Scientific and Social Research, 2021, Volume 3, Issue 3
http://journals.innosciencepress.com/index.php/ssr
ISSN Online: 2661-4332

Study of Micro-Silicon Particles Covered by Graphene

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Abstract: Lithium-ion batteries have become a new hot spot in battery research due to their high-energy density, environmental friendliness, and multiple charge/discharge times. Silicon-based materials have become the best choice of anode materials for lithium-ion batteries due to their advantages of low lithium insertion voltage, high specific theoretical capacity, and large reserves on the planet. However, the silicon-based material has a large volume expansion (about 300%) during cycling, which causes the active silicon to fall off from the surface of the conducting material. This expansion will also break the solid electrolyte interphase (SEI) on the surface of the silicon electrode, and will consume additional Li+, causing the battery's capacity to drop rapidly as the times of circulation increases. In addition, the conductivity of silicon-based materials is lower than that of graphite anode, which have already been used commercially, led to the worse performance of the silicon anode. These drawbacks force silicon-based anode materials to encounter huge resistance in the commercialization process. Therefore, research on the improvement of performance of the silicon-based anode materials is of great significance.

Keywords: Lithium-ion battery; Silicon-carbon composite anode; Vertical graphene; Solid electrolyte interphase; Micro-nano manufacturing

Publication date: September 2021; ***Online publication:*** September 30, 2021

1. Introduction

In this paper, we use the silicon micro-pillar array covered by graphene to study the effect of the graphene cover on the electrochemical performance and structural stability of the silicon micro-pillar electrode. The experimental results show that the coating of graphene increases the coulombic efficiency in the first circulation to more than 90%. After 50 cycles of three-dimensional silicon micron square column graphene composite, the structure of electrode surface is complete, and the surface is covered with a thin solid electrolyte interphase. By contrast, the silicon micro-pillar electrode without graphene is peeled off from the surface of the conducting material. At the same time, in the long-period cycle test, the coulombic efficiency and capacity retention rate of the three-dimensional silicon micron square column graphene composite electrode are better than those of the electrode without graphene.

2. Introduction

With the beginning of the industrial revolution in the 19th century, fossil fuels have become the most common and valued energy source. However, with the advancement and development of science and technology, people have realized the dangers and deficiencies of fossil fuels. Due to its long growth cycle, high mining costs, and harmful effects to the environment, fossil fuels have slowly faded out of our sight [1,2]. With the popularization of electronic equipment, such as mobile phones, computers, and electric vehicles, batteries have gradually become the best solution to replace fossil fuels. Therefore, its demand has risen significantly. Coupled with the concept of sustainable development promoted by the United Nations in recent years, research in the battery field has only increased [3,4].

Since lithium is the lightest metal, discussions about lithium batteries have never stopped. In 1970, Japan's Sanyo company used metal oxide (MnO_2) as a positive electrode for the first time and produced the first commercial lithium battery in human history. In 1971, Greatbatch, W prepared a lithium-iodine solid-state lithium battery and applied it to a new type of solid-state battery designed for implantable prostheses [5]. In 1973, Panasonic began mass production of fluorocarbon cathode active materials as the anode of lithium primary batteries. After the 1980s, lithium batteries entered the commercialization stage, which was mainly due to the decline in the cost of lithium metal mining.

Thanks to the success of lithium metal primary batteries, people began to focus on rechargeable lithium-ion secondary batteries. In 1976, Whittingham [6] first introduced the $Li\text{-}TiS_2$ lithium secondary battery. However, this discovery did not improve the stability and efficiency of the battery during the cycle. This is mainly due to the formation of lithium dendrites during the cycle of the lithium electrode, which pierced the separator and caused a micro short circuit inside the battery, which caused a safety accident. Therefore, scientists realize that it is extremely important to choose suitable materials that can insert/desorb lithium ions as the positive and negative electrodes of the battery. In 1980, the "rocking chair battery concept" was first proposed by Armand [7,8]. In the same year, the Goodenough [9] group proposed $LiCoO_2$ as the cathode material for lithium-ion batteries. In 1991, Sony Corporation of Japan found in the oxides of transition metals that Co oxides can form compounds with metal lithium as the positive electrode of lithium-ion batteries, and successfully developed LiCoO2-C lithium secondary batteries. Ion secondary batteries have greatly improved cycle stability and coulombic efficiency on the original basis, making lithium batteries for civilian use. Lithium batteries are favored by many people because of their good electrical conductivity, high number of charge and discharge times, and light weight. In recent years, in pursuit of more perfect performance, materials such as graphite, sodium, and silicon have been used as the negative electrode of the battery. This article will focus on lithium batteries with silicon as the negative electrode.

