

Research progress of carbon nanomaterials for lithium-ion battery anodes

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Abstract. Lithium-ion batteries (LIBs), one of the most promising energy storage methods, have been widely used in portable electronic devices due to their excellent performance, including no memory effect, great safety performance, and high energy density. The performance of the negative electrode, an essential component of LIBs, has a significant impact on the metrics of the battery as a whole. However, LIBs built with traditional electrode materials have limited durability, inadequate energy and power densities, and high prices. The discovery of carbon nanoparticles enables the design of innovative energy storage materials suitable for LIBs. Its large specific surface area, short diffusion distance, high conductivity, and strong ion conductivity are just a few of the numerous distinguishing characteristics that make it a revolutionary form of carbon material. It has a wide range of application possibilities thanks to LIBs with high reversible capacity, high power density, prolonged cycle stability, and superior safety. The most recent developments in one-, two-, and three-dimensional carbon nanomaterials are reviewed in this article, along with their uses in LIBs. The difficulties and potential benefits of creating high-performance LIBs in the future utilizing carbon nanomaterials were highlighted.

Keywords: Lithium-Ion Batteries, Negative Electrodes, Carbon Nanomaterials.

1. Introduction

Energy storage technologies are crucial for addressing the global energy problem and environmental issues. Several industries, including portable electronics, electric vehicles, and smart grids have turned to LIBs as one of the most widely used energy storage devices because of their long cycle life, safety, and enormous capacity [1].

A standard LIB is composed of a positive electrode, a negative electrode, a separator, and an electrolyte. The negative electrode material is one of the most crucial factors affecting the capacity, cycle, and rate performance of LIBs. Graphite is presently the most often used negative electrode material for commercial LIBs because of its low working potential of 0.1 V vs. Li/Li⁺ and theoretical capacity of 372 mAh g⁻¹. There are a few drawbacks to graphite as well, such as its low rate capability, the scarcity of lithium insertion sites, and the potential dangers posed by lithium dendrite development.

Carbon nanoparticles are potential options for replacing or enhancing graphite as the negative electrode material for LIBs. Carbon nanostructures have unique advantages such as high specific surface area, excellent electrical conductivity, chemical stability, and adaptable structure and form [2]. Carbon nanomaterials can be classified into different categories according to their dimensionalities, such as one-dimensional (1D), two-dimensional (2D), and three-dimensional (3D) carbon nanomaterials.

In this paper, it focuses on the recent progress of carbon nanomaterials with different dimensionalities as negative electrode materials for LIBs. It introduces the structure, synthesis methods, and application performance of 1D carbon nanotubes (CNTs) and carbon nanofibers (CNFs), 2D graphene and graphene nanosheets (GNSs), and 3D carbon nanospheres (CNSs) and nanoporous carbons (NPCs). It also discusses the challenges and future directions of carbon nanomaterials for developing high-performance LIBs.

2. Basic Principles of LIBs

The main principle of LIBs is to rely on the reversible intercalation/de-intercalation of Li-ions between the positive and negative electrodes. Typically, the positive electrode is constructed from metal oxides or phosphates that can discharge lithium ions. Carbon compounds that can store lithium ions in their interlayer gaps or on their surfaces often make up the negative electrode. The separator is a porous membrane that prevents the electrodes from coming into touch with one another but still allows the movement of lithium ions. The medium for the movement of lithium ions is provided by the electrolyte, which is a solution of lithium salts in organic solvents [3].

Li-ions travel through the electrolyte from the positive electrode to the negative electrode during discharge before being injected into the carbon matrix. While this is happening, electrons are released from the positive electrode and go from there to the negative electrode, where they are used up. During charging, the procedure is reversed.

LIBs's performance is influenced by several variables. One of these criteria that most accurately indicates the amount of charge that a battery can hold is its capacity. The capacity of the electrodes, particularly the negative electrode, which is typically the limiting element, determines the capacity of a battery. Thus, the creation of high-capacity negative electrode materials is crucial for LIBs.

3. Carbon nanomaterials for LIBs anodes

Nanoscale materials made of carbon atoms in a variety of configurations and hybridizations are called carbon nanomaterials. There are many different shapes and morphologies of carbon nanomaterials, including 1D CNTs and CNFs, 2D graphene and GNSs, and 3D CNSs and NPCs.

3.1. One-dimensional carbon nanomaterials

One-dimensional carbon nanomaterials have a tubular or fibrous shape with a high aspect ratio. The most representative 1D carbon nanomaterials are CNTs and CNFs.

3.1.1. Carbon nanotubes. CNTs are a category of nanomaterials made of two-dimensional hexagonal lattices of carbon atoms that come together to create hollow cylinders by bending in one direction. Single-wall carbon nanotubes (SWCNTs) and multi-wall carbon nanotubes are two different types of them. CNTs have many attractive properties for LIBs, such as high specific surface area (up to $2600 \text{ m}^2 \text{ g}^{-1}$), high electrical conductivity (up to 10^5 S cm^{-1}), high mechanical strength (up to 150 GPa), and good chemical stability. CNTs can provide abundant lithium storage sites on their inner and outer surfaces, as well as in their intertube spaces. CNTs can also facilitate the electron and ion transport. LIBs vary from 200 to 1000 mAh g^{-1} depending on the structure, purity, morphology, and modification of CNTs. The highest capacity of CNTs reported so far is 1168 mAh g^{-1} achieved by N-doped SWCNTs coated with SnO_2 nanoparticles [4].

