Progress of silicon and graphene composites in lithium-ion battery anodes

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Abstract. As society progresses, the need for high-power, long-life energy supply devices gradually increases. Lithium-ion batteries (LIBs) with large energy reserves and high power have recently become the preferred choice. The anode of LIBs plays a crucial role in battery performance, safety, and cycle life. Typically, graphite materials are used for LIBs anodes. Still, they have drawbacks such as low first-time Coulombic efficiency, capacity degradation, safety issues, short cycle life, insufficient gram capacity, and purity and side reactions, which limit the application of LIBs. Therefore, new harmful electrode materials are in demand. Graphene and silicon are both environmentally friendly and sustainable materials. They both have the advantages of high theoretical capacity and high energy density, which are critical materials for developing LIBs. Combining the two can exert a synergistic effect and jointly improve the cycle stability of the battery. In this paper, we review the preparation methods of graphene and silicon composites in recent years, including mechanical ball milling and hydrothermal and thermal reduction methods. In addition, graphene and silicon composites have been explored for LIBs applications.

Keywords: LIBs; anode; silicon; graphene; composite.

1. Introduction

Energy issues have always been the focus of people's concern as energy is the foundation of social development and human survival; when people demand a high quality of life increases, the energy required gradually rises. For example, aerospace, electric vehicles, etc., all have a high energy demand. However, people's overuse of non-renewable resources, such as natural gas and oil, not only causes energy shortages but also cause environmental problems. To solve this problem, people began to pay attention to sustainable, high-performance, clean energy and energy storage devices. LIBs are one of them, as they have a high cycle life and safety performance and can provide a high energy conversion efficiency.

In recent years, LIBs have emerged as the primary research object. Urban transit, gadgets like tablets and smartphones, and aerospace all have a crucial role. It still has certain shortcomings, though. The need for high-power, long-lasting energy supply devices is growing. Thus, it's essential to research how to make LIBs even more reliable and safe. The negative electrode of a lithium-ion battery is essential to its operation; it affects not only the longevity and performance of the battery but also its safety and sustainability. As a result, enhancing the negative electrode's performance has become essential to assessing LIB performance.

The anode of LIBs requires materials with good conductivity, such as metal materials (such as Si, Tn), carbon materials (such as graphite and graphene), silicon, and composite materials of the above materials. Graphene is the most widely used anode material at present; it shows good electric conductivity (about 5.7×10^6 S/m), high Young's modulus (1.0 TPa), and high thermal conductivity (about 5.0×10^3 W/mk) [1]. Also, silicon contains high theoretical capacity and low voltage profile, making it a popular choice in the battery's anode. However, single materials still have specific shortages, such as the electrical conductivity of graphene, which still has an upper limit and cannot meet people's needs. The volume change of silicon in lithium and dilithium is too significant, and the lack of intrinsic conductivity will lead to continuous loss of electrolytes. Therefore, the researchers changed the structure of the anode material (such as nanostructure, porous structure, and nanocomposite material) by combining silicon and graphene, which will increase the conductivity and service life of the battery [2, 3].

This paper will discuss the application of silicon/graphene composites in LIBs negative electrodes. It has a reference role for future research on lithium-ion batteries.

2. LIBs Anode Materials

Lithium ions will be transferred from the cathode to the anode during the charging process. Electrons will go in opposing directions at the exact moment. Lithium ions that reach the anode will become entrenched in the micropores because of the anode's massive micropores [3]. Batteries can thus hold more charges if they have more micropores. This suggests that batteries' anode is a critical factor in influencing the energy density of LIBs.

Graphite is currently the most commonly used anode material in commercial lithium-ion batteries and is popular due to its low cost, good electrical conductivity, and high chemical stability. As one of the critical materials used to increase the energy density of batteries, graphite has a relatively low theoretical capacity (372 mAh/g), which makes it challenging to meet the demand for high-energy-density batteries [2]. To overcome the limitations of graphite anode, researchers have developed a variety of new anode materials that typically have higher theoretical capacity, better multiplicative performance, and longer cycle life. Silicon, with a much higher theoretical capacity than graphite (~4200 mAh/g) and abundant resources at low cost, is currently used as one of the critical materials to increase the energy density of batteries [3]. However, silicon materials face several challenges in practical applications, mainly their massive volume expansion during lithiation (up to 300% or more) and the resulting problems of material pulverization, active material shedding, and poor cycling stability. In addition, carbon nanomaterials, including graphene, porous carbon, and graphene, with high specific surface area, excellent electrical conductivity and mechanical properties, and good lithium storage capacity, have promising applications in LIBs.