With the development of electric vehicles, the energy storage technology of battery has become an important factor hindering its development. Therefore, scientists have focused on using materials with high specific capacity as the negative electrode of the battery. Silicon has become a new choice for lithium battery negative electrodes due to its high theoretical capacity, low mining cost, and abundant reserves. At the same time, the huge volume expansion (approximately 300%) brought about by the high theoretical capacity makes silicon prone to cracking and chalking during the charge-discharge cycle, causing the SEI to crack. The repeated cracking and formation of the SEI will accelerate the consumption of lithium ion in the electrolyte, increase the side reaction and decrease the coulombic efficiency, and also cause heat generation and even explosion. In addition, the conductivity of silicon is inferior compared to other anode materials, which is also an obstacle for its commercialization. Therefore, the research on the stability of silicon anode is of great significance.

Both the nano-lise and composite silicon anodes can improve the stability of silicon anodes during cycling. This paper will focus on the impact of composites on silicon anodes. The composite silicon anode can effectively prevent the volume expansion caused by silicon lithium insertion and stabilize the SEI to reduce the number of cracks and increase the conductivity of the anode to improve the coulomb efficiency. Graphene materials have many advantages such as high electrical conductivity, high mechanical strength, and low cost, making them an ideal choice for coating materials for silicon anodes. Wang studied the composite electrode of graphene and silicon nanocone. When the discharge capacity is limited to

200μAh/cm^2, the charging of graphene and silicon nanocone composite electrode is compared with that of silicon nanocone electrode. The capacity has reached 95μAh/cm^2 and maintained 1400 cycles. The reversible capacity and cycle life have been improved [10].

3. Fabrication processes

We use micro-/nano-techniques to prepare the coating structure of the GR@SMP@GR electrode. This structure can effectively avoid problems such as difficulty in observation and low area capacity caused by the accommodating structure. At the same time, the silicon micro-pillar array consists of several groups of silicon micro-pillars with exactly the same size, so the composite silicon pillars after the cycle can be displayed more intuitively and accurately.

First, graphene deposition is performed on the surface of nickel current collector through a microwave plasma chemical vapor deposition system (MPCVD, self-developed by the Institute of Physics, Chinese Academy of Sciences), the pressure is 600 Pa, and the process gas is methane and hydrogen: argon (95:5), The air pressure is regulated by the valve of the vacuum pump. During the growth process, it is necessary to regulate the standing wave to the working area. Then silicon is deposited on a nickel current collector with graphene by using a plasma enhanced chemical vapor deposition system (PECVD, Plasmalab System 100, Oxford Instruments). The process gas used is silane and argon, and the pressure is 1000W. After 7 hours of deposition in a system at a temperature of 120 degrees Celsius, a silicon film with a thickness of about 10μm is obtained. The silicon micron square pillars are etched on the deposited amorphous silicon through a masked etching process, the etching time is 3.5 minutes, and then MPCVD is used again to deposit the graphene on the current collector with the micron silicon pillar array to ensure the silicon pillars is uniformly covered by the graphene layer on the electrode surface.

