Design of Silicon-Based Anode Materials for High Energy Density Li-Ion Batteries

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Abstract. Compared to other types of batteries, lithium batteries have an extremely high energy density, which means they can store more energy while maintaining a smaller size and weight. The ideal electrode material must have a high lithium ion capacity to store many lithium ions. In addition, the electrode material must have good electronic conductivity to promote lithium ions' rapid entry and exit. However, traditional carbon materials have limited theoretical specific capacity, and the transmission of lithium-ion batteries in traditional materials is limited, resulting in a significant decrease in capacity. Silicon has a theoretical capacity of up to 4200mAh/g, more than ten times the capacity of commercial graphite negative electrodes. In addition, silicon and lithium can undergo alloying reactions to form Li Si alloys, which helps improve the material's specific capacity. This article first summarizes the advantages of electric vehicles and lithium-ion batteries. Then, the benefits and challenges of using silicon-based materials as negative electrodes for lithium-ion batteries were elaborated in detail, and finally, the prospects of silicon-based materials in lithium-ion battery applications were summarized. This article has reference significance in improving the energy density of lithium-ion batteries.

Keywords: Li-ion batteries, silicon-based materials, anode.

1. Introduction

At present, using energy not only consumes reserves but also pollutes the environment, causing severe problems in the ecological environment. Electric vehicles are powered by electricity, which can reduce dependence on fossil fuels, improve energy security, and stabilize energy prices. Among them, batteries in electric vehicles (EVs) are crucial as they provide power to the car. They store electrical energy and then deliver it to the electric motor to drive the car. In addition, the battery's capacity determines the range of electric vehicles, that is, the distance they can travel after one charge. Lithium-ion batteries have the highest energy density under the same volume and weight as other types of batteries. This enables them to provide an excellent range of electric vehicles. Lithium-ion batteries comprise structures such as a positive electrode, a negative electrode, separators, electrolytes, and current collectors. The importance of the negative electrode in lithium-ion batteries is exceptionally high. The negative electrode material has a layered structure, which can provide space for lithium ion insertion and extraction [1]. Therefore, the storage capacity of the electrode material determines the energy density of the battery. The electrode material must have good electronic conductivity to ensure that the electrons generated after lithium-ion deintercalation can be efficiently transferred to the positive electrode material. Graphite is a commonly used electrode material for commercial lithium-ion batteries. However, graphite has low energy and power density, and its low lithium insertion potential is also prone to safety issues. Therefore, developing an electrode material with high energy density and lithium insertion potential is necessary [2]. The theoretical specific capacity of Si up to 4200mAh/g has attracted significant attention [3]. Using silicon-containing materials as the negative electrode of lithium-ion batteries can significantly improve the battery's energy density, which meets the current mainstream market demand. The article mainly explores the application of silicon-based materials in the negative electrode of lithium-ion batteries, which has a reference value for developing electrode materials for lithium-ion batteries.

2. Factors Affecting the Energy Density of LIBs

2.1. Battery Size

The size of the battery has a significant impact on the energy density of lithium-ion batteries. Generally, larger-sized lithium-ion batteries have higher energy density. This is because larger batteries have a larger volume that can accommodate more electrode materials, and large-sized batteries have higher energy density, thereby giving electric vehicles a more extended range. Lithium-ion power batteries for electric cars are divided into cylindrical, square, and soft-pack batteries according to appearance [1]. Specific shapes, such as cylindrical batteries, have higher volumetric energy density than other shapes, such as square batteries.

2.2. Electrode Materials

The theoretical specific capacity of different electrode materials varies; that is, the amount of lithium ions that can be stored per unit of electrode material is different. Materials with higher theoretical capacity can store more charge at the same mass, thereby increasing the energy density of batteries. The positive electrode material of lithium-ion batteries significantly impacts energy density. The commonly used positive electrode materials currently include lithium cobalt oxide (LCO), lithium manganese oxide (LMO), nickel cobalt manganese ternary materials (NCM/NCA), and lithium iron phosphate (LFP). Among them, ternary materials have attracted much attention due to their high energy density, especially those with high nickel content, such as NMC811, whose energy density is significantly higher than other materials. Graphite is a traditional electrode material for lithium-ion batteries, but its specific capacity is limited. Researchers are exploring new electrode materials, such as silicon-based and lithium titanate, to improve energy density.

