Preparation and Modification of Silicon-Based Anodes in Lithium-ion Batteries

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Abstract: As an anode material, the theoretical specific capacity of silicon is more than ten times that of graphite materials, and its delithiation potential is low. Therefore, it has become a research focus in the field of electronic devices, electronic vehicles and renewable energy storage systems. However, the volume expansion of silicon during charge and discharge process will cause the material to pulverize, which will reduce Coulomb efficiency and shorten the service life. In order to solve these problems, researchers have made a lot of efforts. This article analyzes and discusses the preparation methods, electrochemical properties of representative silicon-based materials, including silicon nano-particles, silicon-carbon composite materials, and SiO_x ($0<x\leq2$). Finally, the existing problems are discussed and future research directions are proposed.

1. Introduction

Lithium ion batteries have the advantages of abundant raw materials, green environment protection, higher energy ratio, high operating voltage, and no memory effect [1-2], and are widely used in the field of electronic products. However, the specific capacity of graphite, a traditional commercial material for lithium ion battery cathode, has been close to its theoretical value (372 mAh/g) [3], which is difficult to improve substantially. Lithium titanate (LTO) has a good cycle security, but its specific capacity is very low (176 mAh/g), which is hard to meet future demand for the application of high-energy battery. The theoretical specific capacity of silicon intercalated-lithium is ten times more than graphite (> 4000 mAh/g) [4]. In addition, it has low cost, low voltage platform, abundant reserves in the earth, and good multiplier characteristics. So it has become a research hotspot in electric vehicles, energy storage systems and other fields. But the conductivity of silicon-based materials is poor, and its volume changes by 400% upon insertion and extraction of lithium, which results in pulverization and capacity fading [2]. In addition, the solid electrolyte layer (SEI) repeatedly formed on the silicon surface increases the polarization and decreases the Coulomb efficiency, resulting in the deterioration of electrochemical performance [5]. To solve these problems, the researchers modified the silicon-based materials by means of nanocrystallization [6], structure design [7], etc.

2. Nanocrystallization

Nano-sized materials have a relatively large specific surface area, which can buffer the stress caused by volume expansion at a certain degree, which is more conducive to maintaining the integrity of the active materials after charging and discharging [8]. Particle size reduction means shorter ion transport distance and less polarization [9]. The experimental results of Li et al. show that the polarization of nano-silicon is less than micron silicon, and the charging curve platform is more inclined and closer to monophasic behavior [10]. In addition, the first coulomb efficiency and capacity retention rate of nano-silicon have also been significantly improved. After the cycling test, the battery was disassembled, and it was found that the micron silicon appeared obvious pulverization, the electrical contact became worse, and the reversible capacity loss was greater. According to another research by Christoph Erk, figure 1 shows the difference in performance of electrodes made from 50 and 100 nm silicon particles. Fig. 1 (g) and (h) shows that in 30 cycles, their lithium specific capacities are all higher than 1000 mAh/g, and the smaller the particle size, the larger the battery capacity.

(a) TEM image of Si-50   (b) EMTEM image of Si-50   (c) HRTEM image of Si-50

(d) TEM image of Si-100   (e) EMTEM image of Si-100   (f) HRTEM image of Si-100
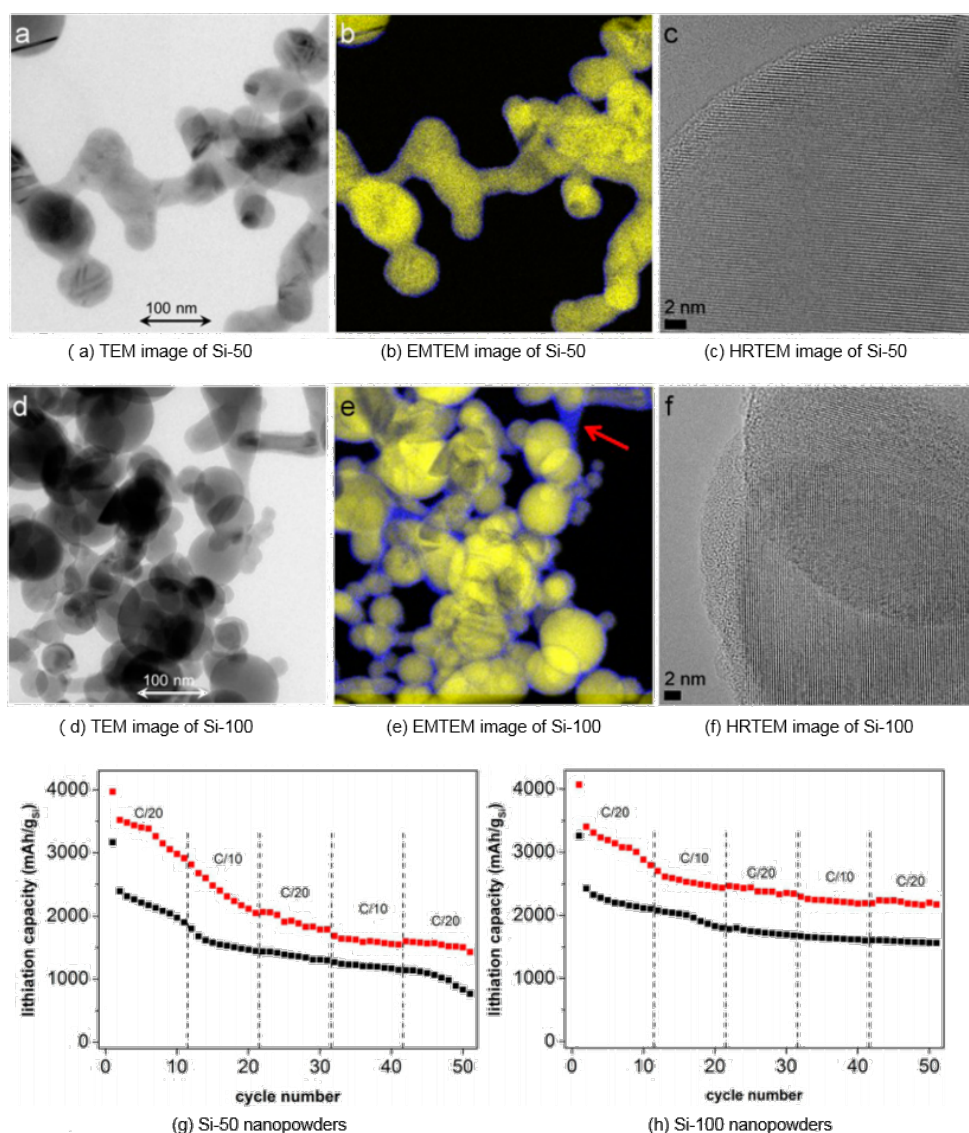
(g) Si-50 nanopowders   (h) Si-100 nanopowders