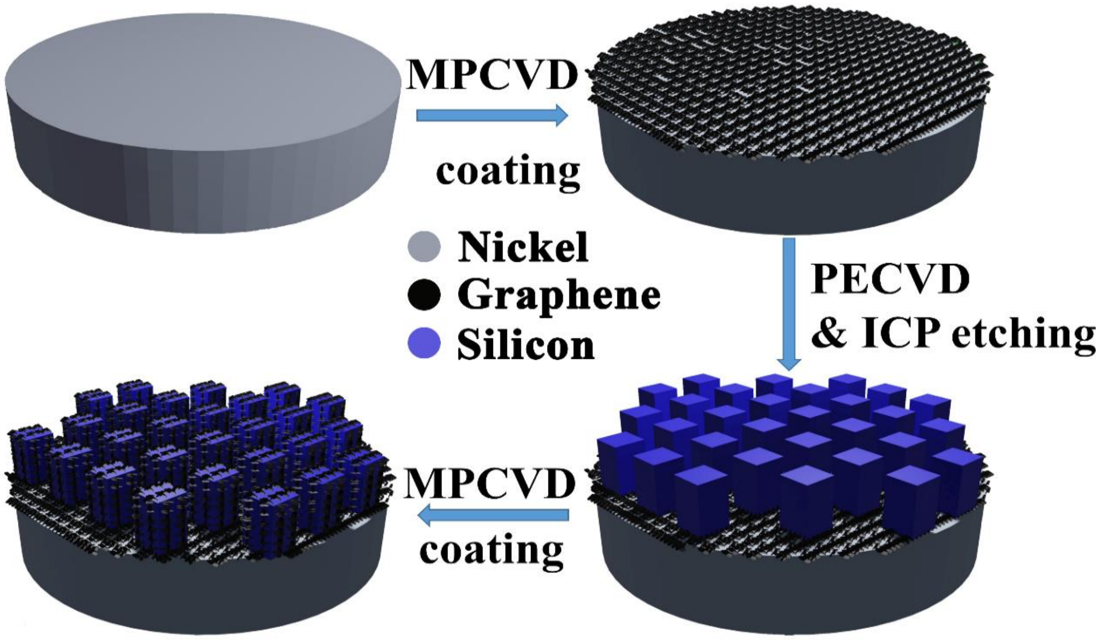


Figure 1. Schematic 3D representation of the main microfabrication process steps for the fabrication of GR@SMP@GR electrode.

The prepared electrode was observed using a Helium Focused Ion Beam (ORION NanoFab, Carl Zeiss AG) to observe the electrode morphology of SMP and GR@SMP@GR. As shown in **Figure 2(a)**, the silicon micro-pillars after ICP etching are neatly arranged and uniform in size. **Figure 2(b)** shows the electrode morphology of GR@SMP@GR. It can be seen that the graphene is uniformly coated on the surface of the silicon column and the morphology of the silicon column has not changed. SMP and GR@SMP@GR were characterized by Raman spectroscopy (as shown in **Figure 3**. Both electrodes showed characteristic peaks related to amorphous silicon at 480 cm^{-1}, while GR@SMP@GR The peak positions of the Raman spectrum of the electrode show that D (1348 cm^{-1}), G (1580 cm^{-1}) and 2D (2700 cm^{-1}) peaks are characteristic peak positions of graphene.

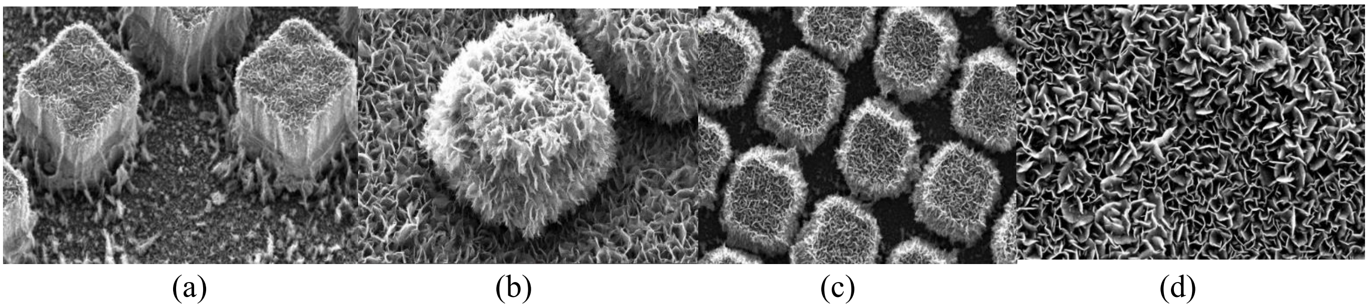

(a) (b) (c) (d)

Figure 2. SEM images of samples at different stages. (a) SMP electrode; (b) GR@SMP@GR electrode; (c) top view of SMP electrode; (d) top view of GR@SMP@GR electrode.

