Electrode Materials for Flexible Lithium-Ion Batteries Based on Carbon Nanomaterials

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Abstract. Due to the increased need for flexible electronic goods in recent years, energy storage technologies with high energy densities and flexibility have been quickly developed. Among various energy storage systems, flexible lithium-ion batteries (LIBs) have high energy density, elasticity to mechanical deformation, and stable electrochemical performance, making them the most promising battery technology for wearable electronic products. As one of the components of flexible lithium-ion batteries, flexible electrode materials play an important role. Carbon nanomaterials, represented by carbon nanotubes, graphene, and others, have excellent mechanical flexibility, large specific surface area, and high conductivity, making them a research hotspot in the field of electrode materials. As a result, this research describes the function of various carbon nanomaterials in flexible lithium-ion batteries and analyzes the difficulties they encounter. Finally, the path of electrode material development in the future is anticipated. It can provide a reference for the research of related electrode materials in future lithium batteries.

Keywords: Flexible lithium-ion batteries, electrical stability, carbon nanomaterials, electrode materials.

1. Introduction

The need for effective and portable energy storage solutions has increased the significance of lithium-ion batteries (LIBs) in today's technologically advanced world. From consumer electronics to electric vehicles and renewable energy systems, LIBs have emerged as crucial components in the powering of a diverse variety of applications. Due to its high energy density, long cycle life, low self-discharge, and good safety, it has become a research hotspot in the field of batteries.

The total efficacy and efficiency of lithium-ion batteries are greatly influenced by the electrode materials utilized inside their intricate structure. Improved electrode materials must be created to boost safety requirements, increase battery life, and enhance energy storage capacity. Examining and making use of the potential of novel electrode materials is essential to the continued development of LIBs. Carbon nanotubes (CNTs), graphene, and carbon nanofibers are being examined as potential possibilities due to their exceptional mechanical, electrical, and structural properties [1]. These carbon nanostructures provide tremendous promise for circumventing the constraints imposed by conventional rigid electrodes when used in flexible electrode design. They have the potential to improve LIBs' flexibility, conductivity, and overall performance thanks to their special properties [2].

Therefore, this article introduces different types of carbon nanomaterials used in LIBs and explores their applications in flexible electrode design. Summarizing the attributes, manufacturing processes, and potential applications of energy storage technology, provides a certain reference value for future research on LIBs.

2. Different carbon nanomaterials and their preparation methods

2.1. Carbon nanotubes (CNTs)

Carbon nanotubes (CNTs) are one-dimensional carbon nanomaterials with good mechanical characteristics, high electrical conductivity, and high thermal conductivity [3]. Its structure, including the angle between the hexagonal carbon grid and the axis and the arrangement of the tubes, all have an impact on electrochemical performance. Carbon nanotube arrays (CNTA) are specially arranged carbon nanotubes, which strengthen the material's properties in a specific direction. When applied to LIB, the CNTA's more neatly arranged structure allows the electrolyte to better permeate and diffuse. The intertube void also provides sufficient channels for ion movement, thus achieving better electrical conductivity. Also, because it is an array composed of countless CNTs, it has a larger specific surface area, which is conducive to loading more electrode-active substances [4].

At the moment, chemical vapor deposition, arc discharge, and laser ablation are the major processes used to manufacture CNTs. The arc discharge technique is the oldest, but it is difficult to modify the chemical process and various byproducts can be created [5]. Both single-walled and multi-walled CNTs can be formed more easily using laser ablation [6], but the equipment is expensive, making industrialization difficult. The most popular technique is chemical vapor deposition (CVD), which works by splitting carbon-containing gas with a catalyst to produce activated carbon atoms, which are subsequently utilized to create CNTs by covalent bonding [5]. Based on this method, certain progress has been made in controlling the structure selection of CNTs.

2.2. Carbon Nanofiber (CNF)

Carbon nanofibers (CNF) are one-dimensional carbon nanomaterials composed of multiple graphene layers. The structure is more complex than CNTs. Different carbon materials and metal particle catalysts used in the preparation process will lead to different stacking methods of graphene layers, and their different structures have different mechanical properties [7]. The degree of graphitization also has an impact on its mechanical and electrical qualities. For instance, heat treatment can cause CNF to develop a more ordered arrangement of graphene, which will result in a more stable support structure and improved electrical conductivity [7]. CNF exhibits excellent performance and can be adjusted and modified by temperature and other aspects, reflecting its potential as an excellent composite material raw material.

