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Application of carbon and silicon nanomaterials in lithium ion battery anode

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Abstract. The world is in an era of increasing energy demand to meet the development needs of modern society. Both nanotechnology and lithium-ion battery technology play an important role in helping the world meet the growing challenges of energy and environmental problems. In this paper, through consulting relevant materials and referring to relevant papers, the influence and progress of nanostructured electrode materials on the design, synthesis and electrochemical performance of Li-ion battery anode materials are comprehensively introduced. Nanomaterials exhibit unique properties that present intriguing prospects for their use in various sectors. Traditional anodes in LIBs suffer from limited charge capacity, poor cycle life. By reducing the size to nanoscale, these structures can better accommodate the volume changes, hence improving durability and charge capacity. Despite current challenges in terms of cost and scalability, the progress in this field suggests the potential for future advancements in high-performance LIBs with the integration of nanostructured anodes.

Keywords: nanomaterials, lithium ion battery, energy demand, application.

1. Introduction

The booming industry of portable electronics and electric vehicles necessitates the quest for more efficient and sustainable power sources. One of the leading technologies in this field is the lithium-ion battery (LIB), which offers a high energy density and longevity. However, the current industry-standard graphite anodes, despite their reliability and good cyclability, are approaching their theoretical capacity limits and struggle to meet increasing energy and power demands. This scenario has catalyzed intensive research in finding alternative anode materials with higher energy storage capacities, such as silicon (Si) and carbon-based nanomaterials.

The significance of research stems from the exceptional potential of these nanostructured materials to enhance the performance of LIBs. Silicon, with a theoretical lithium storage capacity ten times that of graphite, is a promising candidate. Unfortunately, it suffers from a dramatic volume expansion during lithiation and delithiation cycles, leading to pulverization, loss of electrical contact, and consequent rapid capacity fade, issues that must be tackled to achieve commercial viability [1].

Similarly, carbon nanomaterials, such as graphene, carbon nanotubes, and carbon nanowires, possess exceptional electrical conductivity and mechanical properties, making them promising

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candidates for anodes. Nevertheless, challenges concerning their lithiation capacity, rate performance, and stability during cycling, warrant further research and optimization.

This research is focused on a set of research questions: Can the issues linked to nanostructured silicon and carbon anodes be mitigated? What are the viable strategies to augment the capacity, stability, and cyclability of these anodes in LIBs? Could these materials be feasibly scaled for commercial production? This research will extensively discuss the current state of research and development, unresolved challenges, and future perspectives in the application of these nanomaterials in LIB anodes. In particular, this research will detail the synthesis, material properties, electrochemical behavior, and the strategies employed to address the specific problems of each material. This research will also cover how nano-engineering these materials can overcome their individual limitations, and improve the performance of LIBs. Lastly, this research will examine the challenges and perspectives for scaling up the production of these anode materials and their integration into commercial LIBs. This objective is to delve into the nanoscale structuring of silicon and carbon elements. This includes graphene, carbon nanotubes, carbon nanowires, silicon nanowires, silicon nanotubes, and silicon nanofilms. The nanoscale offers the potential to alleviate the volume expansion of silicon, enhance the conductivity of carbon, and overall, to improve the electrochemical performance of the anode materials. This research believe that this comprehensive exploration and discussion of these nanostructured silicon and carbon materials will contribute to the ongoing efforts to enhance the energy storage capabilities of LIBs and their commercial viability [2]. This research is sorted out related applications of nanotechnology, and the specific analysis is carried out from multiple angles, so that readers can quickly establish a general understanding of related technologies.

2. Application of nanostructured carbon

2.1. Graphene

Nano graphene refers to smaller graphene sheets fabricated using nanotechnology techniques. Through precise control offered by nanotechnology, the structure, morphology, and properties of graphene can be tailored, further expanding its application potential. Its high electrical conductivity and wide bandgap make it an ideal material for high-speed electronic transport and efficient energy storage. Furthermore, nano graphene holds great promise in the energy sector. Its high specific surface area and excellent conductivity make it an ideal carrier for efficient catalysts and electrocatalysts, applicable in catalyst preparation, hydrogen energy generation, and storage.

