Design of ultrafine silicon structure for lithium battery and research progress of silicon-carbon composite negative electrode materials

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Abstract—As demand for high-performance electric vehicles, portable electronic equipment, and energy storage devices increases rapidly, the development of lithium-ion batteries with higher specific capacity and rate performance has become more and more urgent. As the main body of lithium storage, negative electrode materials have become the key to improving the performance of lithium batteries. The high specific capacity and low lithium insertion potential of silicon materials make them the best choice to replace traditional graphite negative electrodes. Pure silicon negative electrodes have huge volume expansion effects and SEI membranes (solid electrolyte interface) are easily damaged. Therefore, researchers have improved the performance of negative electrode materials through silicon-carbon composites. This article introduces the current design ideas of ultrafine silicon structure for lithium batteries and the method of compounding with carbon materials, and reviews the research progress of the performance of silicon-carbon composite negative electrode materials. Ultra-fine silicon materials include disorderly dispersed ultra-fine silicon particles such as porous structures, hollow structures, and core-shell structures; and ordered ultra-fine silicon, such as silicon nanowire arrays, silicon nanotube arrays, and interconnected silicon nano-films. The article analyzes and compares the composite method of ultrafine silicon and carbon materials with different structural designs, and the effect of composite negative electrode materials on the specific capacity and cycle performance of the battery. Finally, the research direction of silicon-carbon composite negative electrode materials is prospected.

1. Introduction
As demand increases rapidly for high-performance electric vehicles, portable electronic equipment, and energy storage devices, the development of lithium-ion batteries with higher specific capacity and rate
performance has become more and more urgent \cite{1}. Generally speaking, the total specific capacity of a lithium-ion battery is determined by the components that make up the battery. As the main body of lithium storage, the negative electrode material is the key to improve the total specific capacity, cycle life, charge and discharge performance and other related parameters of lithium-ion batteries \cite{2}. The current commercial negative electrode materials are mainly graphite-based traditional carbon materials, and the theoretical specific capacity of graphite is only 372 mAh/g, which greatly limits the further improvement of the total specific capacity of lithium-ion batteries \cite{1}. Therefore, people have developed a higher specific capacity silicon negative electrode material, the theoretical maximum specific capacity is about 4200 mAh/g, and the source is wide \cite{3}. However, in the process of insertion and extraction of lithium ions, silicon materials are accompanied by severe volume changes (over 300%). This will cause the active material in the electrode to fall off and powder, and then affect the cycle life of the battery \cite{3}. In recent years, intensive research has been carried out at home and abroad to solve this problem. There are two main ideas: one is the nanometerization of silicon; the other is the compositeization of silicon; In the composite phase selection of composite materials, carbon and silicon have similar chemical properties, and the two can be closely combined. Therefore, the combination of silicon and carbon can achieve the purpose of improving the volume effect of silicon and improving its electrochemical stability \cite{3}. This article mainly introduces the structural design of silicon-carbon composite negative electrode materials developed in recent years, and reviews the effects of different structural designs of ultra-fine silicon materials on the specific capacity and cycle performance of composite silicon-carbon negative electrodes for the purpose of studying high-performance lithium batteries negative electrode materials provide reference.

2. Introduction to the design of disorderly dispersed ultra-fine silicon particles and ordered ultra-fine silicon structure

The ultra-fine nano-silicon particles have large reserves and low prices, and the synthesis method is becoming mature. It is compatible with the manufacturing process of lithium batteries. Its size reduction can help release the stress of silicon expansion and prevent silicon powdering, which significantly improves the cycle performance of the battery \cite{4}. However, due to the large change in the volume of silicon, there is a risk that the nano-silicon particles will fall off the current collector and the SEI film will be destroyed during the charging and discharging process. Therefore, many studies have put forward new ideas for nano-silicon materials, and carry out special structural design such as porous, hollow, core-shell and other structures. Compared with disorderly dispersed ultra-fine silicon particles, ordered ultra-fine silicon such as silicon nanowires, silicon nanotubes and silicon nano-films can greatly relieve the stress caused by volume expansion, but it is more expensive and complex to manufacture. In addition, the tap density is relatively low.