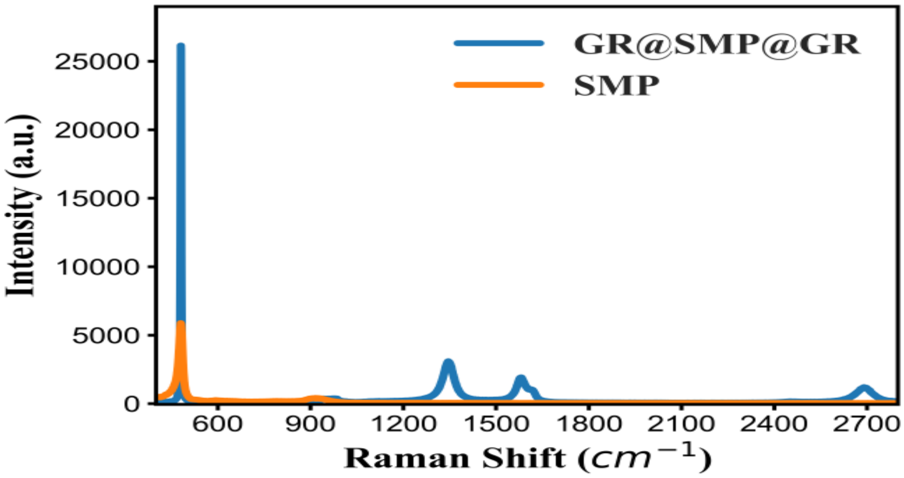


Figure 3. Raman shift of electrodes

4. Electrochemical tests of electrodes

4.1. SMP and GR@SMP@GR electrodes' performance of ten circulation

In order to analyze the influence of the graphene coating on the first charge and discharge cycle of the silicon micron column electrode, we used the Landian test system (LandBA2100A, Wuhan Landian Electronics Co., Ltd.) to charge the SMP and GR@SMP@GR electrodes with constant current. In **Figure 4**, it can be observed that the lithium insertion platform voltage of the two electrodes in the first week is 0.2-0.3V, indicating that the silicon prepared by the PECVD deposition process has a higher degree of amorphization and only requires a smaller activation energy to react with lithium [11]. Therefore, the reaction potential is higher. The reversible specific capacity of the SMP electrode in the first cycle is 2470.9 mAh/g, and the coulombic efficiency is 79.65%. The reversible specific capacity of the GR@SMP@GR electrode in the first cycle is 2956.7 mAh/g, and the coulombic efficiency is 93%. Obviously, the coating of vertical graphene greatly improves the coulombic efficiency of the silicon micron column electrode in the first week, which indicates that the coating of vertical graphene makes the electrolyte difficult to contact with silicon, thereby reducing the consumption of lithium ions in the electrolyte and reduce the generation of irreversible side reactions. At the same time, the vertical graphene network also promotes the transportation of lithium ions and improves the electronic conductivity of the silicon anode, which improves the conductivity of the silicon anode, which significantly improving the coulombic efficiency in the first week [12].