2.3. Membrane

The thickness and porosity of the membrane have a particularly significant impact on its energy density. Thin and high porosity membranes allow more lithium ions to pass through, increasing energy density. However, for power batteries, ensuring that the positive and negative electrodes are not short-circuited under any circumstances is the essential function of the separator, and battery optimization can only be carried out on this basis; thinner membranes may also cause internal short circuits, so careful optimization of thickness and porosity is necessary. Polyethylene (PE) and polypropylene (PP) are low-cost and easy-to-manufacture membrane materials but have lower porosity and thermal stability. [1] Polyimide (PI) membranes have higher porosity, thermal stability, and chemical stability but are more expensive. To ensure high porosity, thermal stability, and chemical stability at a suitable cost, researchers are exploring new ternary copolymer membranes made of a combination of PE, PP, and PI, which provide a good balance of performance.

2.4. Electrolyte

Electrolytes mainly play a role in transporting lithium ions in lithium-ion batteries, serving as a medium for ion exchange between the positive and negative electrodes inside the battery. Its performance directly affects the migration rate of lithium ions and the battery's internal resistance, affecting the battery's energy density and cycling performance. The electrochemical stability of the electrolyte determines its stability during battery charging and discharging processes. A stable electrolyte can reduce the occurrence of side reactions, lower the battery's internal resistance, increase the migration rate of lithium ions, and thus increase the battery's energy density.

The conductivity of the electrolyte also directly affects the battery's output power and energy density. A high conductivity electrolyte can increase the migration rate of lithium ions, reduce the battery's internal resistance, and enable the battery to respond faster during charging and discharging, thereby improving the battery's energy density.

In addition, electrolytes with good wettability can ensure that the electrolyte thoroughly penetrates the electrode material's pores, improves the electrode material's utilization rate, and increases the battery's energy density.

3. Problems with Silicon

The volume effect of silicon-based electrode materials leads to phenomena such as powdering, crushing, and even detachment from the current collector during lithium insertion and extraction, limiting silicon-based negative electrodes' cycling performance. The key to developing silicon-based negative electrode systems is to alleviate or suppress the volume expansion of silicon-based materials and improve cycling stability.

In addition, transition metal compounds MX (M=Fe, Co, Ni, Cr, Mn, Cu, etc.; X=O, S, F, N, P, etc.) also belong to high-capacity electrode materials. [2] This type of negative electrode material generally suffers from problems such as significant volume changes, intense polarization, and unstable structure during the electrode reaction process, resulting in poor cycling stability of the battery during charging and discharging.

During the electrochemical process, silicon nanostructures in Si-containing negative electrodes undergo excessive volume expansion and collapse. Secondly, the overload change in volume will also cause the SEI film on the Si-negative electrode and electrolyte side to continue to break and recombine, resulting in abnormally unstable properties. Over time, this will consume the electrolyte and significantly affect the transmission channel of lithium ions in the negative electrode, thereby reducing the conductivity of lithium-ion batteries. The interest points of universities and research institutes in improving energy density mainly focus on constructing high theoretical specific capacity silicon micropores and silicon composite negative electrodes.

4. Design of silicon anode electrode

4.1. Nanostructure

Nanosizing is currently the most effective method to improve the anode materials for Si-based lithium-ion batteries. Using different preparation methods, nano-Si materials with various dimensions and morphologies can be obtained, and their unique nanostructures and morphologies can be used to reduce the volume expansion of the embedded lithium delithiation process and buffer the internal stress, thus improving the electrochemical cycling stability performance of the anode materials. Meanwhile, the pores inside the nanostructures can promote the penetration of the electrolyte and shorten the diffusion distance of lithium ions, which is also conducive to improving the embedded and delighted lithium kinetic performance of Si-based anode materials [1].

The widely studied nano-Si-based anode materials for lithium-ion batteries mainly include zero-dimensional Si nanoparticles, one-dimensional Si nanowires and nanotubes, two-dimensional Si nanofilms, three-dimensional porous nanosi, etc.