2.1 The porous structure design of disorderly dispersed ultra-fine silicon particles and the properties of silicon-carbon negative electrode materials after compounding

The porous structure of ultra-fine silicon particles is etched with multiple holes on the surface and inside of the silicon to reduce the battery current density and the Li⁺ concentration and stress gradient on the surface of the particles, and shorten the distance of electron and ion transfer, so as to improve the polarization and rate performance. Hu et al\cite{5}, prepared porous silicon by metal-assisted chemical etching of silicon in HF aqueous solution. In HF aqueous solution, the addition of graphite particles and carbon nanotubes accelerated the etching rate of silicon. By replacing precious metals with carbon materials, the author provides a low-cost method to manufacture ultra-fine porous silicon materials. The design of the porous structure offsets the volume expansion effect of silicon. Ge et al\cite{6}, developed a transformable method to prepare ultrafine silicon with a porous structure. The porous nano-silicon particles were prepared by doping with boron atoms and electroless etching. The outer layer of this material is wrapped by graphene, and the inside is ultra-fine porous silicon. After 200 cycles at 0.5 C, the capacity remains at 1,000 mAh/g. Although the porous structure of ultrafine silicon can improve their cycle performance, the volume capacity of the electrode will also be severely impaired. Cho et al\cite{7}, used silicon dioxide as
a raw material and used the sol-gel method to make it into a porous hollow structure, and then converted the silicon dioxide into silicon through a magnesium thermal reduction reaction, and finally chemically etched to remove excess impurities. Obtained hollow ultrafine porous silicon. Because of the increase in the porous structure, the volume expansion of silicon can be further offset, thus exhibiting excellent cycle performance.

2.2. Hollow structure design of disorderly dispersed ultrafine silicon particles and properties of silicon-carbon negative electrode materials after compounding

The hollow structure of ultrafine nano-silicon particles can also buffer the volume expansion of silicon. The maximum tensile stress generated in the silicon during the constant current cycle of the battery is as high as 2 GPa [8], which can be effectively reduced by the design of the hollow structure. Yao et al [8] developed an interconnected hollow structure ultra-fine nano-silicon material. Using SiO$_2$ nanospheres as a template, use chemical vapor deposition to deposit silicon on a stainless steel sheet, pass SiH$_4$ gas into the device containing SiO$_2$ nanospheres, and keep the temperature at 485℃, and deposit a layer of 25nm thickness on the surface of the SiO$_2$ nanospheres the left and right elemental silicon is finally used to etch the inner SiO$_2$ nanosphere template with HF solution to obtain the final interconnected hollow structure ultrafine nano-silicon material. The first reversible capacity of the material electrode is 2725 mAh/g, and the first coulombic efficiency is 77%. The excellent electrochemical performance can be attributed to the structural advantages of the interconnected hollow structure ultrafine nano-silicon. Because the deposited silicon layer is thinner, the diffusion path of lithium ions is shortened, and the rate performance of the material is improved. In addition, the internal hollow structure can buffer the volume expansion of the electrode material during charging and discharging. Yoon et al [9] synthesized hollow-structured ultra-fine nano-silicon cubes (m-Si HC) (as shown in Fig.1 [9]). The internal size of the cube is about 60 nm, and the thickness of the silicon layer at the junction of the cube is about 15 nm. The internal space is calculated to be enough to accommodate the volume expansion of the silicon material. Compared with the spherical structure, the cubic structure enhances the contact area between the m-Si HC material and the electrolyte, and the outer contact surface of the cubic accelerates the diffusion efficiency of lithium ions. The m-Si HC material coated with amorphous carbon has the first reversible capacity as high as 1728 mAh/g, and the first coulombic efficiency is as high as 80%.

2.3. The core-shell structure design of disorderly dispersed ultrafine silicon particles and the properties of silicon-carbon negative electrode materials after compounding

Si@C is the most common composite material among core-shell silicon nanomaterials [10]. Liu et al [10] used a special method to seal the ultra-fine nano-silicon particles in a thin and uniform carbon shell, leaving a gap between the ultra-fine nano-silicon and the carbon shell to meet the expansion of silicon. The first reversible capacity of this core-shell electrode material is as high as 2833 mAh/g at a rate of 0.1 C, and the capacity retention rate after 1000 cycles is 74%. Chen et al [11] developed a double-layer carbon shell-coated ultra-fine nano-silicon negative electrode material (DCS-Si). The inner carbon shell provides sufficient internal space for the large-volume changes of ultra-fine nano-silicon. The shell contributes to the formation of a stable SEI interface. The first reversible specific capacity of DCS-Si electrode material is relatively high, and it performs well under 1000 cycles. The author used LiNi$_{0.45}$Co$_{0.1}$Mn$_{1.45}$O$_4$ as the cathode material and assembled a button battery. The average discharge
voltage of the battery is 4.2 V and the energy density is as high as 474 Wh/kg.