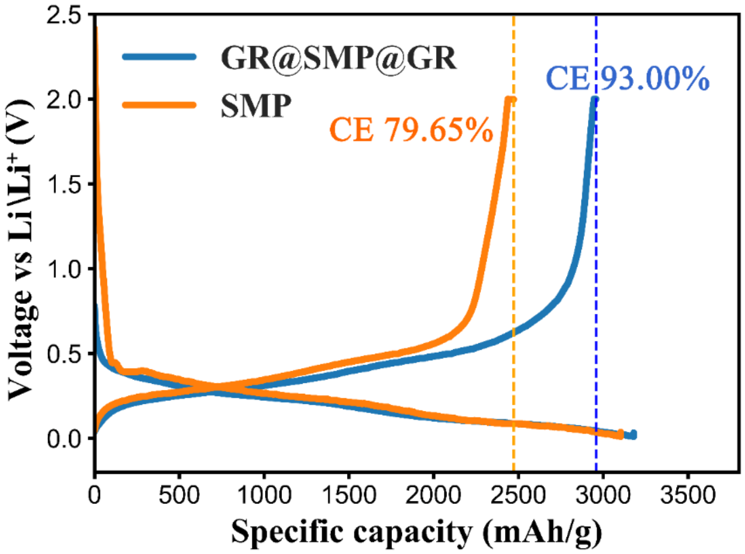


Figure 4. The charge/discharge cure for SMP and GR@SMP@GR electrodes.

4.2. Rate performance test of SMP and GR@SMP@GR electrodes

The curve reflects the process of insert and desorb of lithium on the electrode at a constant sweep rate. **Figure 5(a)** and **Figure 5(b)** shows the CV curves of the first two cycles of the SMP and GR@SMP@GR electrodes. It is not difficult to see from the figure that the lithium insertion and removal peak positions of the two electrodes both contain the LixSi alloy peak positions of 0.1-0.25 V, and the lithium-silicon alloy delithiation peak positions near 0.3 V and 0.5 V. At the same scanning speed of 0.1 mV/s, the area enclosed by the lithium insertion curve and delithiation curve of the GR@SMP@GR electrode is higher than that of the SMP electrode, and the area enclosed by the CV curve in the second circle of scanning changes It is smaller, indicating that the use of vertical graphene effectively reduces the loss of active silicon. It can be observed in the inset that the two electrodes contain broad peaks at 0.5-2 V, corresponding to the decomposition of electrolyte and electrolyte additives. Among them, the side reaction of the silicon electrode coated with vertical graphene disappeared in the second week, indicating that the irreversible side reaction of the electrode and the electrolyte was suppressed, the consumption of lithium ions was reduced, and the electrochemical performance of the battery was enhanced.

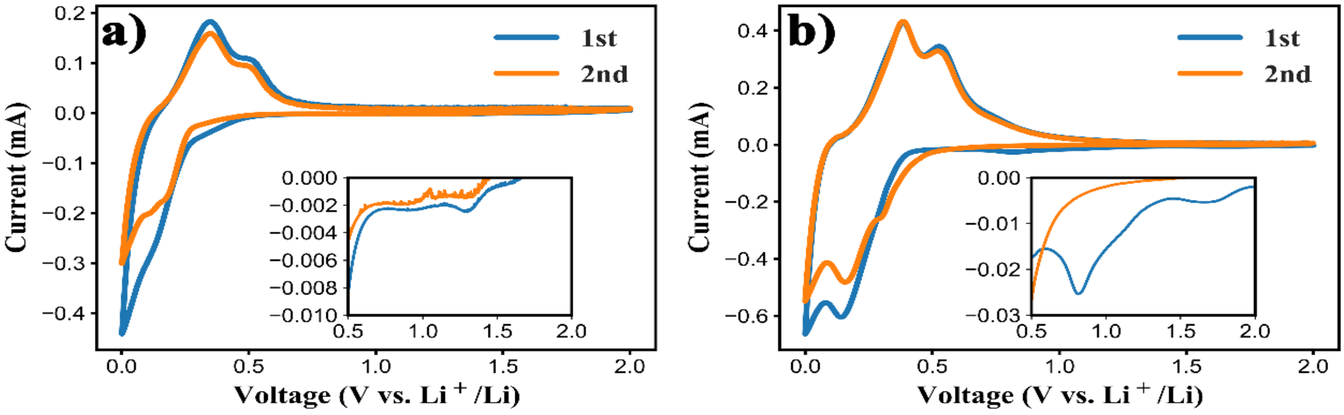


Figure 5. The the CV curves of (a) SMP and (b)GR@SMP@GR electrode.