The Si nanoparticles, which have a low self-stress and a high mechanical strength, are further composited with matrices capable of acting as buffers, and they can sufficiently alleviate the volume expansion and release the internal stresses, which can substantially improve the electrochemical performance. One-dimensional Si-based nanowire anode materials can relieve the tension generated by the anisotropic volume expansion and realize the electron transport in the one-dimensional direction without adding additional conductive agents.

The electrochemical properties of 2D Si nanofilms mainly depend on the thickness of the film. The thinner the film thickness, the more favourable to the release of volume expansion stress, but at the same time will cause the specific capacity of the electrode material to decrease. Combining high capacity and long cycling performance is difficult when researching 2D materials.

Porous nano-Si and its complexes can effectively inhibit the volume expansion and irreversible side reactions, while the cladding layer is conducive to stabilizing the formation of SEI. The pore size, porosity, pore depth, and additives of porous Si have an impact on its electrochemical performance: graded three-dimensional structures such as polysilicon wires and porous membranes have the advantages of both three-dimensional and other dimensional materials, and they are expected to be a key direction for the future development of Si anode materials.

To improve the electrochemical performance of the hollow core-shell structure, Liu et al. synthesised a nanoparticle Si/C composite electrode material with an egg yolk-eggshell type structure. This structure has a fragile, stable, and self-supporting carbon shell protecting inner Si particles. The hollow structure can buffer the volume expansion effect well and shows good cycling stability (first capacity of 2833mAh/g at 400mA/g, capacity retention of 74% after 1000 cycles) and high Coulombic efficiency (99.84%) [2].

Zhang [3] et al. prepared Si/graphene sheet composite films by combining electrophoretic deposition and RF magnetron sputtering. As an anode material for Li-ion batteries, the Si/graphene sheet composite film has enhanced electrochemical properties with weaker polarisation, higher capacity, better assortment, and cycling performance than the simple Si film.

Liu et al. constructed a 'sandwich' structure of c@Si@C nanotubes, a fragile, stable, and self-supporting carbon shell. The first charge/discharge capacities of 2545mAh/g and 4130mAh/g were achieved at a current density of 0.07 C. The discharge capacity of c@Si@C nanotubes reached 2246mAh/g after 15 cycles [4].

4.2. Alloying

Si can form metal silicides with many metal elements. These compounds generally have a lower lithium storage capacity when used as anode materials for lithium-ion batteries than monolithic Si. Still, the volume change is minor, which is conducive to the material maintaining structural stability during de-embedded lithium to obtain cycling stability performance superior to that of monolithic Si. In addition, Si alloys tend to have higher electrical conductivity, which is conducive to improving the electrochemical performance of si-based anode materials.

There are two main types of metal parts in Si-based metal composites (SiaMb, M is metal and a, b is the ratio of elements): the first type of metal element, M, can not provide additional capacity, which is mainly to alleviate the volumetric effect of de-embedded lithium and to improve the electrical conductivity of the anode material, and it primarily includes metal elements such as Fe, Ni, Cu, Ti, and so on; the other type of metal element M is the metal element that can provide additional capacity and is compatible with the first type of metal element M, which is also compatible with the first type of metal element M. Another type of metal element, M, provides additional capacity and is compatible with the functions of the first type of metal element, M, such as Ge, Sn, and Pb [5, 6].

Although Fe, Co, Ni, etc. cannot perform electrochemical lithium embedding reactions at low potential, Fe-Si, Co-Si, and Ni-Si alloys can perform lithium substitution reactions under an electrochemical environment to precipitate the inert metal and form Li-Si alloys [7].

Liu et al. [8] deposited silicon on CuO by chemical vapour deposition, and finally reduced CuO at 450°C to form Cu/Si alloy. The Cu/Si alloy has a specific capacity of 1869mAh/g at 1.6A/g, and the capacity retention rate reaches 66.6% after 500 cycles.

Hyun et al. [9] based on Al-Si-Ni alloy, during the selective etching process, silicon forms a porous structure, and a thin nickel layer spontaneously forms on the silicon surface, with a high initial discharge capacity of 3225mAh/g and a reversible capacity of 806mAh/g after 500 cycles.

The presence of Si inert metal alloy can buffer the volume expansion of the Si-based anode material, improve mechanical stability, and help release the mechanical stress of Si during the charging and discharging process. The carbon coating can further enhance the electrical conductivity and is conducive to forming a stable SEI film. However, the addition of inert metal will cause the loss of active Si, coupled with the alloy's low embedded lithium activity and relatively heavy mass, inevitably leading to a decline in the mass-specific capacity of the material itself [10].