Graphene is predominantly utilized in the development of graphene-based ion batteries, with graphene lithium-ion batteries being the most prevalent. These batteries employ graphene as a negative electrode material to leverage its unique properties and enhance overall battery performance. Theoretically, graphene batteries offer numerous advantages. (1) Enhanced capacity: The inclusion of graphene materials significantly expands the battery's capacity per unit volume. (2) Rapid conductivity: Graphene facilitates improved charging efficiency of the ion battery, without compromising its structural integrity. (3) Reduced volume and weight: Graphene-based batteries achieve smaller dimensions and reduced weight, while substantially increasing energy storage density. (4) Extended lifespan: The incorporation of graphene theoretically minimizes resistance, thereby enhancing battery stability, safety, and lifespan.

There are many advances in graphene research, here is a list of some content. Graphene-based quasi-solid-state Li-oxygen battery: This battery theoretically exhibits ultrahigh energy density. It consists of a 3D porous graphene cathode and a Li anode, achieving high capacity, high charging efficiency, and stable cycling performance. In integrated circuits, it can effectively address issues related to unstable electrolytes and dendritic growth of the anode. Graphene-based three-dimensional conductive network for energy storage electrode materials: Graphene possesses a unique 2D structure, which grants it exceptional charge conductivity. However, there have also been reports on various three-dimensional network structures of graphene composite electrode materials. The principle involves assembling different structured materials through integration, resulting in a more advanced

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three-dimensional composite structure that enhances ion and electron transport. (3) Graphene applied in quasi-solid-state rechargeable Na-CO_2 batteries: The incorporation of graphene in this battery improves its ionic conductivity and other capabilities, making it safer and more suitable for efficient charging and cycling. (4) Graphene-based composite electrodes in asymmetric supercapacitors: Graphene can be combined with various materials to achieve different performance characteristics. For instance, combining it with metal oxides such as RuO_2, MnO_2, CuO yields high energy density, while combining it with conductive polymers like polyaniline enhances electrical conductivity. Graphene can also be combined with metal hydroxides like $Co(OH)_2$ for high specific capacitance or with metal sulfides to achieve outstanding pseudocapacitive properties [3].

Graphene batteries are currently in the experimental stage and have not yet achieved widespread adoption. However, their successful development holds promising prospects for delivering significant advantages to society. Standardization initiatives for graphene are being actively pursued at both international and domestic levels, leading to the emergence of various standardized production techniques and testing methodologies.

2.2. Carbon nanotubes (CNTs)

CNTs are cylindrical structures composed of carbon atoms arranged in a hexagonal lattice. They possess extraordinary mechanical, electrical, and thermal properties, making them a subject of intense research and interest. CNTs can be categorized into two main types: single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs). SWCNTs consist of a single layer of carbon atoms rolled into a seamless tube, while MWCNTs consist of multiple concentric layers. The unique structure of CNTs grants them exceptional strength, high electrical conductivity, and efficient heat transfer capabilities. Moreover, their large surface area and nanoscale dimensions make them suitable for various applications, including electronics, energy storage, sensors, and composites.

The capacity of CNTs as negative electrode materials in lithium-ion batteries generally depends on their structural characteristics, including chirality, diameter, length, and defects, which can result in varying capacities ranging from 300 to 1,500 mA·h/g [4]. Here is an example of the properties of carbon nanotubes as thin films in batteries. Place the purified CNTs in deionized water and add them dropwise alcohol, spread into a uniform film. Transfer CNTs film to processing.

Dry the back of a good c-Si battery with nitrogen gas. Under surface tension, it adheres to the back of the c-Si battery, forming a back electrode. It uses silver glue and silver wire to lead out the two electrodes and create a C-Si/CNTs solar cells. As shown in Figure 1, CNTs were characterized by scanning electron microscope (SEM), transmission electron microscopy, Raman spectroscopy, and transmittance spectroscopy membrane. The surface roughness of polished c-Si batteries was characterized by using a white light interferometer roughness [5].