After cycling for ten weeks at a rate of 0.1 C, scan the CV curve. As shown in **Figure 6**, both SMP and GR@SMP@GR electrodes contain characteristic peaks of silicon-lithium alloying around 0.2 V and de-alloying characteristic peaks of 0.3-0.5 V[13]. However, the SMP electrode still has the characteristic peak position due to electrolyte additives and electrolyte decomposition in the first cycle around 1V-1.3 V, which indicates that the SEI formed on the surface of the SMP electrode does not effectively reduce the reaction between silicon electrode and electrolyte. The side reaction of the electrolyte causes the lithium ions to be consumed, which reduces the coulombic efficiency. The GR@SMP@GR electrode does not have this peak position except for the first week. At the same time, the oxidation and reduction peaks of the electrode are higher than those of the SMP electrode, indicating that the addition of vertical graphene makes the electrode capacity more stable than that of the SMP electrode. At the same time, the oxidation peak intensity is approximately the same as the reduction peak intensity, indicating that the electrode containing upright graphene is more reversible, which also indicates the high coulombic efficiency of the GR@SMP@GR electrode in the previous charge-discharge cycle test.

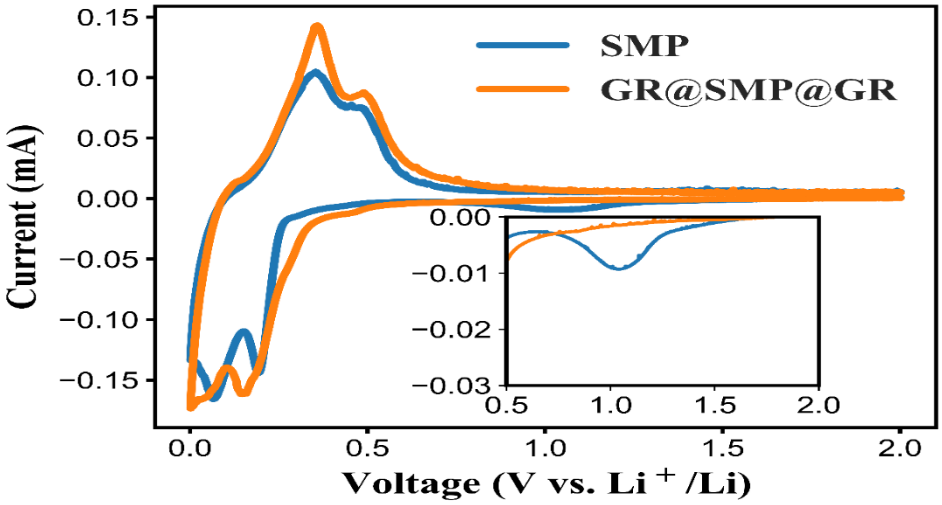


Figure 6. CV curves after ten circulations of electrode.

4.3. Electrochemical impedance test of SMP and GR@SMP@GR electrodes

After the first cycle, electrochemical impedance measurement was performed on the SMP and GR@SMP@GR electrodes, and the test results are shown in **Figure 7**. It can be observed that the AC impedance spectrum components of the two electrode materials are the same, with a semicircular shape in the middle and high frequency region and a diagonal line in the low frequency region. The semicircle in the middle and high frequency region is designated as the diffusion and migration of ions through the SEI and between the SEI and the electrode surface, and the oblique line in the low frequency region is the lithium-ion diffusion resistance inside the electrode. The electrochemical impedance of the SMP electrode is relatively high, mainly because the SEI film on the electrode surface fails to effectively protect the silicon electrode, which reduces the growth rate of the SEI. These irreversible side reactions further increase the charge transfer resistance (Rct), and the deactivation of silicon also increases the diffusion distance of lithium ions, reduces the diffusion rate of lithium ions inside the silicon electrode, and increases the diffusion resistance (Wo), resulting in the impedance spectrum as a whole shows a higher impedance. The coating of upright graphene reduces the contact between the electrode and the electrolyte, reduces the occurrence of side reactions, and controls the formation rate of the SEI on the electrode surface. At the same time, the high toughness and good conductivity of the upright graphene network make the electrode transfer the charge impedance is lower, and the silicon electrode is effectively protected, which reduces the dead lithium capacity in the silicon electrode, thereby reducing the diffusion resistance and making the overall performance lower impedance. The use of upright graphene also makes the lithium insertion and extraction process less resistant, the charge and discharge capacity of the electrode is approximately equal, and the reversibility is high. These characteristics are intuitively manifested as a higher coulombic efficiency and a stronger peak current in the CV.