CNF, like CNT, can be prepared by the CVD method and also has methods including electrospinning and template methods. By electrospinning, the precursor polymer solution is sprayed and stretched to form a nanofiber film under the action of an applied electric field [8]. The template method uses different substrates to form suitable nanofiber filaments, and through heat treatment or carbonization to form CNF [8]. Electrospinning is the most used method, and some current studies have innovated it, such as preparing magnetic CNF by adjusting precursor solution [9], which has broadened its application range and demonstrated the research value in this direction.

2.3. Graphene

Two-dimensional carbon nanomaterial graphene is made of a single sheet of carbon atoms arranged in a honeycomb pattern. From graphene, many carbon nanomaterials may be created. The zero-dimensional nanomaterial fullerene can be obtained by wrapping single-layer graphene into a spherical shape, and the one-dimensional nanomaterials CNTs and CNF can be obtained by curling graphene into a cylinder [10]. It can be seen that graphene has the same excellent electrical conductivity and other material properties as other carbon nanomaterials. Graphene oxide (GO) is obtained by connecting different oxygen-containing groups with carbon atoms, and reduced graphene oxide (rGO) is formed by reducing GO, but changing chemical structure by removing functional groups leads to certain defects in the rGO structure and reduces its electrochemical performance. Therefore, the electronic properties of rGO have not surpassed that of pristine graphene obtained by mechanical exfoliation [10].

Mechanical stripping, chemical vapor deposition, epitaxial growth, and redox are the four basic ways to produce graphene. As the earliest method of graphene production, mechanical stripping has limitations and cannot be mass-produced. The CVD method requires a metal substrate as a platform, and the subsequent chemical separation of products and substrates is required, which increases the cost to some extent [11]. The epitaxial growth method is used to grow graphene by removing the non-carbon part of the raw material from the crystal substrate [13]. This has certain requirements for the substrate and also requires subsequent separation operations, and there may be product damage during separation. The Hummer technique, which involves introducing oxygen-containing functional groups between graphite layers that have been strongly oxidized, is often used by the redox method to produce graphene oxide (GO). After utilizing various techniques to obtain the right number of layers, reducing agents are utilized to eliminate the oxygen-containing groups [11]. The method is low-cost and easy to operate. Some current improvement makes the oxidation degree in the process better controlled and the properties of the product improved**.**

3. Application of carbon nanomaterials in LIBs

One of the research directions of flexible LIB is to prepare high-capacity electrode materials. Flexible wearable devices usually have a small volume, and an electrode material with a high areal capacity can allow it to be integrated into a small space and have enough energy to drive the device, which has important application value. At present, the two research angles in this direction are to reduce the proportion of inactive materials inside the electrode or to increase the thickness of the electrode to increase the content of active materials per unit area [12]. However, the increase in thickness hinders the ion transport speed and reduces the battery efficiency. CNT increases the conductivity of the material and the gap of CNT can effectively provide channels for ion movement. Its tubular design also acts as a support. The electrode materials most frequently used in LIB are lithium titanate (LTO) and lithium iron phosphate (LFP). LFP/CNT/EVA and LTO/CNT/EVA thick electrodes were created by Zhang et al. using the suspension-casting technique [12]. EVA is a kind of ethylene vinyl acetate copolymer that is used in composite materials. It creates a network with CNT and improves the benefits of CNT. The calculated fracture elongation is 11.3%, showing excellent flexibility. Also, this composite material showed higher specific capacity and cycle stability in the charge-discharge cycle comparison test with similar materials, reflecting the help of its composite structure in electrolyte transport. It can be seen that the combination of CNT/EVA provides an angle for the application of organic materials and other carbon nanomaterials in flexible electrodes.