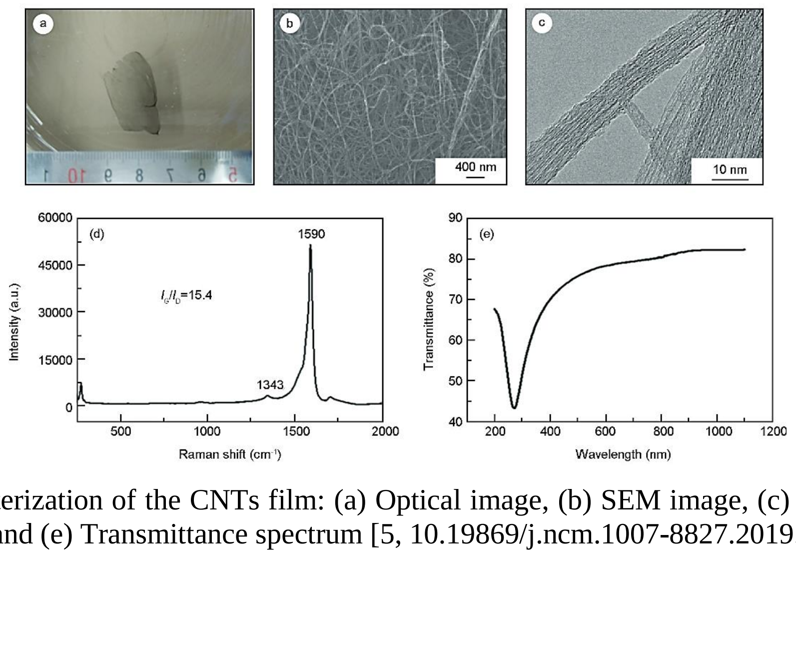

Figure 1. Characterization of the CNTs film: (a) Optical image, (b) SEM image, (c) TEM image, (d) Raman spectrum and (e) Transmittance spectrum [5, 10.19869/j.ncm.1007-8827.2019.03.006].

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The incorporation of CNTs with other active nanomaterials to form composite materials as negative electrode materials in lithium-ion batteries has gained attention. This is due to the high mechanical stability, large surface area, and high conductivity of CNTs, which enhance the electrochemical performance of such negative electrode materials. In composite materials, CNTs act as a supportive framework for active nanomaterials, buffering the structural changes and improving their conductivity and cycling stability, thus enhancing the rate performance of lithium-ion batteries. Among them, CNT/silicon-based composites have attracted considerable interest due to their high specific capacity. Further reduction of their irreversible capacity during initial cycles, along with improved cycling stability and rate performance, would make them a promising negative electrode material for lithium-ion batteries.

2.3. Carbon nanofiber

Nanofibers have shown significant potential in enhancing the performance of batteries due to their unique properties and versatile applications. Nanofibers, typically with diameters in the nanometer range, possess a high aspect ratio and a large surface area, offering enhanced electrochemical reactivity and efficient charge transfer kinetics. In the context of batteries, nanofibers can be employed in various roles. Firstly, as electrode materials, nanofibers can serve as a three-dimensional (3D) conductive scaffold, providing a conductive network for electron transport and facilitating ion diffusion. The 3D interconnected structure of nanofibers enhances the active material utilization, increases the electrode-electrolyte contact area, and reduces the diffusion path length for ions.

Furthermore, nanofibers can be utilized as a support or carrier for active materials. By incorporating active materials onto nanofiber surfaces or within their porous structure, the overall electrochemical performance can be enhanced. Nanofibers provide a stable and uniform platform for anchoring active materials, preventing their aggregation and ensuring efficient utilization. In addition to their roles in electrode materials, nanofibers can be used as separators or membranes in batteries. Their high porosity and tunable pore size enable efficient electrolyte transport, while effectively blocking the migration of active material particles, thus enhancing battery safety and stability.

