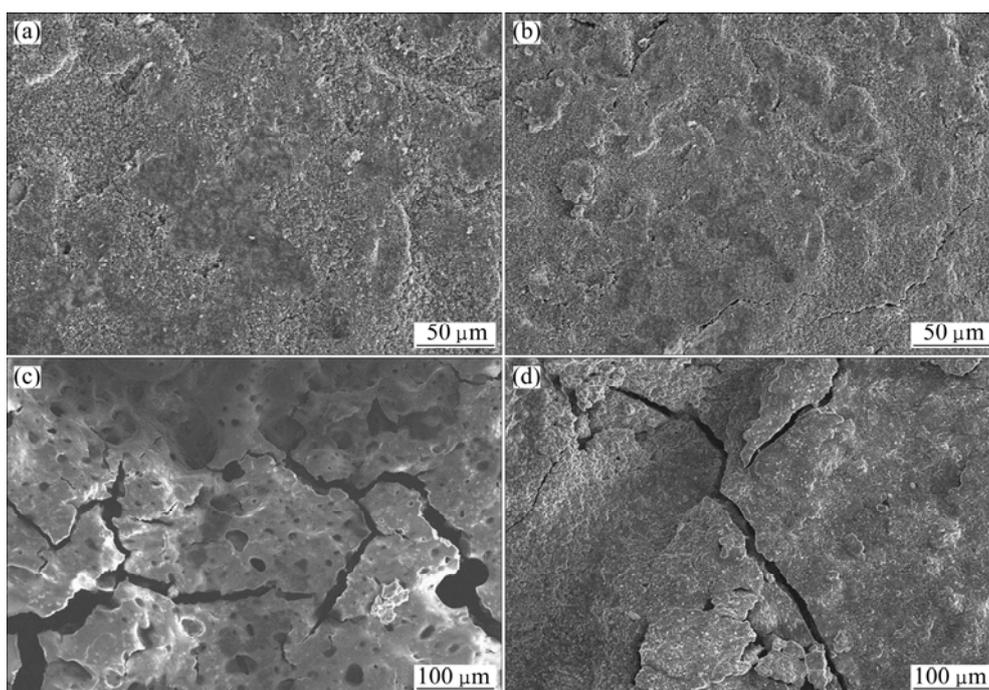


Fig. 4 SEM images of slurry-coated electrodes: (a) Smooth current collector before cycling; (b) CCBH before cycling; (c) Smooth current collector after 40 cycles; (d) CCBH after 40 cycles

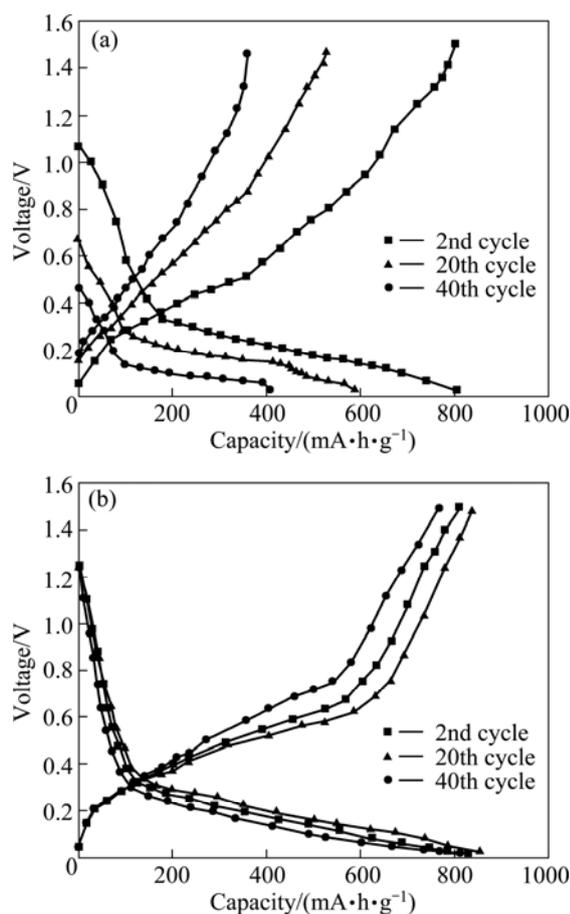


Fig. 5 Voltage–capacity profile of electrodes with smooth current collector (a) and CCBH (b)

greater polarization of electrode with smooth current collector occurs. In addition, the discharging plateau gradually becomes lower voltages and the discharging capacity rapidly reduces with cycling, as shown in Fig. 3(a). The severe polarization springs from a gradual disintegration of the electrode structure, which promotes the growth of impedance of the electrode. These indicate that the silicon-based anode materials have lost the electric contact with smooth current collector. Therefore, the cycle life of the electrode does not keep longer. On the other hand, judging from the curves, the capacity of lithium insertion shows the order CCBH>smooth current collector, and the voltage of lithium insertion of the electrode with CCBH is stable, higher than the electrode with smooth current. The result indicates that silicon-based materials do not lose the electric contact with CCBH, the contact resistance is lower and the cycling performance is excellent.

To sum up, the good mechanical adhesion and low interfacial contact resistance between electrode layer and the current collector are most important features. The use of a current collector with surface functional structures can satisfy the two features to improve cycle performance. The CCBH by laser machining has

coincident surface structures, which guarantees the performance stability of electrodes. It must be pointed that the CCBH is about 150 μm thick, which limits practical application. But it deserves further study to overcome this problem for active materials with high specific capacity and huge volume changes.

4 Conclusions

1) The electrode with CCBH exhibits excellent cycle performance. The great structure shows superiority in keeping good mechanical adhesion between the active materials and CCBH, because the blind holes can offer reasonable interface restraint to hold the electrode layer.

2) The charging-discharging curves have confirmed that the electrode with CCBH has a lower contact resistance.

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盲孔铜集流体制备及其对硅基阳极循环性能的改善

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摘 要: 为提高硅基阳极的电化学性能, 采用激光加工制备表面具有盲孔的铜集流体。将具有盲孔的铜集流体及表面光滑的铜集流体制成电极片, 并组装成纽扣电池进行充放电循环测试。与表面光滑的铜集流体相比, 多孔铜集流体显示出性能优势。电压—容量曲线表明, 带有盲孔的集流体可以保持电极结构, 进而保证较小的界面接触电阻。结果表明: 多孔铜集流体可以提高硅基阳极的循环性能和库伦效率。

关键词: 锂离子电池; 集流体; 硅; 循环性能

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