A Silicon Anode Material with Layered Structure for the Lithium-ion Battery

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Abstract. Although the theoretical capacity is 4200 mAh/g, it suffers from a large volume expansion (over 300%). We design a novel stratified rGO/CNT/Si structure by the vacuum filtration method. rGO is used to form a multilayer structure which is supported by CNT and the silicon nanoparticals (SiNPs) are dispersed in the CNT gap. This structure can effectively protect the SiNPs from forming SEI in the first lithiation and de-lithiation process. The anode material owns the specific capacity of 1794.23mAh/g in the first cycle, and remains 1211.15mAh/g after 100 cycles.

Keywords Si anodes, Lithium-ion battery, stratified structure

1. Introduction
Rechargeable Li–ion batteries have been successfully commercialized, which has a widespread application, such as electric vehicles and energy storage systems for grid support [1]. So, much efforts have been devoted to study advanced energy storage technologies to order to enhance the performance of current Li–ion batteries [2,3]. To meet the ever increasing high-performance requirements, scientist need find a kind new anode materials which has high energy density and long cycle life.

Silicon reserve is very rich in nature, which is 26.4% ranked only second to oxygen. Recently, silicon has emerged as one of the most attractive high-capacity anode materials for it has the highest theoretical capacity (4200 mAh/g in a composite of Li₄.₄Si) compare with conventional graphite anodes (theoretical capacity of 372 mAh/g) [4]. However, silicon has a large volume change (over 300%) during lithium-ion intercalation and deintercalation [5]. The volume change can lead to a series of problem for example, causing continuous consumption of the active material and Li-ion for reformation of solid electrolyte interphase (SEI) layers [6].

The lithium-plating mechanism of Silicon does not is very different from graphite with a layered structure for graphite-based materials, however silicon depends on the alloying and de-alloying of
lithium ions in the lithiation and de-lithiation process, its electrode reaction can be written as the following formula in the charge and discharge process [7].

\[ \text{Si} + x\text{Li}^+ + xe^- \leftrightarrow \text{Li}_x\text{Si} \]

There is a huge change in volume when Silicon and lithium together form alloy [7]. To overcome volume problem, many researchers have done a lot of research. People has researched some nanostructure strategies, such as thin films [8], nanowires/nanotubes [9,10] and nanoparticles [11,12]. These special structure facilitate relaxation of the stress associated to the intercalation/deintercalation process and thus demonstrating high capacities in initial cycles. In addition, many researchers design a shell to protect the silicon a, the silicon particles wrapped in the shell inside. The shell could provide a void space for silicon’s volume expansion and a stable shell to prevent electrolyte react with silicon directly was demonstrated in Si-SiO2 hollow tubes [13] and the Si-C yolk-shell [14,15]. The conductivity of pure silicon is very poor, carbon-based anode material has a good conductivity. Therefore, the Silicon - carbon composites which has a high-performance get more and more attention for lithium-ion anode material. The composite of silicon and carbon is gaining more and more attentions in the search of new high-performance Li-ion battery anodes. Much progress in terms of cycle stability has been made by designed silicon/carbon nanocomposite anodes from various carbon sources, such as graphene, PVDF, pitch, acetylene and polydopamine [16].

In summary, in order to solve the problem of volume expansion and conductivity of silicon, we have designed the anode material of rGO / CNT / Si with a layered structure as shown Figure.1. The layered structure can effectively protect the silicon so that the SEI film does not form on the surface of the silicon particles and uses a highly conductive graphite material to improve the electrical conductivity of the material.

