A novel silicon/carbon nanocomposite anode for high performance lithium-ion micro-battery

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Abstract. This paper reports a novel nanocomposite anode for lithium-ion battery, with high initial specific capacity (1200 mAh/g) and good capacity retention (850 mAh/g remaining after 30 cycles). Sufficient silicon nanoparticles (SiNPs) at anode make a significant contribution to specific capacity increase. Moreover, nano void space between SiNPs and carbon scaffold provide enough space for expansion and contraction of SiNPs during the process of lithium ion intercalation and deintercalation to ensure a long cycle life. The porous carbon scaffold is obtained from Si/SiO\textsubscript{2}-templated SU-8 photoresist. As such, this design and fabrication makes it possible to implement direct prototyping of three dimensional (3D) micro-battery on chip.

1. Introduction

Lithium-ion secondary batteries are widely considered as the most useful devices for electrochemical energy storage in the 21st century. Because of their high gravimetric and volumetric capacity, Li-ion batteries have a wide application range from portable electronics to electric vehicles and other renewable energy [1]. With the ever increasing power requirements for applications, the Li-ion batteries are in desperate need of anode materials that can yield a much higher specific capacity than the traditional graphite anode (theoretical capacity of 372 mAh/g). Silicon is one of the most attractive anode materials for next-generation Li-ion batteries because of its natural abundance, low discharge potential, and most importantly, high theoretical capacity (4200 mAh/g in a composite of Li\textsubscript{4.4}Si), which is an order of magnitude beyond that of conventional graphite anodes [2]. Unfortunately, silicon undergoes large volume change (over 300\%) during lithium-ion intercalation and deintercalation [3]. The volume change can lead to anode structure failure and electrical contact loss, and can also cause continuous consumption of the active material and Li-ion for reformation of solid electrolyte interphase (SEI) layers [4]. As a consequence, the electrode suffers rapid capacity decay.

Recent works have shown that silicon nanostructures can effectively solve this limitation. A number of silicon nanoscale morphologies have been investigated to reduce the structural degradation due to the volume change during cycling and therefore to overcome the mechanical instability in bulk Si. These nanoscale morphologies, including thin films [5, 6], nanowires/nanotubes [7, 8] and nanoparticles [9-11], facilitate relaxation of the stress associated to the intercalation/deintercalation process and thus demonstrating high capacities in initial cycles. However, after long cycles, most of these all-Si anodes still demonstrate obvious capacity fade due to silicon’s separation from current collector. Many materials with good conductivity have been tested to stabilize Si-collector contact.
Among these efforts, anodes of nano-Si/C demonstrate the most outstanding performance. Carbon is effective not only in enhancing the electronic conductivity but also in stress relief due to its lightweight and ductile nature. A lot of promising results in terms of cycle stability have been obtained by designed nanocomposites of silicon and various carbon sources, such as graphene, PVDF, pitch, acetylene and polydopamine [12]. Some of these Si/C nanocomposite anodes also introduce suitable networks of interconnected pores in order to further buffer the volume change of the silicon. However, none of these techniques are compatible with standard microfabrication protocols.

In this work, a novel Si/void/C nanocomposite anode is designed and fabricated. Aiming at the direct prototyping of 3D micro-battery on chip, we use SU-8 photoresist as the carbon source to construct a scaffold to support SiNPs for the first time. The SiNPs make the main contribution to the high specific capacity, and the carbon scaffold from SU-8 builds an efficient conductive pathway. With rationally designed void space to accommodate silicon expansion and contraction during cycling, the anode maintains a stable structure and achieves a long cycle life.

2. Design and fabrication

The composite of silicon and carbon is gaining more and more attentions in the search of new high-performance Li-ion battery anodes. The limitations of carbon-based or all-silicon-based anodes could be addressed by designing and controlling the microstructure of Si/C composite anode, with the help of nanoscale fabrication techniques. The principle is based on the fact that graphitic carbon is able to release the stress generated by expansion and contraction of silicon, meanwhile the high conductivity of carbon can make up the electrical connection failure caused by silicon volume change.

In this work, we use SiNPs as the main active materials and SU-8 photoresists as the carbon source, which consist of epoxy resin SU-8, triaryl sulfonium salt and organic solvent. When exposed to ultraviolet light, the resin will form a highly structured cross-linked matrix. Moreover, SU-8 can retain micro patterns after high-temperature carbonization, which has been widely utilized in carbon microelectromechanical systems (C-MEMS) and micro power devices, such as micro supercapacitors [13] and three-dimensional micro batteries [14]. The good thermal stability and chemical resistance of SU-8 shown in these researches inspire a brand new way to fabricate on-chip batteries with Si/C composite anode, using a Si/SiO$_2$-templated synthetic procedure.