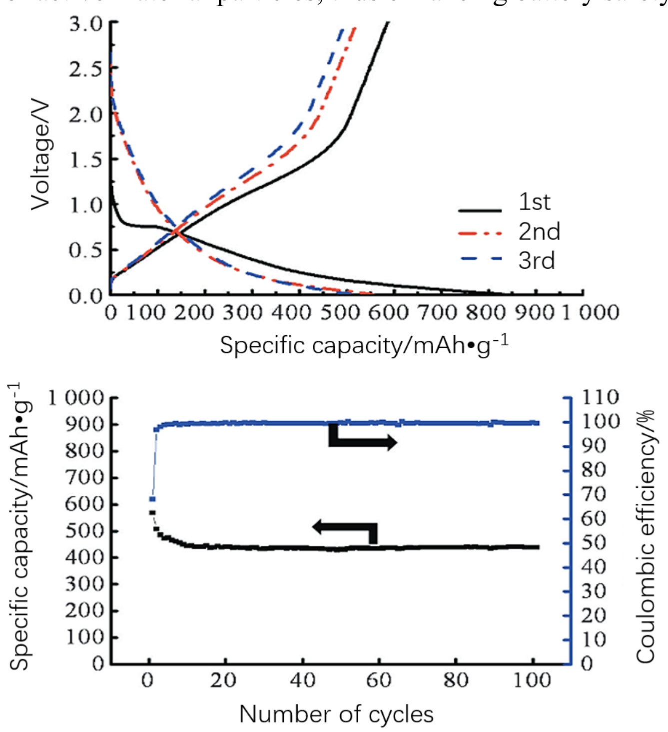

Figure 2. First three charge-discharge curves and cycling performance of carbon nanofibers [6, http://journal.zjtextile.com.cn/EN/10.19398/j.att.202011004].

Carbon nanofibers were synthesized through the utilization of electrospinning and carbonization techniques to investigate the impact of preparation parameters on their morphology and properties. The obtained results are as follows. (1) Pre-oxidation treatment resulted in fiber contraction and bending, accompanied by a reduction in fiber diameter with increasing pre-oxidation temperature and duration. After parameter optimization, fibers prepared under pre-oxidation conditions of 250°C for 120 minutes and subsequent carbonization at 800°C for 120 minutes exhibited desirable morphology. (2) Elevating the carbonization temperature led to an increase in the carbon content proportion within the fiber membrane. Specifically, fibers carbonized at 800°C for 120 minutes displayed a carbon content proportion of 73.7%. (3) The degree of cyclization in pre-oxidized fibers exhibited continuous enhancement with elevated temperatures and prolonged holding times, subsequently resulting in increased ordering within the carbonized fibers. (4) Lithium-ion batteries employing carbon nanofiber-based negative electrode materials demonstrated favorable electrochemical performance, with an initial reversible capacity of 568.4 mAh/g and a capacity retention rate of 77.3%, indicating superior charge-discharge characteristics and cycling stability [6], as shown in Figure 2.

Overall, the integration of nanofibers in batteries offers improved electrochemical performance, including enhanced capacity, higher rate capability, and prolonged cycle life. The unique properties of nanofibers make them a promising component for the development of advanced batteries with enhanced energy storage and conversion capabilities.

3. Application of nanostructured silicon

3.1. Silicon nanowires (SiNWs)

SiNWs have emerged as a promising technology for enhancing the performance of lithium-ion batteries. SiNWs possess unique structural and electrochemical properties that make them highly suitable for energy storage applications. The high surface-to-volume ratio of SiNWs facilitates efficient lithium-ion diffusion and provides ample active sites for electrochemical reactions. Additionally, SiNWs offer superior mechanical stability, enabling them to withstand the volume changes that occur during lithiation and delithiation processes. By incorporating SiNWs into the electrode architecture, lithium-ion batteries can achieve enhanced capacity, improved rate capability, and prolonged cycle life. Various synthesis methods, such as vapor-liquid-solid (VLS) growth and metal-assisted chemical etching (MACE), allow precise control over the diameter, length, crystal structure, and doping of SiNWs, enabling tailored optimization for specific battery applications.