![Figure 1](image)

**Figure 1.** The schematic of lithiation and delithiation processes of different silicon-based materials (1) the anode material is fabricated by natural evaporation. The SEI films is continuously destroyed and meanwhile formed because the silicon has a huge volume expansion during the reaction process; (2) the anode material is fabricated by vacuum filtration. The layered structure protects the silicon, and prevents the SEI layer forming directly on the silicon surface.
2. Materials and Methods

Figure 2 describes the process of fabricating for the rGO/CNT/Si anode materials, the process is divided into four steps: the first step, fabricating the precursor solution of GO/CNT/SiNPs (the mass ratio of each substance is 38:12:50) ——SiNPs are dispersed in deionized water containing a certain amount of GO and CNT, SiNPs are used as active material which provides main battery capacity, GO will form a layered structure to protect silicon and the CNT acts as a support role between the GO layers; the second step, the rGO/CNT/Si material is obtained by different ways, (a) the mixed solution of GO/CNT/Si is transferred to the culture vessel with a dropper and naturally evaporates the excess liquid (b) we deal with the compound of GO/CNT/Si by vacuum filtration; The third step, the compound requires a high-temperature sintering process in 900 °C about 2h (the process called as carbonation), in order to transform the GO into rGO; the fourth step, the surface of silicon particles has been oxidized to silica when it exposes to the air, so the SiO₂ need etch by using hydrofluoric acid. Finally, we fabricate the rGO/RGO/CNT/SiNPs composite.

![Diagram of fabrication process](image)

**Figure 2** Fabricating the process of rGO/CNT/SiNPs composite anode by different ways(a) natural evaporation; (b) vacuum filtration.

3. Results and Discussion

The SEM of the rGO/CNT/Si composite is shown in Figure. 3 and Figure. 4. Figure. 3(a) and Figure. 4(a) show morphological features of this material by natural evaporation. The layered structure can’t been found in Figure. 4(a) which is a sectional view, so the rGO failed to encapsulate the silicon particles. From the figure.3(b) and figure.4(b), We can clearly find a layered structure for the composite which is manufactured by vacuum filtration, thus it can protect the silicon particles. This is a good proof to our design.
Figure 3. SEM images of the anode material (a) natural evaporation; (b) vacuum filtration.

Figure 4. SEM images of the anode material for the sectional view (a) natural evaporation; (b) vacuum filtration.

Figure 5. (a) The profiles of the rGO/CNT/Si composite anode for different cycles on continuous current charge and discharge; (b) The specific capacity of rGO/CNT/Si composite anode under galvanostatic cycling tests.

We fabricate the two kinds materials into half-cell. Figure 5(a) shows the charge and discharge diagram of the layered structure in constant current for different cycles. The first cycle has a longer discharge plateau compared with others. This is because the effective silicon content is most at the first cycle, so the initial capacity is the highest and the process of discharge is the longest. The discharge plateau for the second and third is almost similar, which indicates that the battery structure has been stable and the layered structure has protected the SiNPs. The cycle performance of half-cell is shows in
Fig 5(b) for the two kinds materials. The first specific capacity is as high as 1804.12mAh / g for the first method, but it rapidly drops to 497.01mAh / g after the 100 cycles, and the capacity decays by 72.45%. This demonstrates that the rGO can’t protect the silicon, the continuous formation of SEI layers consumes a mass of lithium in the silicon surface, which makes the battery capacity rapid decrease. The anode material is prepared by the second method, its first specific capacity is 1794.23mAh / g, and capacity falling to 1211.15mAh / g after 100 cycles, so the capacity still remains 67.50%. Thus, these can verify that the rGO / CNT / Si composite with layered structure not only effectively protects the silicon, but also greatly enhances the specific capacity.

The reason why the rGO/CNT/Si fabricating by vacuum filtration can form a layered structure lies in the high precipitation speed. During the natural evaporation, the graphene with great mass precipitates at the bottom and the silicon precipitates at the upper. However, for the vacuum filtration, the solvent is rapidly filtered. The compositor materials are synchronously precipitated, which can retain the layered structure.

4. Conclusions
To solve the volume expansion problem of silicon, we designed the rGO/ CNT/Si composites with stratified structure, which shows high capacity compared with graphite material. The experiment demonstrates the anode which has a later structure own the initial specific capacity of 1794.23mAh / g when the battery performs the first cycle, and remain 1211.15mAh / g after 100 cycles. Meanwhile the preparation process of material is simple and benefit for the large scale production.

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