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

The scheme of the overall design and fabrication of the Si/void/C nanocomposite anode is shown in Fig.1. In the 1st step, SiNPs (30–50 nm in diameter) coated by SiO$_2$ layer are obtained by typical Stöber method, with hydrolysis and condensation of tetraethoxysilane (TEOS) in a water-alcohol-ammonia medium [15]. The thickness of the SiO$_2$ sacrificial layer and therefore the void space size can be easily controlled by controlling the coating time, PH, and TEOS concentration. In order to accommodate the maximum volume expansion (300%) of each SiNPs, the thickness of sacrificial coating layer should be over 10nm. In following experiments, the thickness of the SiO$_2$ layer is controlled to be about 10–15 nm, considering size variation. In step 2, the Si/SiO$_2$ particles are dispersed in SU-8 photoresist to form Si/SiO$_2$-templated SU-8 composite, where SU-8 serves as the
precursor of subsequent carbon scaffold. Considering both specific capacity and stability of the electrode, the ratio of each component in this step is 20wt% for Si/SiO$_2$ particles and 80wt% for SU-8. After spin-coated on silicon substrate, the Si/SiO$_2$-templated SU-8 composite is exposed under ultraviolet light, forming highly structured cross-linked polymer matrix. In step 3, the polymer contained in the materials is pyrolyzed in nitrogen atmosphere at 900°C for 2h. And the SU-8 is turned into carbon scaffold to provide a considerably strong mechanical support for the particles. At last, to remove the SiO$_2$ sacrificial layer, the Si/SiO$_2$/C composite is etched in HF aqueous solution and the space once occupied by the nano SiO$_2$ layer becomes void space.

The working electrodes are fabricated using a typical aqueous slurry method. Si/void/C nanocomposite electrode is prepared by homogeneously mixing appropriate amount of Si/void/C nanocomposite, carbon black and carboxymethyl cellulose sodium (CMC) binder to form a slurry, with a mass ratio of 8:1:1. The mass loading of silicon in the mixture is kept at 35%. The viscous slurry is then cast onto a copper foil and dried at 80 °C under vacuum. For electrochemical tests, coin-type cells (CR2025) are fabricated inside a N2-filled glove box, using circular Si/void/C nanocomposite electrode as the working electrode and Li metal foil as the counter electrode. As shown in Fig.2 (a), two electrodes are separated by a Celgard 2400 separator, which is soaked in the electrolyte. 1 mol/L LiPF6 in a mixture of ethylene carbonate, diethyl carbonate and dimethyl carbonate (EC : DEC : DMC, 1 : 1 : 1 by volume) is used as the electrolyte, and with 10% fluoroethylene carbonate (FEC) as the electrolyte additive to increase the cycling efficiency and improve cycling stability. Fig.2 (b) shows the composite anode on a copper foil and the packaged cell for testing.

The SEM image of the cross-section of the Si/void/C nanocomposite anode before cycling is shown in Fig.3. We can see that SiNPs are embedded in carbon scaffold with some nano void space between them clearly, which provides enough space for expansion of individual SiNPs during lithium-ion intercalation.

### 3. Results and discussion

The galvanostatic charge-discharge tests 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$^+$. Specific capacity

![Figure 2](image2.png)  
**Figure 2.** a) Packaging diagram of Li-ion battery: Si/void/C nanocomposite as the anode; Li foil as the cathode.; b) Photograph of Si/C composite anode (right) and packaged testing cell (left).

![Figure 3](image3.png)  
**Figure 3:** SEM image of the cross-section of Si/void/C nanocomposite anode before cycling.
is calculated based on the total mass of Si/void/C composite. The current density of charge/discharge is 400 mA/g, corresponding to a rate of 0.1C.

The SiNPs account for about 35% of the anode composite by weight, thus the anode has a theoretical capacity of 1470mAh/g, on the premise that the capacity contributed by carbon is negligible when compared with silicon. From the discharge/charge voltage profiles for different cycles in Fig.4, the actual initial capacity is about 1200mAh/g. In the first few discharge processes, there is a long discharge plateau below 0.3V due to the SiNPs crystalline structure. The discharge/charge curves remain similar in shape from 1st to 10th cycle with a small decrease in the capacity, indicating a stable electrochemical behavior.

This excellent cycling stability is attributed to the presence of void space and the structural stability of carbon scaffold from SU-8, therefore individual SiNPs can expand and contract inside the carbon scaffold without rupturing the outer shape of the structure. The capacity retention is 71% after 30 cycles. The irreversible capacity loss is a result of the irreversible insertion of Li into silicon and amorphous carbon. Besides, the continuous formation of SEI layers could make a significantly influence, because the carbon accounts for over 60% of the composite and directly contact the electrolyte, with a high surface area structure.

The Si/void/C nanocomposite demonstrates much higher capacity and better capacity retention when compared to pure SiNPs and Si/C composite without void space, as shown in Fig.5. Our Si/void/C nanocomposite anode has an initial specific capacity of 1200mAh/g and a capacity of 850mAh/g remaining after 30 cycles. Under the same conditions, the pure SiNPs anode has a high initial capacity but decays quickly to almost zero after only several cycles, due to its structure failure, SEI formation and poor electrical conductivity. Si/C composite, which is without void space inside, shows a similar initial capacity to Si/void/C structure. However, poor capacity retention of less than 10% is observed after only 15 cycles. The above comparison has strongly proved that the Si/void/C composite anode shows outstanding performance, mainly because of the advantage of allowing the Si particles to expand freely, with a stable and conductive carbon scaffold to support silicon.

4. Conclusions

In summary, we have designed and fabricated a Si/void/C nanocomposite anode from Si/SiO$_2$-templated and demonstrated its high capacity (1200mAh/g) and stable cycling behavior (71% capacity retention after 30 cycles). These results suggest that Si/void/C nanocomposite can improve the
structural stability and cycling performance of the silicon-based anode, with rationally designed void space to accommodate volume expansion during cycling, and stable carbon scaffold to release the stress and provide an efficient conductive pathway. Besides, the SU-8 carbon source along with the fabrication technology opens up a new route for direct prototyping of Si-based on-chip 3D microbattery in the future.

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