3. Preparation Method of Graphene/Si Composites

Combining graphene and silicon to make composite material, the advantages of the two materials are combined, while the disadvantages are eliminated. Thus, the energy density and the stability of the LIBs increase sufficiently. Here are some practical and feasible ways of combination.

3.1. High Energy Ball Milling Method

If the two substances are mechanically mixed directly, the stability of the composite material formed is low; at the same time, the degree of dispersion is also not satisfactory, so the material produced is not stable in the cycle process. For the energy ball milling method, using a high-efficiency ball mill, those materials added will be mechanically ground and mixed under the impact of high-energy balls. Particles will be deformed and fractured, leading them to achieve the purpose of high dispersion of the material and interface bonding strength. Also, due to the high energy produced by the ball mills, the temperature will increase, and the material added will be reacted chemically. As shown in Figure 1, milling bodies and powder particles were well mixed in the container and moved. The substances will be combined by the high energy produced by the balls [4].

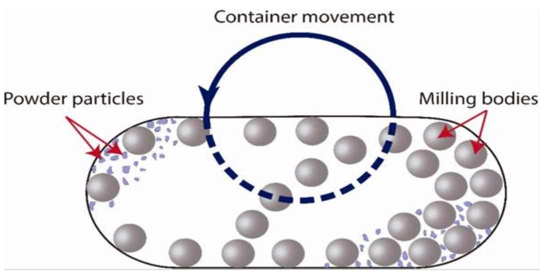

Fig 1. The high-energy ball milling method is used to fabricate composite materials [4].

Hang et al. [5] mentioned that when combining silicon nanoparticles and graphene sheets, amino and carboxyl groups can effectively cause the surface of the two materials to contain opposite charges, producing static electricity. Under the action of electrostatic force, the silicon nanoparticles will become more dispersed; at the same time, the attraction between graphene and silicon will increase so that the silicon particles will be anchored to the graphene surface or between different layers. The high-energy ball milling method provides considerable energy, enhancing the reaction rate and the attraction between the graphene sheet and the silicon nanoparticles. The data illustrate that the stability of this structure is high, and the circulation efficiency has also been improved (under the current density of 1000 mA/g, the data reaches 1516.23 mAh/g after 100 cycles and 1151.5 mAh/g under 1000 cycles).

3.2. Hydrothermal Method

Hydrothermal methods are usually used in the synthesizing of organic or inorganic compounds. It is generally carried out in a closed reaction vessel. With high temperatures and high pressure, when reactants are dissolved in the water, the surroundings will quickly accelerate the reaction rate and enhance the selectivity of products. Also, high-purity products can be synthesized using this method under mild conditions.

Luo et al. [6] point out that the hydrothermal method plays a vital role in synthesizing coaxial silicon-coated carbon nanotubes, which effectively solves the problem of the synthetic material not fully absorbing the volume stress in the process of fossilization/demolitization. Also, after 1000 cycles, the reversible discharge capacity remains very high (1508.5 mAh/g).

3.3. Thermal Method

Thermal reduction is a standard method used to synthesize graphene. This kind of reaction is mainly carried out in the pyrolysis furnace. At the same time, it is usually carried out with reducing agents like sulfate, hydrogen, etc. The primary purpose is to remove or reduce the functional group in graphene oxides with the surroundings of high temperature to produce reduced graphene. Then, further purification occurs to remove the impurities. The advantage of thermal reduction is that it could be more efficient and produce large amounts of graphene. Also, graphene can react with other materials to produce composite material.

By employing the MMR approach with Si_2O nanospheres as the reactant and Mg_2Si as a Mg source, Xiang et al. [7] create porous silicon nanospheres that resemble blackberries. Subsequently, it combines with rGO to create a Si and graphene composite. After 1000 cycles at 1.0 C, this material exhibits excellent cycle stability and rate, with 1034 mAh/g.

4. Application of Graphene and Si Composites in LIBs

The composite material of silicon and graphene prepared by the method above effectively solves the shortages of insufficient stability caused by the problem of large volume changing of single materials. Based on composite materials, the researchers optimized the number of graphene nanoparticles to maximize silicon protection from the structure's expansion, further achieving higher circularity and conductivity for LIBs. The next part of this passage will discuss the properties of composites formed by combining different silicon materials and graphene.

4.1. Graphene/Si

Graphene has excellent electrical conductivity and is one of the thinnest and best-conducting materials known. Compositing it with silicon can significantly improve the composite material's conductivity, reduce the battery's internal resistance, and improve its charging and discharging efficiency and multiplier performance. The addition of graphene can effectively mitigate the structural damage and capacity degradation caused by the volume change of silicon during the charging and discharging process (mainly when lithiation volume expansion can occur several times).

The flexibility and mechanical strength of graphene provide a buffer for the volume change of silicon and maintain the integrity of the electrode structure, thus extending the battery's cycle life.

