Progress in Application of Nano-technology in Silicon-Based LIBs

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Abstract. With the growing global demand for clean energy and efficient energy storage technologies, improving the performance of lithium-ion batteries, as one of the most mainstream energy storage devices, has become the focus of scientific research and industrial attention. Lithium-ion batteries (LIBs) have been widely used in portable electronic devices, electric vehicles, smart grids, and large-scale energy storage with their advantages of high energy density, long cycle life, no memory effect, and environmental friendliness. However, with the increasing battery performance requirements in these fields, traditional lithium-ion battery materials have gradually exposed their limitations in energy density, cycle stability, and safety. In this context, nanosilicon, a new anode material, has become a research hotspot in lithium-ion batteries due to its unique physicochemical properties and excellent electrochemical performance. Nano silicon, i.e., silicon materials with dimensions on the order of nanometers, has a larger specific surface area, shorter lithium-ion diffusion paths, and higher mechanical stress tolerance than bulk silicon. These properties make nanosilicon exhibit higher lithium storage capacity, faster charge/discharge rate, and better cycle stability in lithium-ion batteries. Therefore, this paper focuses on the progress of the application of nanosilicon in LIBs and the future development direction.

Keywords: LIBs, nanotechnology, Si.

1. Introduction

With the continuous progress of science and technology and the growing global demand for clean energy, lithium-ion batteries, as highly efficient and portable energy storage devices, have shown great potential for application in electric vehicles, portable electronic devices, renewable energy, and other fields. However, due to its limited capacity, the graphite anode of traditional lithium-ion batteries has made it challenging to meet the market demand for high-energy-density batteries. Therefore, the exploration and development of new high-performance anode materials have become hotspots in current battery research [1].

The application of silicon-based materials in lithium-ion batteries has received increasing attention, mainly due to the advantages of their high specific capacity, low embedded lithium potential, and abundant resource reserves. However, the application of silicon-based materials in Li-ion batteries also faces some challenges, such as volume expansion, poor electrical conductivity, and unstable SEI film. The application of nanotechnology can be an excellent solution to these problems. In recent years, the application of silicon nanomaterials in lithium-ion batteries has received widespread attention due to their high specific capacity and excellent electrochemical properties [2].

With an incredibly high specific surface area and porous structure, nano silica powder provides more storage space and can accommodate more lithium ions, thus achieving a higher storage capacity. According to research, the theoretical storage capacity of nano-silica powder can reach 4200 mAh/g, which is much higher than the specific capacity of traditional anode materials such as graphite. In addition, the smaller size of nano-silica powder has better mechanical elasticity and smaller volume expansion, which results in more minor volume changes during lithium ion embedding/de-embedding and reduces the stress and damage of the electrode material, thus improving the cycling stability and long-term service life [3]. Meanwhile, the high electrical conductivity and short ion/electron transport paths of the silica nanopowder help to improve the charge/discharge rate and battery power density. Therefore, this paper focuses on the application of nano-silica in LIBs.

2. Working Process of LIBs

2.1. Composition of LIBs

LIBs have emerged as one of the most essential energy storage solutions for portable electronic devices, electric vehicles, and renewable energy systems. LIBs consist of four essential components: anode, cathode, electrolyte, and separator, all components that make up the battery and are relevant in the working of batteries.

An anode is the negative electrode of a lithium-ion battery and usually consists of graphite, a very stable material that can easily accommodate lithium ions between the carbon layers [3]. Nevertheless, the theoretical capacity of graphite is 372 mAh/g, and therefore, the energy density of LIBs is restricted. Silicon has been considered one of the most attractive materials for anode because of its much higher theoretical capacity of about 4200 mAh/g.

The cathode is a positive electrode and is typically made of lithium metal oxides like lithium cobalt oxide ($LiCoO_2$), lithium iron phosphate ($LiFePO_4$), or lithium nickel manganese cobalt (NMC) oxide [4]. The cathode is used as the source of lithium ions during the charging and discharging process, and the material used in making the cathode plays a vital role in determining the battery's energy density, cost, and performance.

The electrolyte is the medium through which lithium ions are transported across the anode and the cathode, either in liquid or solid form. The electrolyte of most LIBs is an organic solvent, which contains a lithium salt or an organic lithium salt, of which the most common lithium salt is $LiPF_6$ [5]. The electrolyte is another significant factor in affecting the ionic conductivity of the battery, which must be chemically stable over a wide range of voltage levels and chemically compatible with the electrodes.