One key advantage of SiNWs is their high surface-to-volume ratio, which allows for efficient lithium-ion diffusion and provides a large number of active sites for electrochemical reactions. This property significantly enhances the electrode-electrolyte interface, leading to improved charge and discharge rates. Additionally, the nanoscale dimensions of SiNWs reduce the diffusion length for lithium ions, enabling faster charge transfer kinetics and enhancing the overall battery performance [7].

Moreover, SiNWs possess excellent mechanical flexibility, which enables them to accommodate the volume changes that occur during the lithiation and delithiation processes. This flexibility mitigates the detrimental effects of volume expansion and contraction, reducing the risk of electrode degradation and enhancing the cycling stability of the battery. The robust mechanical properties of SiNWs make them well-suited for long-term battery cycling applications.

Furthermore, SiNWs can be tailored and optimized through precise control over their dimensions, crystal structure, and doping. Various synthesis methods, such as VLS growth and MACE, allow for the production of SiNWs with desired characteristics. By optimizing these parameters, researchers can enhance the performance of SiNW-based electrodes, achieving higher energy storage capacity and improved cycling performance [8]. SiNWs exhibit immense potential in advancing lithium-ion battery technology. Their unique properties, including high surface-to-volume ratio, mechanical flexibility, and tunability, make them excellent candidates for improving battery performance. Through further research and development, SiNWs can contribute to the realization of high-energy-density, longlasting, and efficient lithium-ion batteries, driving the progression of portable electronics, electric vehicles, and renewable energy storage systems.

3.2. Silicon nanotubes (SiNTs)

SiNTs have garnered considerable attention as a viable technology for advancing lithium-ion batteries. The tubular structure of SiNTs offers several advantages for energy storage applications. Their large inner surface area facilitates faster lithium-ion diffusion and enhances the electrode-electrolyte interface, resulting in improved electrochemical performance. SiNTs also exhibit excellent mechanical flexibility, which mitigates the strain caused by volume changes during cycling, thus enhancing the cycling stability of the battery. Furthermore, SiNTs can be engineered with tailored properties by incorporating additional materials, such as metal oxides or carbon-based materials, to further enhance their electrochemical properties. By integrating SiNTs into the electrode design, lithium-ion batteries can achieve enhanced energy storage capacity, prolonged cycle life, and improved rate capability.

One primary advantage of SiNTs lies in their tubular structure, which provides a large inner surface area. This characteristic enables faster lithium-ion diffusion and offers numerous active sites for electrochemical reactions, resulting in enhanced charge and discharge rates. Additionally, the tubular structure allows for effective accommodation of volume changes during lithiation and delithiation processes, mitigating detrimental effects such as electrode degradation and improving cycling stability.

Moreover, SiNTs can be tailored and modified by incorporating additional materials, such as metal oxides or carbon-based substances. This synergistic combination enhances the electrochemical performance of SiNTs by promoting charge transfer kinetics and overall energy storage capacity. The integration of these complementary materials enhances structural stability, alleviates volume expansion concerns, and facilitates prolonged cycling with minimal capacity degradation. SiNTs can be synthesized using various techniques, including chemical vapor deposition and template-assisted methods, allowing precise control over their dimensions, length, and surface properties. By fine-tuning the synthesis parameters, researchers can optimize SiNTs for specific battery applications, resulting in improved energy storage performance and electrochemical stability [9].

SiNTs offer distinct advantages for advancing lithium-ion batteries. Their tubular structure, characterized by a large surface area and volume change accommodation, combined with the ability to be engineered with complementary materials, leads to enhanced energy storage capacity, improved cycling stability, and expedited charge and discharge rates. Continued research and optimization of SiNT-based electrode designs hold the potential to drive the development of high-performance batteries with extended lifespans, increased energy densities, and enhanced safety features.