Ababtain et al. [8] combined silicon with graphene to create a composite material with a three-dimensional porous structure. The strong adhesion between the electrode and the surface area of the electrochemically active material would be increased by the three-dimensional porous structure, potentially improving the performance of the current ratio and further enhancing the conductivity of lithium ions. Because of this, the silicon electrode made of this material shows reasonable current rates up to 5C and has a capacity of 0.37 mAh/cm^2 for a plane thickness of 500 nm. Sanad et al. [9] discuss the optimum proportion between silicon and graphene. They set the ratio of graphene to silicon: 10, 20, 30, and 40 wt%, respectively. Based on electrochemical impedance spectroscopy (EIS) findings, graphene decreases capacity fading during sequential galvanostatic cycling of G@Si composite anode materials vs Li/Li+ while inhibiting the volume change through conductive shielding. This indicates that during the first and hundredth cycles, the 30%G@Si battery's specific discharge capacity supplied around 1240 and 900 mAh/g, respectively. The characteristics of this type of material are shown in Figure 2. After 60 cycles at 500 mA/g, the anode in VC-modified electrolyte still has a capacity of more than 900 mAh/g, demonstrating an impressive cycle life.

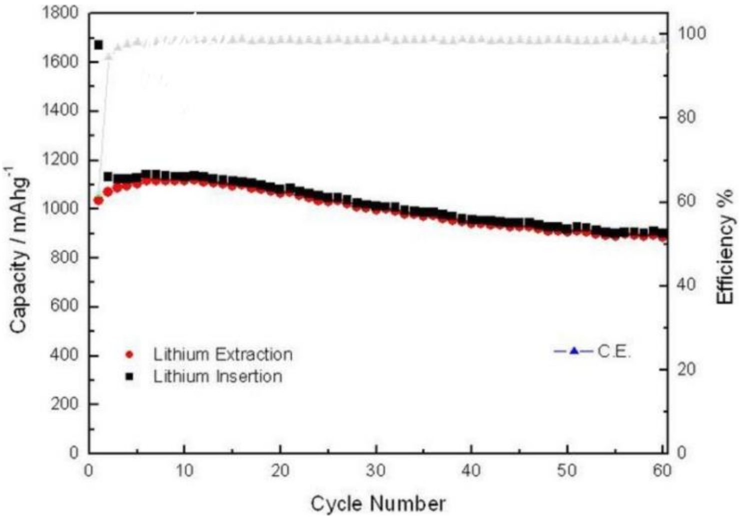

Fig 2. Properties of silicon/graphene composite anode [9].

4.2. Graphene/Silicon Oxide

Graphene and silicon oxide composites are relatively simple to prepare, have low cost, and have good electrochemical properties and cycle stability. Combining the two can exert a synergistic effect and jointly improve the cycling stability of the battery. Graphene acts as a conductive network to ensure rapid electron transfer. At the same time, silicon oxide prevents the destruction of the electrode structure and rapid capacity decay by promoting lithium ion conduction and forming a stable interfacial layer. Adding silicon oxide also promotes lithium ion conduction and the lithiation-delithiation process, improving the battery's charging and discharging efficiency and cycle stability. In addition, silicon oxide can provide the solid electrolyte interface (SEI) membrane with higher electrolyte affinity, chemical stability, and Young's modulus, further inhibiting the growth of lithium dendrites.

Lv et al. [10] researched GF@SiO_2. Figure 3 shows that they added SiO_2 into graphene sheets in a vacuum. Due to the strong interaction between the SiO_2 and graphene layers, the current density is reduced, and the nucleation of Li metals is easier. Furthermore, the volume expansion effects of this composite material during the lithium and dilithium processes are less pronounced than those of the two components introduced beforehand. Thus, the minor volume modification will enhance the LIBs' cycle life and electrochemical performance. After 500 cycles of steady cycling using this material and one mAh/cm^2 of metallic Li deposited at one mAh/cm^2 current density, the Li-GF@SiO_2 battery's coulombic efficiency remains as high as 97%. It is noteworthy that, following steady cycling for 234 cycles, the average coulombic efficiency of the Li-GF@SiO_2 battery is still very high (96%) even at three mA/cm^2 current density and three mAh/cm^2 deposition capacity. Bie et al. [11] investigated silicon oxide as well. Silicon polyester is made of ethylene glycol and phthalic anhydride (Si-PET). The resulting material will be hydrothermally coated with glucose and carbonized again to make SiO_x with layers of 3D network graphene. As a result, SiO_x was covered on the surface of this material by a flexible layer of amorphous carbon. Furthermore, forming a solid electrolyte interphase (SEI) layer will produce excellent cycle stability for the LIBs. The reversible capacity of the SiO_x/C-rGO material is 660 mAh/g for 100 cycles at a current density of 100 mA/g and 469.7 mAh/g for 300 cycles at a density of 200 mA/g. additionally, an average of 98% Coulomb efficiency was maintained.