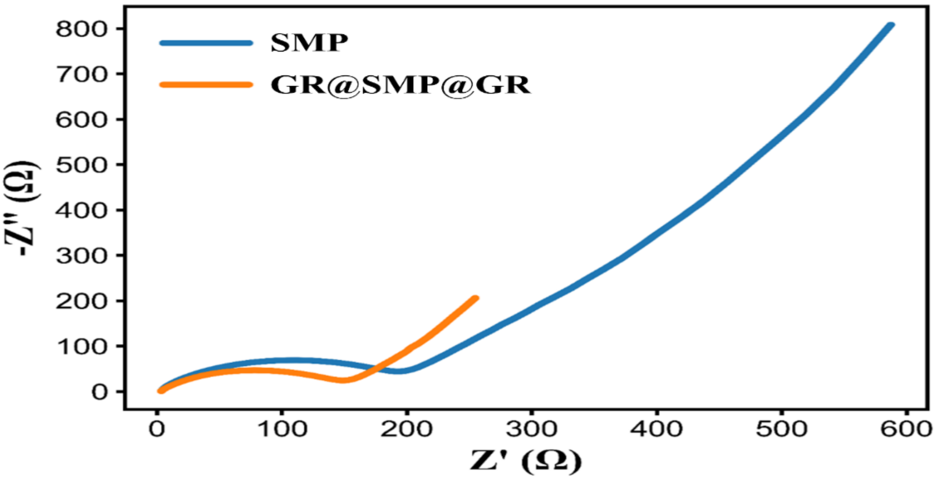
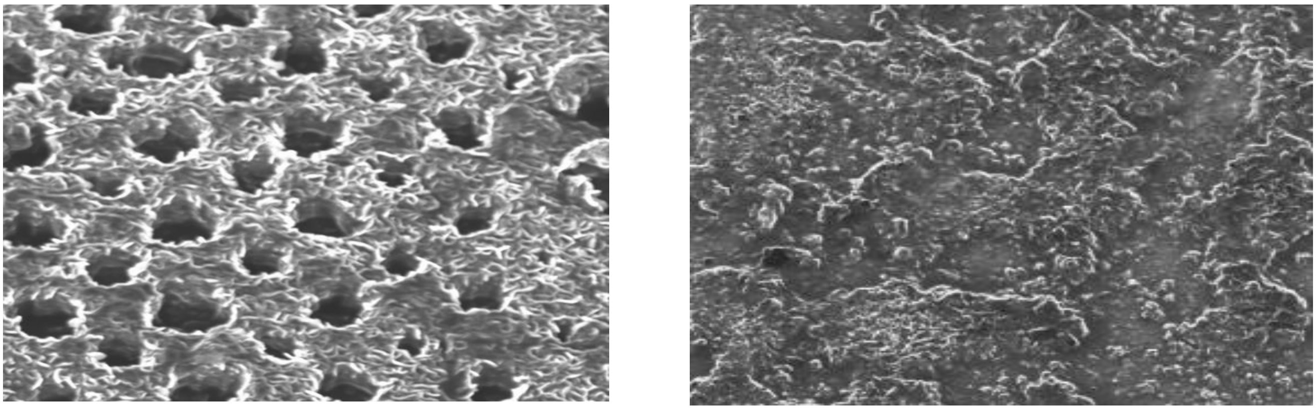


Figure 7. Electrochemical impedance spectra of SMP and GR@SMP@GR electrodes after the first cycle.

4.4. Morphology analysis of SMP and GR@SMP@GR electrodes

The vertical graphene has an important influence on the micron silicon pillar morphology on the SMP electrode and the SEI morphology of the silicon pillar surface. We used SEM to characterize the morphology of the SMP and GR@SMP@GR electrodes after 50 cycles. After a long-period test under specific conditions, the battery was disassembled in a glove box full of Ar (H2O<0.1 ppm, O2<0.1 ppm), and the nickel current collector with micron silicon column array was repeatedly cleaned several times to completely remove the residue. The electrolyte solution on the surface of the current collector is then put into a transparent glass bottle, sealed and transferred to a vacuum drying box to stand still, so that the DMC is dried and volatilized. Finally, the sample was transferred from the drying oven to the He ion microscope for morphological characterization.