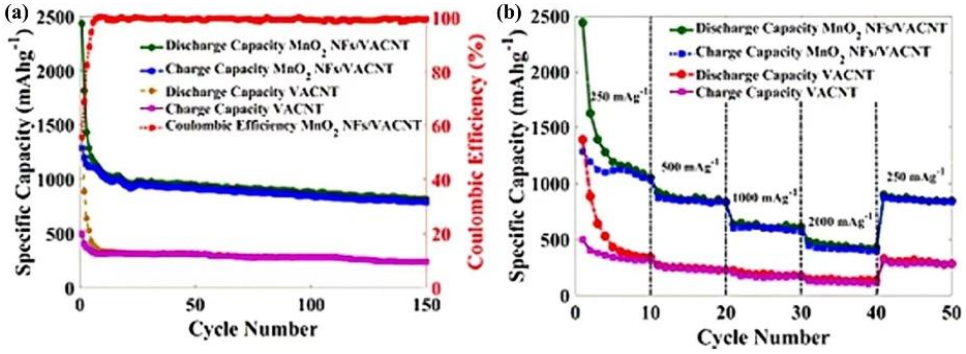


Figure 1. (a) cycling performance of materials with and without MnO_2 NFs/VACNT structure; (b) rate performance diagram of materials with and without MnO_2 NFs/VACNT structure [4]

CNT can also be used as a material for making a flexible conductive framework, on which active materials are loaded to achieve good electrical conductivity. Vertically aligned carbon nanotubes (VACNT) are a kind of CNTA. The highly ordered structure brings better electrical conductivity and also enhances the mechanical strength of the electrode to a certain extent. Transition metal oxides such as MnO_2 have a high theoretical capacity and have the potential to become lithium-ion battery electrode materials, but they are prone to volume expansion during the exchange of lithium ions,

resulting in particle crushing and SEI film undergoing continuous formation and regeneration process, thereby consuming a large amount of lithium ions and reducing the charge-discharge efficiency, resulting in a decrease in battery capacity and affecting the long-term stable operation of the battery [4]. By compounding with VACNT, the network structure composed of carbon atoms alleviates the volume change, increases stability, and brings better electrical conductivity. Abdollahi et al. grew VACNTs on stainless steel (ss) by CVD and allowed $KMnO_4$ and HNO_3 to react on the surface to form MnO_2 films to obtain MnO_2 NFs/VACNTs composite flexible electrode materials [4]. As shown in Figure 1, the battery cycle performance and rate performance are significantly improved. However, due to the existence of the SEI film, there is still research value in improving the first Coulombic efficiency and controlling its consumption of lithium ions.

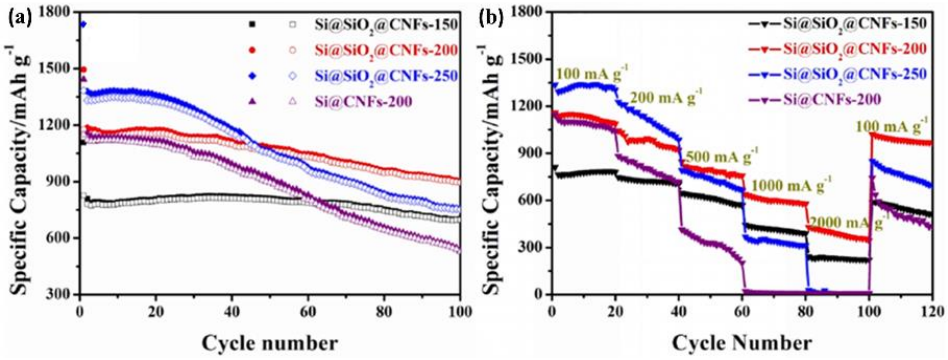


Figure 2. (a) Cycling performance at 100 mAg-1; (b) rate performance at different current densities [13]

Another point of the electrospinning method is that it can be adjusted to produce hollow carbon nanofibers, which can not only buffer the volume expansion of traditional electrode materials through the network structure but also enhance the buffer effect through the appropriate thickness and hollow structure. Ni et al. prepared hollow multi-nanochannel carbon nanofibers (NHMCFs) with a three-dimensional structure by electrospinning method and prepared NHMCFs/$MoSe_2$ composite flexible electrode materials by growing $MoSe_2$ on its surface [14]. It exhibits greater electrochemical performance than comparable composite materials based on the properties of the material. Meanwhile, its three-dimensional structure leads to the internal and external multi-dimensional growth space of MoSe2, which further reduces the ion transport distance and increases the transport efficiency, reflecting the influence of the material structure on the electrode performance. This presents another entry point for improving material properties.