In recent years, high-capacity anode materials without lithium (e.g., s, etc.) have received extensive attention, which urgently requires the development of lithium-containing anode materials, especially

Li-Si alloys. The initial volume of Li-Si alloys is large, which can reduce the volume rate of change of the process of de-embedded lithium in Si anode materials, thus improving their cycling stability. Although Ca, Mg, Al, Zn, Ag, and other metal monomers can embed lithium to form the corresponding lithium alloy, the activity of these metal monomers embedded lithium is low and unsuitable as separate electrode materials. On the contrary, these metals and Si form a metal Si alloy, showing better-embedded lithium activity.

Si-based active metal alloys are chemically active and more easily oxidise in air. They will be deactivated by violent chemical reactions with water, which is the main reason for limiting the research and application of si-based active metal alloys [11]. In addition, many Si-based active metal alloys also have volume expansion effects, causing capacity decay during cycling. Surface cladding (e.g., carbon cladding) and preparation of nanomorphology should be the main ways to improve their electrochemical properties [12].

In addition, poly-Si-based alloys can combine the advantages of both inert and active metal alloys, providing a buffer layer for the volume expansion of si and reducing the relative content of the non-lithium embedded active phase. However, such materials have disadvantages: the inert phase cannot embed lithium, some alloys are active, the preparation process is relatively complicated, the multiple phases are difficult to control, etc [13].

Jung et al. prepared Si-Ti-Ni nanomaterials in which the Ti-Ni alloy is an elastic buffer for the non-embedded lithium activity. As a non-lithium-embedded active elastic buffer, the Ti-Ni alloy could significantly alleviate the volume change caused by the lithium-embedded Si charging process and improve the cycling stability of Si anode materials [14].

5. Conclusion

Against the background of the energy crisis and the rapid development of electric vehicles, this paper explores the effects of cell size, electrode material, diaphragm, and electrolyte on the energy density of LIBs. Silicon is effective in increasing the energy density of LIBs due to its high theoretical capacity. However, it faces challenges such as volume expansion, low initial charging efficiency, and poor conductivity. Based on these challenges, this paper explores the design methods of silicon anode from three aspects, namely, nanostructure design, silicon/metal oxide composites, and silicon/carbon composites, to improve the energy density of LIBs.

However, the significant increase in the specific surface area of the silicon material after nanosizing leads to the formation of more SEIs during the first charge/discharge process, which consumes more lithium ions and reduces the first-time coulombic efficiency. The high specific surface area of the silicon nanomaterials may increase the contact area with the electrolyte, leading to more side reactions occurring, which may affect the safety performance of the battery. Although metal oxides can somewhat buffer silicon's volume expansion, the significant volume change of silicon during charging and discharging remains a challenge. This volume change may lead to stresses within the composite material or even cause material pulverization or structural damage, thus affecting the cycling stability and lifetime of the battery. Although metal oxides have some electrical conductivity, they are still low compared to silicon. This may result in the composites exhibiting poor capacity release during high-rate charging and discharging, limiting their performance in high-power applications. In addition, although silicon-carbon composites have relatively high electrical conductivity, they are still low compared to conventional conductive materials. This may increase the battery's internal resistance, affecting the charge and discharge rate and performance.

Future research should be conducted by designing rational composite structures, such as core-shell structures and porous structures, to better buffer silicon's volume expansion and improve the composites' conductivity. For example, silicon nanoparticles can be encapsulated in a metal oxide shell layer, or metal oxides can be dispersed in nano form in the silicon matrix. Other elements (e.g., lithium, boron, etc.) or materials (e.g., carbon nanotubes, graphene, etc.) are introduced into the composite material to improve further the electrical conductivity, cycling stability, and safety. For example, carbon nanotubes can be embedded in composites as conductive networks to enhance electron transfer efficiency. More importantly, it is also necessary to strengthen the research on the failure mechanism of silicon-based composites during charging and discharging to reveal the root cause of their performance degradation and propose effective improvement measures accordingly. This helps guide the development of new materials and the optimization of the preparation process.

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