The SEM images of SMP and GR@SMP@GR electrodes after 50 cycles are shown in **Figure 8(a)** and **Figure 8(b). Figure 8(a)** shows the SEM image of the GR@SMP@GR electrode, and **Figure 8(b)** shows the SEM image of the SMP electrode. It can be clearly observed that after 50 cycles of the GR@SMP@GR electrode, the electrode structure is complete and no cracks appear on the surface. At the same time, it can be observed that the SEI formed on the electrode surface is embedded in the graphene film. However, the SEI film does not completely cover the vertical graphene layer on the surface. Moreover, the electrode structure has changed from a silicon micro-pillar array structure to a cross-shaped grid structure. This is mainly due to the adhesion of the vertical graphene grown on the surface of the silicon micro-pillar, and the growth of the SEI. It can be observed that the SEI is attached to the surface of the graphene, which increases the thickness of the graphene. This is mainly due to the fact that graphene participates in the electrochemical reaction during the electrode cycle, and the carbon-based material has a low degree of expansion due to its low specific capacity, but still forms an SEI. In **Figure 8 (a)**, it can be observed that the silicon pillars on the surface of the SMP electrode are destroyed and disappeared, and only the base of the silicon pillars remains, and the silicon active material disappears. These findings also confirm the low coulombic efficiency of the SMP electrode, and the rapid decrease of the electrode capacity is also intuitively reflected in the CV curve.



(a) (b)

Figure 8. SEM images of (a) GR@SMP@GR electrode and (b) SMP electrode.

5. Conclusion

The research and development of silicon anode materials with high specific capacity and low cost is an important journey of silicon anode to commercialization. The key to solving the problem lies in how to deal with the high-volume expansion during the charging and discharging process of silicon, so that the active silicon is quickly consumed and the low battery life and coulomb efficiency are caused. In order to solve the above problems, this paper uses micro-nano processing technology to prepare a silicon-carbon composite anode composed of upright graphene-coated silicon particles. After assembling the button cell, the effect of the composite anode on the battery performance is studied from the perspective of composition and electrochemistry.

From the experiment that electrolyte additives can improve the performance of SEI membranes, it can be known that blocking the contact between the silicon anode and the electrolyte can effectively reduce the occurrence of irreversible side reactions. Therefore, we propose to use graphene as a coating material to improve the Coulombic efficiency of the battery and prepare graphene-coated silicon micropillar arrays to study the effect of vertical graphene on amorphous silicon micropillar electrodes. The vertical graphene network blocks the direct contact between the silicon electrode and the electrolyte to the greatest extent, reduces the occurrence of irreversible side reactions and improves the electronic conductivity of the silicon anode. Compared with uncoated materials, the first week coulombic efficiency of the amorphous silicon micropillar negative electrode coated with vertical graphene increased from 79.65% to 93%. The electrode surface after 50 cycles was observed by SEM, and the silicon containing vertical graphene was found the micro-pillar electrode has a complete structure, low degree of cracking, no shedding, and the SEI film formed on the electrode surface is thin. It shows that the graphene-coated silicon anode is more stable under long-term cycling. However, the surface of the uncoated silicon micron column electrode is severely powdered, the silicon active material falls off in a large area, and the electrode capacity loss is serious.

In this paper, the coulombic efficiency and long-cycle cycle stability of silicon anodes have been significantly improved by using graphene composite anodes. This research will help improve the performance of silicon anodes and reduce their use costs, and deepen people's understanding of SEI membranes and composite anodes. The micro-nano processing method used in this experiment can also provide a new understanding and platform for other battery-related experiments. At the same time, it is also hoped that the silicon composite anode can be used in commercial lithium-ion batteries as soon as possible

Disclosure statement

The author declares no conflict of interest.

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