A flexible lithium-ion battery electrode made of graphene is perfect because of its outstanding theoretical characteristics, large specific surface area, and stable two-dimensional carbon nanostructure; GO and rGO also have similar qualities. Additionally, rGO makes an excellent single-atom platform for the growth of other nanomaterials. Abdollahi et al. prepared GO by the Hummer method and reduced it in H2 to obtain reductive active graphene oxide (a-rGO) first [15]. Then, VACNT was grown on its surface by the CVD method to obtain VACNT/a-rGO composites. It combines the advantages of the two carbon nanomaterials, alleviating the defect of low surface reactivity of the graphene material, as described in Figure 3, by storing lithium on the more active surface of the VACNT, which achieves a higher electrode capacity. Meanwhile, its three-dimensional structure creates more electrolyte transport space for the layered graphene. This demonstrates the research value of electrode structures and the composite between different carbon nanomaterials.

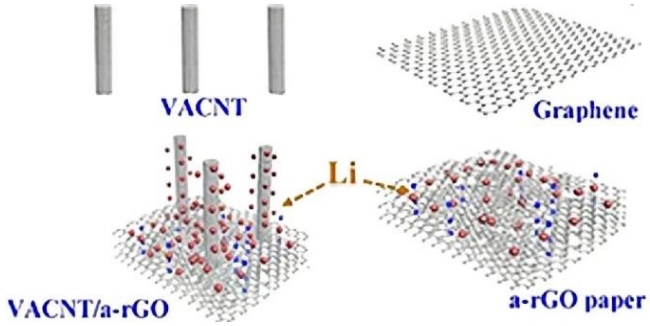


Figure 3. Diagram of more Li+ on the surface of VACNT [15]

The electrochemical characteristics of the rGO will also improve the electrical conductivity of the composite material, which is of great application value. The rGO is frequently utilized to help mix various electrode materials without the need for adhesives. Gao et al.'s approach to producing several, ultra-thin graphene sheets from a single piece of cellulose resulted in flexible, high-surface-area carbon paper [16]. Figure 5 shows a comparative diagram of rGO increasing film stability. The CP@Fe_3O_4@rGO composite flexible material with sandwich structure was composed of composite carbon paper (CP) with good electrode material Fe_3O_4 and wrapped with rGO on the outside of Fe_3O_4. It exhibits excellent electrochemical flexibility and performance, and the sandwich structure lessens Fe_3O_4 volume expansion, lessens the irreversible impact of SEI coating on the electrode, and increases electrode longevity. This serves as a useful reference for researching how composite structures affect electrode characteristics and how well graphene materials can load other electrode materials.

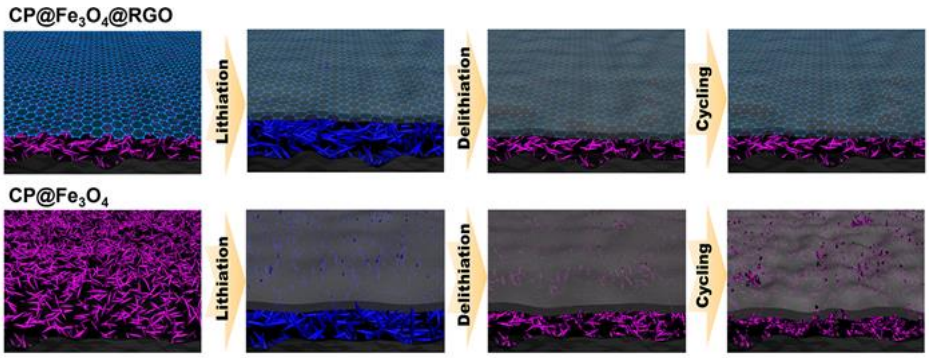


Figure 4. Diagram of rGO increasing stability [16]

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4. Summarize

4.1. Advantages of carbon nanomaterials

Due to their special characteristics, carbon nanomaterials including carbon nanotubes (CNTs), graphene, and carbon nanofibers have emerged as viable electrode materials for flexible lithium-ion batteries. These materials are appropriate for flexible battery applications because of their superior mechanical flexibility, high specific surface area, and high electrical conductivity.

Firstly, carbon nanomaterials exhibit high electrical conductivity, which is crucial for efficient charge transport in lithium-ion batteries. The high conductivity of carbon nanomaterials allows for rapid electron transfer during charge and discharge processes, leading to improved battery performance. This is particularly advantageous for flexible batteries, as it enables fast charging and discharging, enhancing the overall power output of the device.