2.4. The structure design of ordered ultrafine silicon and the properties of silicon-carbon negative electrode materials after compounding

The ordered ultra-fine silicon structure design includes structures such as silicon nanowire arrays, silicon nanotube arrays, and silicon nanofilms. This structure can better reduce the volume expansion effect, the silicon nanowires are entangled with each other, and there are many contact points, which can speed up the transmission of lithium ions. There are two methods for preparing ordered ultra-fine silicon structures: one is based on the vapor-liquid-solid (VLS) growth mechanism to produce silicon nanotubes on the substrate using chemical vapor deposition (CVD) and molecular beam epitaxy (MBE); the other uses metal ions as a catalyst to etch silicon wafers to obtain arrayed nanowire structures. However, compared with ultra-fine nano-silicon particles, silicon nanotubes are more complicated to manufacture and more expensive. Hu et al. put the P(100) and N(100) silicon wafers with a resistivity of 1-10Ω•cm deposited with a metallic silver film on a carbon plate conveyor belt and soaked them in an oxygen-impregnated reaction in hydrofluoric acid solution. The carbon plate substrate effectively accelerates the rate at which the metal-catalyzed silicon corrosion reaction occurs, and realizes the continuous preparation of ordered silicon nanowire arrays by enhancing the metal-catalyzed corrosion of the carbon substrate. This structure reduces the volume expansion effect of silicon. The first discharge cycle specific capacity of this electrode is as high as 3124 mAh/g, and the cycle performance is also high. However, toxic HF is used in the material synthesis process, and the cost is relatively high. In order to study a simple and low-cost production process, Zhang et al. prepared SiO2 coated crystalline silicon nanowires. The specific process is to mix silica and titanium powder, and heat treatment at a high temperature at 1600 °C in an argon atmosphere. The reversible capacity of the synthesized electrode material maintained at 1640 mAh/g after 100 cycles at a current density of 1 A/g. Wu et al. prepared silicon nanotubes coated with SiOx on the outer layer. This design prevents the inner silicon nanotubes from directly contacting the electrolyte, and the SEI film can exist stably. During the specific production process, the author using electrospinning technology and carbonization treatment to obtain a carbon fiber template, then using CVD technology to deposit a layer of silicon on the surface of the carbon fiber. Finally, the material is heat-treated at 500 °C in an O2 atmosphere to remove the carbon fiber, and the silicon on the outer layer is oxidized to SiOx as a protective layer. The material has a reversible specific capacity of up to 1780 mAh/g for the first time at a rate of 0.2C, and a capacity retention rate of up to 94% after 300 cycles. Zhang et al. used a magnesium thermal reduction method to prepare a kind of silicene sheets, which have different orientations and are interwoven into a flower shape. This material still has 1100 mA/g remaining after 600 cycles at 2000 mA/g, and the cycle performance is excellent. The specific energy and energy density of a full battery made by combining this material with a traditional positive electrode are as high as 543 Wh kg−1 and 1257 Wh L−1.

3. Conclusion

Silicon is the material with the largest theoretical specific capacity. In the application of silicon materials for battery negative electrodes, the biggest problem is the poor cycle performance caused by the huge volume expansion effect of silicon during the charging and discharging process. The design of ultra-fine nano-silicon structure and the composite with carbon materials can effectively solve this problem. In the preparation of silicon-carbon composite negative electrode materials, the porous structure, hollow structure and core-shell structure of the disorderly dispersed ultra-fine silicon particles can effectively alleviate the volume expansion effect of silicon materials. In the orderly design of ultra-fine silicon structure, the negative electrode material prepared after the combination of silicon nanowires and carbon materials has the advantages of high specific capacity, high silicon content, and stable cycle performance. However, the process is relatively complicated and the cost is high. Therefore, for this type of anode material, it is necessary to improve its cycle performance and reduce its irreversible specific capacity. In addition, the influence mechanism of the different structure design of disorderly dispersed ultrafine silicon particles on the properties of the final composite material needs urgent research, such as the
influence of the specific surface area of the ultrafine silicon particles with different structure designs on the formation of the electrode material SEI film, the influence of the carbon content in different silicon-carbon composite negative electrode material systems and the structure design of ultra-fine silicon particles on the irreversible specific capacity of the battery.

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