Figure 1: Microstructure of (a-c) Si-50 and (d-f) Si-100 nanopowders. (a, d) Bright-field TEM images. (b, e) EFTEM mapping of the areas shown in panels a and d. The red arrow in panel e indicates an oxygen-rich domain. (c, f) HRTEM images and lithiation (discharge) capacity as a

function of cycle number for electrodes prepared from Si-50 (solid squares in red) and Si-100 (solid squares in black) nanopowders and AA as binder. (g) EC-based electrolyte. (h) FEC-based electrolyte [11].

Mi-Hee Park et al. [12] prepared Si nanotubes by reductive decomposition of a silicon precursor in an alumina template and etching. These nanotubes show impressive results, which shows very high reversible charge capacity of 3247 mAh/g with Coulombic efficiency of 89%, and also demonstrate superior capacity retention even at 5C rate (= 15 A/g). Furthermore, silicon nanotube anode has good cycling performance: the capacity in a Li-ion full cell consisting of a cathode of LiCoO2 and anode of Si nanotubes demonstrates a 10 times higher capacity than commercially available graphite even after 200 cycles.

However, silicon nanoparticles have a large specific surface area and will come into greater contact with the electrolyte, forming more SEI films. Besides, the small nanoparticles are easy to agglomerate, resulting in rapid capacity decay. Therefore, in practical applications, some measures should be taken to prevent the agglomeration of nanoparticles and thus stabilize the silicon anode.

3. Silicon-Carbon Composite Materials

Dispersing silicon into the reduced graphene oxide (rGO) is a good solution to solve the problem of the significant volume changes of silicon during the lithiation/delithiation process, because the graphene can buffer the volume change and improve the electrical conductivity of silicon active materials. Moreover, rGO can be fabricated in large scale at low cost, so rGO is usually used as a substitute for the pristine graphene in electrodes [13].

Bin W et al. [14] develop a novel kind of self-supporting binder-free silicon-based anodes by encapsulating silicon nanowires (SiNWs) with dual adaptable apparels (overlapped graphene (G) sheaths and reduced graphene oxide (RGO) overcoats). The flexible and conductive RGO overcoats accommodate the volume change of embedded SiNW@G nanocables and thus the structural and electrical integrity of the SiNW@G@RGO are maintained. The SiNW@G@RGO electrodes exhibit high reversible specific capacity of 1600 mAh/g at 2.1 A/g, 80% capacity retention after 100 cycles, and superior rate capability (500 mAh/g at 8.4 A/g) on the basis of the total electrode weight.

H.Tang et al. [15] fabricated the Si/rGO-P composite film which consists of top-down two layers (GO layer and silicon layer) through evaporation method. The rGO sheets in the hybrid porous films not only display a porous structure that enhanced electrochemical performance, but also interact well with the silicon particles to release the volume expansion and reduce the transfer resistance of Li+ in the electrode and increase the conductivity of the material. The initial discharge capacity of the composite film is 3404 mAh/g with a reversible charge capacity of 2250 mAh/g (the specific capacity is calculated according to the total mass), and the first Coulomb efficiency is 66%. The composite film is a flexible and binder-free electrode, which displays a good cyclic retention of 1261 mAh/g after 70 cycles and improved rate capability. Its Coulomb efficiency can be stabilized above 99%, which is an excellent value for silicon materials.