Second, the huge specific surface area of carbon nanomaterials makes them a rich source of active sites for lithium-ion intercalation and deintercalation. The high surface area enables a higher number of lithium ions to be stored, resulting in a higher capacity and improved energy density of the battery. Additionally, the large surface area also facilitates the diffusion of lithium ions, reducing ion transport resistance and enabling faster charge/discharge rates. This is crucial for flexible batteries, as it ensures rapid energy storage and release, enabling the device to meet the demands of various applications.

Furthermore, the exceptional mechanical flexibility of carbon nanostructures also enables them to tolerate repeated bending and stretching without noticeably degrading performance. These materials' distinctive structural characteristics, such as their high aspect ratio and capacity to form linked networks, are credited with giving them flexibility. These characteristics make carbon nanomaterials perfect for use in flexible batteries because they allow them to keep their structural integrity even when put under mechanical stress. For the development of flexible and wearable electronic gadgets, the flexibility of carbon nanomaterials is crucial since it ensures that the battery can adapt to unusual forms and endure outside influences.

4.2. Current Problems and Challenges

Despite the numerous advantages of carbon nanomaterials, there are still several challenges and issues that need to be addressed for their successful integration into flexible lithium-ion batteries.

One major challenge is the scalable synthesis of carbon nanomaterials with consistent quality and desired properties. The current methods for producing carbon nanomaterials often involve complex and time-consuming processes, limiting their large-scale production. To overcome this challenge, researchers need to develop scalable and cost-effective synthesis techniques that can produce high-quality carbon nanomaterials in large quantities, ensuring their commercial viability.

The improvement of the electrode design and electrode-electrolyte interaction presents another difficulty. The effective transfer of lithium ions between the electrode and the electrolyte is a key factor in the battery's performance. Carbon nanomaterials have a large surface area, yet they are porous, which can result in higher contact resistance and constrained ion transport. To address this issue, researchers need to explore innovative electrode designs and develop advanced electrolyte formulations to enhance the electrode-electrolyte interface and improve the overall battery performance.

Moreover, the stability and cycling life of carbon nanomaterials in lithium-ion batteries remain a concern. During repeated charge and discharge cycles, carbon nanomaterials may undergo structural degradation, resulting in capacity loss and reduced battery lifetime. To tackle this challenge, researchers should focus on enhancing the structural stability of carbon nanomaterials through surface functionalization or composite strategies, ensuring their long-term performance and durability.

4.3. Future research directions and development trends

In the future, research on carbon nanomaterials as electrode materials for flexible lithium-ion batteries should focus on several key areas to further improve their performance and enable their widespread adoption.

One important research direction is the development of novel carbon nanomaterials with enhanced properties. This includes exploring new carbon allotropes, such as carbon nanobelts or carbon quantum dots, which may exhibit unique electrical and electrochemical properties for improved battery performance. Additionally, the synthesis of hybrid carbon nanomaterials, such as CNT-graphene composites, could combine the advantages of different carbon materials, leading to synergistic effects and enhanced battery performance.

Another crucial research direction is the design and fabrication of advanced electrode architectures. This involves the development of three-dimensional (3D) hierarchical structures or flexible thin films that can maximize the utilization of carbon nanomaterials and improve ion diffusion. Furthermore, the integration of other functional materials, such as metal oxides or polymers, into the electrode architecture can enhance the overall electrochemical performance and stability of the battery.

Future studies should also concentrate on improving the electrolyte system for batteries made of carbon nanomaterials. This involves creating gel electrolytes or solid-state electrolytes to increase the reliability and safety of flexible lithium-ion batteries. Moreover, the exploration of new electrolyte additives or solvents with improved compatibility and reduced reactivity with carbon nanomaterials could further enhance the performance and lifespan of the batteries.

In conclusion, strong electrical conductivity, a sizable specific surface area, and exceptional mechanical flexibility are only a few of the benefits that carbon nanomaterials provide as electrode materials for flexible lithium-ion batteries. However, challenges such as scalable synthesis, electrode architecture optimization, and stability concerns need to be addressed for their successful integration. Future research should focus on the development of novel carbon nanomaterials, advanced electrode architectures, and optimized electrolyte systems to further improve the performance and enable the widespread application of carbon nanomaterial-based flexible lithium-ion batteries.

Authors Contribution

All the authors contributed equally and their names were listed in alphabetical order.

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