3.1.2. Carbon Nanofibers. CNFs are continuous fibers that are composed of stacked graphene layers along the fiber axis. CNFs have similar properties to CNTs, such as high specific surface area (up to $400 \text{ m}^2 \text{ g}^{-1}$), high electrical conductivity (up to 10^4 S cm^{-1}), high mechanical strength (up to 10 GPa), and good chemical stability. CNFs can also provide abundant lithium storage sites on their surfaces and edges, as well as in their interlayer spaces. The synthesis methods of CNFs include electrospinning, template-assisted methods, and CVD. Among these methods, electrospinning is the most widely used due to its simplicity, low cost, and scalability [5].

3.1.3. The structure, purity, shape, and modification of CNFs, as well as their use as negative electrode materials for LIBs, all affect how well they function in applications. CNFs typically have a lesser capacity than CNTs because of their bigger diameter and smaller surface area. However, because of their continuous fiber form and interlayer interactions, CNFs are more flexible and structurally stable than CNTs. As a result, CNFs can perform better than CNTs in terms of cycle and rate. Another crucial element that influences the performance of CNFs in applications is their purity. As a result, CNFs must be purified using techniques including acid treatment, filtering, centrifugation, or ultrasonication. The performance of CNFs in applications might also be impacted by their shape. By changing the synthesis parameters, such as the polymer type, solvent type, voltage, flow rate, temperature, or time, one may modify the morphology of CNFs. CNFs' porosity, surface area, packing density, and contact area with the electrolyte can all be influenced by their shape. By adding more lithium storage sites or enhancing their compatibility with other materials, modifications to CNFs can improve their application performance. The modification methods of CNFs include doping with heteroatoms (such as N, B, or S), coating with metal oxides (such as TiO_2 , SnO_2 , or Fe_3O_4), or compositing with other carbon materials (such as graphene or carbon black) [6].

3.2. Two-dimensional carbon nanomaterials

Two-dimensional carbon nanomaterials have a sheet-like shape with a thickness of one or a few atoms. The most representative 2D carbon nanomaterials are graphene and GNSs.

3.2.1. Graphene/reduced graphene oxide. Graphene has many outstanding properties for LIBs, such as high specific surface area (up to $2630 \text{ m}^2 \text{ g}^{-1}$), high electrical conductivity (up to 106 S cm^{-1}), high mechanical strength (up to 130 GPa), and good chemical stability. Graphene can provide abundant lithium storage sites on both sides of its surface, as well as in its defects and edges. Additionally, graphene can buffer the volume shift that occurs during lithiation and delithiation as well as enhance electron and ion movement in the electrode. Mechanical exfoliation, liquid-phase exfoliation, epitaxial growth, and chemical reduction are all ways to make graphene. Chemical reduction is the most used technique among them because of its affordability, productivity, and scalability [7].

Graphene/rGO's application performance as negative electrode materials for LIBs depends on several variables, including its structure, purity, shape, and modification. Because of its greater crystallinity and lower oxygen concentration, graphene typically has a larger capacity than rGO. Van der Waals forces and π -stacking interactions, which decrease graphene's effective surface area and enhance its aggregation tendency, cause it to frequently form irreversible agglomerates. Therefore, to enhance graphene's dispersion and electrochemical performance, functional groups or other substances must be added. Due to its poorer crystallinity and greater oxygen concentration, rGO has a lesser capacity than graphene. However, due to its wrinkled or folded structure and lingering oxygen groups, rGO has greater structural stability and flexibility than graphene. As a result, rGO can perform better than graphene in terms of cycle and rate. Another crucial element that influences the effectiveness of graphene/rGO in applications is their purity. Graphene/rGO can have its specific surface area, electrical conductivity, and lithium storage capacity decreased by impurities such as amorphous carbon, leftover metal catalysts, or other pollutants. Consequently, graphene/rGO must be purified using techniques such as acid treatment, filtering, centrifugation, or ultrasonication. The performance of graphene/rGO applications can also be impacted by their shape. By changing the synthesis variables, such as the graphite source, oxidizing agent, reducing agent, temperature, or time, one may alter the morphology of graphene/rGO. The porosity, surface area, packing density, and contact area with the electrolyte of graphene and rGO can all be influenced by their shape.