It can be seen from the above two literatures that the advantages of silicon-carbon composite are mainly reflected in two aspects. First, carbon material can increase the conductivity of silicon electrode, thus reducing the polarization of electrode, improving the coulomb efficiency of battery, and meeting the demand of silicon negative electrode charging and discharging at large ratio. The other is that carbon coating can maintain the structure stability of silicon anode, improve mechanical strength, relieve the volume change in the process of silicon de-imbed lithium, and inhibit the agglomeration of silicon nanoparticles. In addition, carbon materials can improve the compatibility of silicon surface with electrolyte and act as a protective layer to prevent the continuous reaction of silicon and electrolyte to produce SEI film, thus extending the service life of silicon electrode.

4. SiOx and Related Modified Materials

In recent years, as an industrial raw material, silicon oxide (SiOx, $0< x \leq 2$ or less) has attracted special attention because SiOx has higher specific capacity compared with carbon graphite materials, and good cycle stability compared with Si anode [16]. Materials such as oxidation of the most common silicon material (the SiO, $x \approx 1$), has been used in lithium ion battery anode materials and show great potential at present.

SiO is a nanocomposite formed by the uniform dispersion of nano-silicon into amorphous SiO2. The capacity of SiO comes from nano-silicon, its actual reversible capacity is about 1500 mAh/g, and its cycling performance is better than that of Si/C composites [17].

However, compared with silicon materials, the electrochemically active lithium storage phase (a-Si) in SiOx materials is reduced, so the specific capacity and the first Coulomb efficiency are gradually reduced. Although the presence of O atoms will generate the inert buffer matrix phase, the overall volume effect is still large, and there is a problem of poor matching with some electrolytes [18]. Because of these reasons, the cycling performance of SiOx anode material is seriously attenuated. Therefore, a lot of work has been done to modify and optimize SiOx anode materials to improve their electrochemical properties, such as disproportionation [19], composite with other materials [20] and other technologies [21-22].

Mamiya et al. [23] placed amorphous SiO in an inert atmosphere of 850 °C and calcined at high temperature. The disproportionation reaction took place and the nanocrystalline silicon with an average particle size of 4-5 nm was formed. They found that as the calcination time increased, the amount of nanocrystalline silicon gradually increased, and the particle size remained unchanged. If the calcination temperature is increased to more than 1000 °C, the generation rate of monocrystalline silicon will be accelerated rapidly, and the particle size will gradually increase. Remarkably, with the generation of nanocrystalline silicon accompanied by the gradual increase of Si4+, the lithium embedded platform for the first time gradually approached to the elemental Si, and the electrochemical performance of SiOx gradually improved.

In addition, it is a good method to combine SiOx with metal. On the one hand, metal materials have good conductivity, which can enhance the dynamic properties of silicon alloy materials. On the other hand, the metal can act as a supporting framework to improve the silicon volume effect, thus effectively improving the electrochemical performance of SiOx anode [24].

For example, Song and others [25] convert amorphous Si (a-Si)-coated copper oxide (CuO) core-shell nanowires (NWs) into hollow and highly interconnected Si-Cu alloy (mixture) nanotubes with high-capacity and self-conductive structure and robust mechanical support. A high specific capacity of 1010 mAh/g (or 780 mAh/g) has been achieved after 1000 cycles at 3.4 A/g (or 20 A/g), with a high capacity retention rate ($\approx 88\%$), without the use of any binder or conductive agent. Remarkably, they can survive an extremely fast charging rate at 70 A/g for 35 times (corresponding to one full cycle in 30 s) and recover 88% capacity. This novel alloy-nanotube structure could represent an ideal candidate to fulfill the true potential of Si-loaded LIB applications.

SiOx has the advantages of high specific capacity and good cycle stability. The modified conductive performance is better, which further reducing expansion effect, and the first Coulomb efficiency and cycle performance is increased. However, the preparation steps of porous anode materials or hollow structure SiOx is mediocre and low yields. The removal of the template or the etching process will cause the collapse of structure. Therefore, the preparation and commercial application still need further research.

5. Conclusions

In this paper, the properties of silicon anode and the modification of related materials are summarized, which mainly includes nanorization, element doping to prepare composite materials, and the preparation of SiOx. Nano-sized silicon particles have the advantages of releasing stress generated in the process of lithium deintercalation, inhibiting the generation of crack, maintaining the integrity of the material, good circulation and large-scale preparation. Si/C composite material combines the high capacity of silicon and the superior retention capacity of carbon, which possesses the advantages of high conductivity and low volume change. Si/C materials can inhibit the excessive growth of the SEI film, and prevent nano-silicon agglomeration. However, their first Coulomb efficiency is low and the rate performance is not good enough, which still needs to be further improved. SiOx has good cyclic stability and high initial Coulomb efficiency, but it is difficult to prepare and has low yield, which increases the cost of the electrode material and hinders its practical application. Thus come to the conclusion that the composite of silicon nanoparticles and carbon or high energy density of lithium metal, etc., to prepare high-capacity and stable anodes may be a future research direction. This in turn requires the improvement of existing electrolytes or the development of new electrolytes with better compatibility with silicon nanoparticles. A lot of effort is still needed in the development of high energy density and safe silicon-based anode materials。

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