It is a thin film that provides a mechanical barrier between the anode and cathode to avoid the formation of a direct electrical connection while simultaneously allowing the passage of lithium ions. The separator must have the desired characteristics because its performance determines the battery's safety and operational efficiency.

2.2. Charging and Discharging Processes

In the operation of a LIB, lithium ions are shuttled between the anode and the cathode in charging and discharging. While charging, an external power source inputs a voltage across a lithium-ion battery, causing the ions to flow from the cathode to the anode through the electrolyte [6]. When lithium ions move into the anode material, graphite or silicon, for example, electrons go through an external circuit, and this is the electric current that can be utilized to power gadgets. In discharge, the process is the opposite; the client takes their time and reverses the program. The lithium ions move from the anode to the cathode, and in the process of doing so, the stored chemical energy is converted to electrical energy. This electric current flows through an external circuit and supplies the required power to an external device. It is thus evident that the performance of a LIB is directly associated with the efficiency of the occurring ion and electron transfers.

3. Preparation Methods for Nanosilicon

The synthesis of nanosilicon for application in LIBs has been done using physical and chemical methods and even by combining the two methods, which have pros and cons.

3.1. Physical Methods

Through mechanical milling, planetary ball milling is used to reduce silicon to the nanoscale. Ball milling involves subjecting the larger silicon particles to mechanical force whereby the particles are broken down into smaller sizes, thus increasing the surface area reactivity of the silicon [6]. This method is straightforward and inexpensive, but it is often found to generate particles with large distributions and non-spherical shapes. The disadvantage of ball milling, which arises with milling balls, is that the milled particles are usually irregular in shape and large in size and have a large particle size distribution. Also, the process can contaminate the milling equipment through constant wear. It is also energy-costly and relatively slow and thus not very appropriate for bulk or highly accurate synthesis of nanosilicon.

Laser ablation involves irradiating the silicon material with high-energy laser pulses, which causes the vaporization of the material to form nano-sized silicon particles. This method can create tiny and uniform particles, often with high purity, but the technique is expensive and usually difficult to use on a large scale. The disadvantages of laser ablation include the cost intensity and the complex complications that hinder the industrial application of laser ablation in industries with many pieces of manufacturing. It is critical, time-consuming, and requires costly laser systems for implementation. Further, it can be energy-consuming and may not always provide the controlled particle size, although it allows for relatively high purity and uniform particle size for nanosilicon.

In the sputtering process, silicon is implanted into a target material through a high-energy particle, forming a thin nanosilicon layer. Sputtering is widely applied to form nanosilicon coatings on substrate materials with enhanced electrochemical performance. Although sputtering is capable of creating high-quality nanosilicon films, the process of sputtering is very time-consuming and expensive.

3.2. Chemical Methods

Chemical Vapor Deposition (CVD) is one of the well-known techniques for coating nanosilicon onto the substrate. Silicon precursors are decomposed at high temperatures in this process, and silicon atoms are deposited to form nanostructures. Some drawbacks of CVD are high operation costs, high temperatures, and toxic chemicals, which can be unprofitable and require a large amount of energy for high production.

Sol-gel synthesis is a process in which a system changes from the liquid phase “sol” to the solid phase “gel,” which results in nanosilicon particles. This method is relatively cheap and hence can be applied in large-scale production. The technique is also straightforward to use. However, it becomes difficult to control the size and shape of the particles produced after the process. The drawbacks of sol-gel synthesis are that the morphology and size of the particles cannot be easily controlled, there might be an accumulation of particles, and it takes a very long time for the gel to set to a solid.

Nanosilicon is produced through chemical reactions in an aqueous solution at high temperatures and pressures, called hydrothermal synthesis [5]. This method can generate very high crystallinity, uniform size, and shape of nanosilicon, and it also has some drawbacks in terms of scalability and equipment requirements.

4. Nanosilicon in LIBs

Silicon is one of the most explored nanomaterials for LIB anodes, with a theoretical capacity of approximately 4200 mAh/g, which is ten times greater than that of graphite. This renders silicon one of the most promising materials for next-generation LIBs, especially in systems that require high energy density, such as electric vehicles and portable electronics [7]. Nevertheless, the application of silicon in LIBs has been restricted by several serious issues. One of the most critical concerns is the significant volume change, which can reach up to 300% during the lithiation process, where silicon actively incorporates lithium ions. This expansion can cause the silicon particles to crack and pulverize. Thus, the electrical contact between the silicon particles and the current collector will be lost, causing rapid capacity fading and poor cycle life.

