HIGH RECYCLABILITY AND POWER PERFORMANCE OF A THIN MICRO LITHIUM-ION BATTERY ANODE

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Abstract. We report a high recyclability and fast charging/discharging speed of a thin silicon/carbon anode, which can implement direct prototyping of three dimensional (3D) micro-battery on chip. The silicon/carbon material uses SU-8 as carbon source, and forms Si/void/C structure to provide enough space for volume expansion of the SiNPs during lithium-ion intercalation. By using roll forming, the anode has been demonstrated to enjoy the superior recyclability (563.42 mAh/g in the third cycle, while 472.96 mAh/g after 500 cycles) and the high charging/discharging speed (1.35 hour to finish a whole charge/discharge cycle) with only 60μm thickness.

1. Introduction

Electrochemical energy storage has been demonstrated as one of the most critical technology for a variety of applications, such as portable electronic devices, electric vehicles and renewable energy storage. Silicon has been thought as the most attractive high-capacity anode materials because of its high theoretical capacity (4200 mAh/g), which is more than 10 times to conventional graphite anodes (372 mAh/g) [1]. In order to improve the low conductivity of silicon and enhance the recyclability, which is quite low caused by silicon’s large volume expansion (over 300%) during cycling, many silicon and carbon composite materials have been tested [2]. In previous work, X. Li et al. has developed a silicon/void/carbon anode by using SU-8 photoresist as carbon source, and so that it is possible to implement direct prototyping of 3D micro-battery on chip as shown in Figure 1 [3].

However, the anode is always broken when carbonizing the graphical SU-8/nanocomposite particles with high depth-to-width ratio structure, just like what we have fabricated in Figure 2 shown. Figure 2a demonstrates that the graphical interdigital Si/void/C anode after lithography. The structure is easily broken as shown in Figure 2c, while carbonizing the SU-8 photoresist because the high stress releasing.

Here, we have fabricated a film anode by using Si/void/C composite and it maybe a new way to form lithium-ion battery on chip. And this study also tests out the best rolling thickness of the 200 μm anode film by balancing capacity retaining and charging/discharging speed.
2. Fabrication

The Si/void/C composite material is prepared by using the method in the previous work as shown in Figure 1 [3]. In the first step, SiNPs (about 30–50 nm diameter) coated by SiO$_2$ layer are fabricated with hydrolysis and condensation of tetraethoxysilane (TEOS) by using typical Stober method [4]. The thickness of SiO$_2$ shell is 10–15 nm by choosing the weight ratio of silicon and TEOS as 1:10. In the second step, the Si/SiO$_2$-templated SU-8 galatin are formed by dispersing the Si/SiO$_2$ particles into the SU-8 photoresist. Milling and rolling the composite materials, and then filling them into the interdigital electrode maybe another way to form the battery on chip. Also, this method can be used in the industrial production without changing the fabrication process. The silicon/void/C composite is mixed with Super-P and CMC (9:0.5:0.5) by ball milling, and coated on the Cu foil with 200μm thickness. Then, the roll forming is used to improve the volume specific capacity by rolling the anode electrode into thinner thickness.

Figure 1. Schematic design and fabrication of the graphical Si/void/C anode based on SU-8. (1) TEOS oxidation process to generate SiO$_2$ sacrificial layer; (2) Mixing Si/SiO$_2$ composite particles with SU-8 photoresist and spin-coating on Si substrate; (3) Pattern and pyrolysis process to carbonize SU-8; (4) Etching away SiO$_2$ layer, forming void space between carbon scaffold and SiNPs. [3]

Figure 2. (a) and (b): The images of graphical interdigital Si/void/C anode after lithography with different resolution. (c): The broken interdigital structure of Si/void/C anode after carbonization.
3. Results and Discussion

Figure 3 shows the SEM images of the Si/void/C anode before and after milling. In Figure 3a, the Si/void/C structure can be seen clearly, and the carbon network is intact. While in Figure 3b, although some structure on the surface are broken during milling, numerous silicon still remains in the carbon shells or holes (broken shells). Therefore, this structure with carbon shells or holes can still contain the volume expansion during the lithium-ion intercalation and deintercalation.

![Figure 3](image)

**Figure 3.** The SEM of Si/void/C anode with different forming process: (a) The direct forming interdigital Si/void/C anode; (b) The Si/void/C anode after ball milling.

The anode material is compacted to different degree by roll forming as shown in Figure 4. The thickness of anode is approximately determined by the thickness of rolling model and Cu foil. For example, the rolling model used in Figure 4a is 40 μm and all the Cu foil is about 20 μm (the Cu foil also is condensed in this step). It can be easily found that the structure is more loose with a thicker anode than the thinner one. In another word, the transmission of lithium-ion will be hampered while increasing the mass per unit volume of the anode material.

![Figure 4](image)

**Figure 4.** The SEM of the Si/void/C anode with different thickness after rolling forming: (a) The thickness of rolling model is 40μm; (b) The thickness of rolling model is 80μm.

*the thickness of anode = the thickness of rolling model - the thickness of Cu foil

The galvanostatic charge-discharge tests of the anode are performed using a battery testing system (BTS-3000, Neware) at room temperature, with voltage cutoffs set at 0.01V and 1.2V vs. Li/Li+. The charge/discharge rate is calculated with respect to the theoretical capacity of silicon (4200 mAh/g). Therefore, a current density of 1C corresponds to 4200 mA/g.
Figure 5 gives the recyclability test of four samples with different thickness (20μm, 40μm, 60μm, and 80μm). It can be found that the weight specific capacity is decreased while the thickness decreasing, because the void space structure is destroyed more seriously with thinner anode. In all four anodes, the anode with 60μm shows the highest recyclability (563.52 mAh/g in the third cycle, and 472.96 mAh/g after 500 cycles), cause the opportune compression degree. The thicker anode has a lower capacity retain caused by the reaction between more electrolysis and silicon, and the thinner anode shows capacity fading rapidly as there is few void space for silicon expansion.

The charge/discharge profiles of various Si/void/C anode with different thickness are tested to verify the power performance in Figure 6. From these curves, the thinner anode shows the faster charging/discharging speed than the thicker one. for the non-compacted ionic transport channel.

![Figure 5](image1.png)  ![Figure 6](image2.png)

**Figure 5.** The specific capacities of Si/void/C anode with different thickness after roll forming under 0.2C galvanostatic cycling tests.

**Figure 6.** Charge/discharge profiles of various Si/void/C anode with different thickness.

4. Conclusion

We have fabricated a high recyclability and fast charging/discharging speed of a thin anode by using Si/void/C composite, and it can implement direct prototyping of three dimensional (3D) micro-battery on chip in the future. By balancing the capacity retaining and charging/discharging speed, this anode demonstrates a superior recyclability (563.42 mAh/g in the third cycle, while 472.96 mAh/g after 500 cycles) and a high charging/discharging speed (1.35 hour to finish a whole charge/discharge cycle) with only 60μm thickness.

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