3.3. Silicon nanofilms (SiNFs)

SiNFs have emerged as a promising technology for enhancing the performance of lithium-ion batteries. SiNFs, with their tunable thicknesses and high surface area-to-volume ratios, offer unique advantages in energy storage applications. The incorporation of SiNFs into the electrode structure enhances lithium-ion diffusion kinetics and provides a larger interface for electrochemical reactions, leading to improved battery performance. SiNFs can be fabricated using various techniques, such as chemical vapor deposition and sputtering, allowing precise control over film thickness and morphology. Additionally, the integration of SiNFs with other nanomaterials, such as carbon nanotubes or metal nanoparticles, can further enhance their electrochemical properties and stability. The exceptional electrical and optical properties of SiNFs make them promising candidates for developing advanced lithium-ion batteries with higher energy density, prolonged cycle life, and improved safety.

One key advantage of SiNFs is their high surface area-to-volume ratio. This characteristic allows for efficient lithium-ion diffusion and provides a larger interface for electrochemical reactions. The increased surface area enhances the electrode-electrolyte interface, leading to improved charge transfer kinetics and enhanced overall battery performance. Additionally, the tunable morphology of SiNFs enables optimization of the surface properties, further enhancing the electrochemical activity and stability of the battery. Moreover, SiNFs can be fabricated with precise control over their thickness and morphology using techniques such as chemical vapor deposition, sputtering, and thermal evaporation. This precise control allows tailoring of the SiNF properties to optimize their performance for specific battery applications. By adjusting the film thickness and surface modifications, researchers can enhance the electrode-electrolyte interactions, minimize the diffusion path for lithium ions, and improve the overall energy storage capacity of the battery. Furthermore, SiNFs can be integrated with other nanomaterials, such as carbon nanotubes or metal nanoparticles, to form hybrid structures. This integration creates synergistic effects, combining the unique properties of different materials to further enhance the electrochemical performance of the battery. The combination of SiNFs with other nanomaterials can enhance the stability of the electrode and improve the charge/discharge efficiency, resulting in higher energy density and longer cycle life [10].

In summary, SiNFs offer significant potential for enhancing lithium-ion battery performance. Their high surface area-to-volume ratio, tunable morphology, and compatibility with other nanomaterials make them promising candidates for advanced battery applications. Continued research and optimization of SiNFs-based electrode designs hold the promise of developing high-performance batteries with improved energy storage capacity, longer cycle life, and enhanced stability.

4. Conclusions

The application of nanotechnology in lithium-ion battery electrodes, specifically focusing on carbon and silicon-based materials, has shown great promise for enhancing battery performance. The utilization of carbon nanotubes, carbon nanowires, and carbon nanofibers provides unique advantages such as high surface area-to-volume ratio, mechanical flexibility, and improved charge transfer kinetics. These carbon-based materials exhibit excellent electrochemical properties, including enhanced energy storage capacity, rate capability, and cycling stability. Similarly, silicon nanowires, silicon nanotubes, and silicon nanofilms have emerged as key players in advancing lithium-ion battery technology. These silicon-based nanostructures offer advantages such as efficient lithium-ion diffusion, accommodation of volume changes, and compatibility with other nanomaterials for enhanced electrochemical performance. Silicon nanowires and nanotubes, with their tubular structure, provide large surface areas and fast charge transfer, leading to improved energy storage capacity and cycling stability. Silicon nanofilms, on the other hand, with their thin and tunable morphology, offer high surface area-to-volume ratio and optimized electrode-electrolyte interfaces, resulting in improved charge and discharge rates.

Overall, the integration of these six nanotechnology techniques has the potential to revolutionize lithium-ion battery technology by addressing key challenges such as low energy density, limited cycle life, and slow charging rates. By combining the unique properties of carbon and silicon-based nanomaterials, researchers can design and optimize electrode architectures for superior battery performance. Further advancements in the synthesis methods and optimization of these nanomaterials' properties will pave the way for the development of high-performance batteries with improved energy storage capacity, longer cycle life, and enhanced safety features. The ongoing research and development in the field of nanotechnology for lithium-ion batteries hold great promise for meeting the increasing demand for advanced energy storage systems in portable electronics, electric vehicles, and renewable energy applications.

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