The prospect associated with silicon-based LIBs is massive. The following are some of the challenges that face the development of silicon-based LIBs: The much higher capacity of silicon anodes could potentially result in battery energy densities several folds higher, thus providing longer lives to portable devices and an increased driving range of electric vehicles [8]. For instance, current ‘advanced development’ research includes the synthesis of complex composite anodes where silicon is combined with other high-capacity materials such as lithium metal or sulfur to design even more energetic density batteries than the existing ones. These hybrid systems could offer the best of both worlds: the high capacity of silicon and the stability of other more stabilized materials used in comparatively large quantities.

Nano silicon has been considered a potential material for enhancing the performance of LIBs, especially the high-capacity anode material. The lithium-ion storage capability in silicon nanoparticles is due to their high surface area, but these nanoparticles are known to swell during cycling, which causes mechanical deterioration [9]. Silicon nanowires, having a one-dimensional structure, can resolve the volume change of silicon associated with lithiation. Thus, their aspect ratio is high to facilitate efficient electron transport, and they have been reported to enhance the cycle life of LIBs. The problems with pure silicon anodes can be partially solved by incorporating carbon materials like graphene or carbon nanotubes with silicon. Carbon plays the role of a conductive structure capable of compensating and stabilizing the volume changes of silicon while enhancing both the anode's mechanical properties and electrical conductivity. Other research findings indicate that LIBs incorporating nanosilicon have a higher capacity than graphite-based LIBs. These have enhanced aspects such as energy density, cycling capability, and the capability of the cell to operate at a desired rate. For example, it has been found that silicon nanowire anodes have energy densities over ten times those of conventional graphite anodes and have an even longer cycle life when silicon anodes are combined with suitable binders and electrolytes.

Different nanostructuring techniques have been proposed to overcome such issues and enhance the efficiency of silicon-based anodes [10]. The nanoscale silicon can be in the form of nanoparticles, nanowires, or porous structures, and it has been proven that it can easily accommodate the volume changes that result from lithiation and delithiation processes, thus improving the mechanical stability of the anode. For instance, silicon nanowires have been reported to exhibit strength and electrical contact with the current collector through charge-discharge cycles with enhanced cycle life compared to bulk silicon.

Besides the nanostructuring, further approaches have been studied, such as applying Si–C composites that incorporate silicon with conductive carbon materials, including graphene, CNTs, or amorphous carbon [11]. It is possible to use these composites to improve the electrical conductivity of the silicon anode while serving as a buffer matrix that can accommodate changes in volume. For example, it was found that the cycling stability of the anode can be significantly enhanced using silicon nanoparticles encapsulated in a carbon shell or silicon nanoparticles embedded in a conductive carbon matrix.

Despite these developments achieved through nanotechnology in silicon-based LIBs, some challenges remain. The first issue is the challenge of creating large-scale synthesis of nanostructure silicon materials [12]. Most of the methods employed in research work, like CVD, laser ablation, etc., are unsuitable for large-scale production due to their high cost and technical difficulties. The other issue is the stability of the SEI layer, which is formed on the silicon anode during the first few cycles. The high Duch coefficient of silicate causes the se layer to continually rebuild and repair, which in turn causes the lithium ions to be constantly consumed. Hence, the total capacity of the battery is depleted. Scientists are now looking for electrolyte supplements and surface treatments that will help control the growth of the SEI layer.

5. Conclusion

Nanosilicon undergoes significant volume expansion and contraction during the embedding and disembedding of lithium ions, leading to structural damage of the electrode material and affecting the battery's cycling stability and capacity retention. This is one of the major bottlenecks in the application of nanosilicon in lithium-ion batteries. At the same time, nanosilicon has relatively poor conductivity, limiting the battery's performance under high-current charging and discharging conditions. Although its conductivity can be improved by compounding it with conductive materials, this also increases the complexity and preparation cost of the materials. In addition, the preparation of nanosilicon requires advanced nanotechnology and high-cost equipment, which leads to the relatively high cost of nanosilicon-based lithium-ion batteries.

Future research should form binary or ternary composites by compositing nanosilicon with carbon materials, metals, or other materials with good electrical conductivity, which can effectively improve the electrical conductivity and structural stability of nanosilicon, thus prolonging the cycle life of the battery and improving the capacity retention rate. One can also design reasonable nanosilicon structures, such as nanowires, nanotubes, and porous silicon, which can reduce the diffusion path of lithium ions, alleviate the volume expansion problem, and improve the multiplier performance of the battery. In addition, the preparation cost of nanosilicon is expected to decrease gradually with the continuous progress of preparation technology. Improving the yield and purity of nanosilicon by optimizing the preparation process will further promote its commercial application.

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