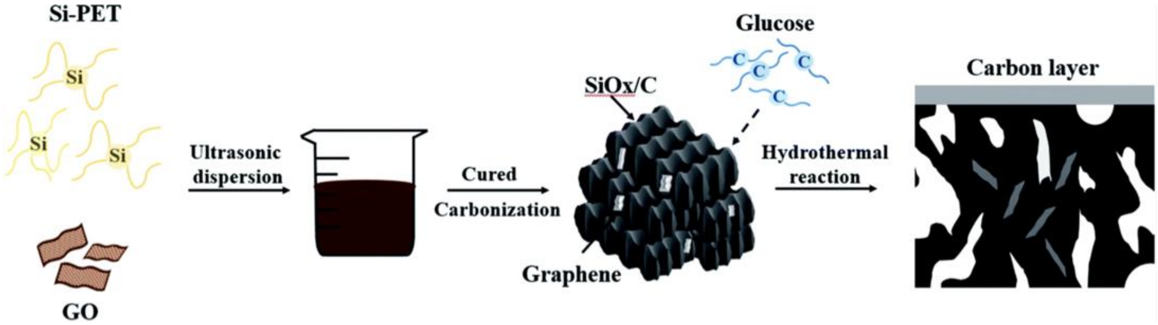

Fig 3. Preparation of the carbon layer by using Si-PET and GO [11].

4.3. S Graphene Oxide/Si

Applying silicon and graphene oxide composites in LIBs has significant advantages, mainly stemming from silicon's high theoretical capacity and the excellent electrical conductivity, thermal conductivity, and mechanical strength of graphene oxide. The addition of graphene oxide can effectively mitigate silicon's structural damage and capacity degradation due to volume changes (e.g., the volume expansion of silicon can reach up to 400% during the lithiation process) during the charging and discharging process. Graphene oxide's flexibility and mechanical strength can support silicon's volume change and maintain the electrode's structural integrity. Graphene oxide has excellent electrical conductivity, which helps to improve the overall electrical conductivity of the silicon-based anode material and reduces the internal resistance of the battery, thus improving the multiplication performance and charge/discharge efficiency. In addition, thermal conductivity helps lithium-ion batteries perform effective thermal management during operation, preventing battery failure or safety hazards due to overheating. The structural stability of the material can be further improved by designing the appropriate microstructure and silicon/graphene oxide size. This structure provides enough space for the volume expansion of silicon but also promotes the rapid diffusion and transport of lithium ions.

By employing microwave radiation, Pier et al. prepared a composite material (nSi/RGO) of silicon nanoparticles (nSi) and graphene oxide (RGO) and used it as an anode material for LIBs. It was found that the LIBs composed of nSi/RGO and lithium iron phosphate had excellent electrochemical properties. The prepared LIBs had a capacity of up to 230 mAh/g under a current cycle of 0.08 mA [12].

5. Conclusion

LIBs contain high energy density and long service life, which help them become the preferred choice in energy supply devices. By combining graphene and silicon, the volume expansion effect of silicon is effectively reduced, and an excellent conductive network is provided; thus, the silicon negative electrode's cyclic stability and magnification performance are further improved. This is also the primary means to enhance the performance of LIBs. This paper summarizes the standard methods of preparing composite materials: high-energy ball milling, hydrothermal, and thermal reduction.

These material preparation methods have low cost and high production efficiency and are suitable for multiple manufacturing environments.

However, LIBs still have a vast space for development—for example, the volume expansion problem. Although the addition of graphene can alleviate the volume expansion of silicon anode, this problem still exists, especially under high rate charge and discharge conditions, and may affect the cycle life and performance of the battery. At the same time, the preparation process of silicon and graphene composite materials is relatively complex, requiring a high level of technology and equipment investment, resulting in relatively high manufacturing costs. This may limit its use in some cost-sensitive areas. Finally, the stability in long-term cycle use still needs to be further studied and verified. In particular, it is necessary to evaluate its performance in different temperatures, humidity levels, and other environments.

Future research will focus on finding efficient ways to reduce silicon's volume growth to extend the battery's cycle life. These methods may include strengthening the composite structure, adding buffer layers, or employing cutting-edge binders. Second, considering the cost issue, straightforward and effective preparation techniques must be investigated to lower the cost of producing silicon and graphene composite materials. For instance, researchers are improving heat treatment procedures and employing inexpensive precursors. Fulfilling these developmental trajectories would facilitate the advancement of lithium-ion battery technology to accommodate diverse application situations.

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