The modification of graphene/rGO can enhance their application performance by introducing new lithium storage sites or improving their compatibility with other materials. The modification methods of graphene/rGO include doping with heteroatoms (such as N, B, or S), coating with metal oxides (such as TiO_2 , SnO_2 , or Fe_3O_4), or compositing with other carbon materials (such as CNTs or CNFs). The reported capacities of graphene/rGO as negative electrode materials for LIBs vary from 300 to 1500 mAh g^{-1}

depending on the structure, purity, morphology, and modification of graphene/rGO [8]. The highest capacity of graphene/rGO reported so far is 1568 mAh g⁻¹ achieved by N-doped rGO coated with SnO₂ nanoparticles.

3.2.2. Graphene nanosheets. Graphene nanosheets (GNSs) are small pieces of graphene with a lateral size of less than 100 nm and a thickness of one or a few atoms. GNSs have a similar structure and properties to graphene but with more exposed edges and defects. GNSs have many advantages for LIBs, such as high specific surface area (up to 2000 m² g⁻¹), high electrical conductivity (up to 10⁵ S cm⁻¹), high mechanical strength (up to 100 GPa), and good chemical stability. GNSs can provide abundant lithium storage sites on both sides of their surface, as well as in their defects and edges. Additionally, GNSs can buffer the volume change that occurs during lithiation and delithiation as well as the transit of electrons and ions in the electrode. GNS can use different synthesis techniques. The top-down strategies entail the physical or chemical procedures of ultrasonication, ball milling, or acid treatment to cut or break graphene or rGO into smaller bits. Assembling or growing GNSs from smaller carbon precursors using techniques like CVD, hydrothermal synthesis, or solvothermal synthesis are examples of bottom-up procedures [9].

The structure, purity, shape, and alteration of GNSs, as well as their use as negative electrode materials for LIBs, all affect how well they function in applications. Due to their higher defect density and greater edge-to-area ratio than graphene/rGO, GNSs often have higher capacity. However, van der Waals forces and - stacking interactions, which decrease their effective surface area and enhance their aggregation tendency, cause GNSs to frequently form irreversible agglomerates. Therefore, to enhance their dispersion and electrochemical performance, GNSs must be modified with functional groups or other substances. Another crucial element that influences the performance of GNSs in applications is their purity. The specific surface area, electrical conductivity, and lithium storage capacity of GNSs can be decreased by impurities such as amorphous carbon, metal catalyst byproducts, or other pollutants. To remove contaminants from GNSs, techniques including acid treatment, filtering, centrifugation, or ultrasonication are required. The performance of GNSs in applications might also be impacted by their shape. By changing the synthesis variables, such as the graphene source, cutting agent, growth agent, temperature, or time, one may modify the morphology of GNSs. GNSs' porosity, surface area, packing density, and contact area with the electrolyte can all be influenced by their shape. The modification of GNSs can enhance their application performance by introducing new lithium storage sites or improving their compatibility with other materials. The modification methods of GNSs include doping with heteroatoms (such as N, B, or S), coating with metal oxides (such as TiO₂, SnO₂, or Fe₃O₄), or compositing with other carbon materials (such as CNTs or CNFs). The reported capacities of GNSs as negative electrode materials for LIBs vary from 400 to 1200 mAh g⁻¹ depending on the structure, purity, morphology, and modification of GNSs. The highest capacity of GNSs reported so far is 1216 mAh g⁻¹ achieved by N-doped GNSs coated with SnO₂ nanoparticles [10].

3.3. Three-Dimensional Carbon Nanomaterials

Three-dimensional carbon nanomaterials have a spherical or porous shape with a large volume and a complex structure. The most representative 3D carbon nanomaterials are CNSs and NPCs, which have been widely used as negative electrode materials for LIBs.

3.3.1. Carbon Nanospheres. CNSs are hollow or solid spheres that are composed of carbon atoms with different hybridizations and arrangements. CNSs have a diameter of 10-1000 nm and a wall thickness of 1-100 nm. CNSs have many advantages for LIBs, such as high specific surface area (up to 1000 m² g⁻¹), high electrical conductivity (up to 10⁴ S cm⁻¹), high mechanical strength (up to 10 GPa), and good chemical stability. CNSs can provide abundant lithium storage sites on their inner and outer surfaces, as well as in their interlayer spaces. CNSs can be synthesized by CVD, hydrothermal synthesis, solvothermal synthesis, and template-assisted techniques. Due to its simplicity, low cost, and scalability, hydrothermal synthesis is the approach that is most frequently utilized among them. In a sealed vessel,

carbon precursors (such as glucose, sucrose, or citric acid) are heated at temperatures between 100 and 300 °C and subjected to pressures between 1 and 10 MPa. Carbon precursors can become CNSs through methods of self-assembly or nucleation [11].

The application performance of CNSs as negative electrode materials for LIBs depends on several factors such as the structure, purity, morphology, and modification of CNSs. Generally, hollow CNSs have higher capacity than solid CNSs due to their larger surface area and lower density. However, hollow CNSs have lower structural stability and conductivity than solid CNSs due to their thinner walls and larger void spaces. Therefore, it is necessary to modify hollow CNSs with functional groups or other materials to improve their electrochemical performance. The purity of CNSs is another important factor that affects their application performance. The specific surface area, electrical conductivity, and lithium storage capacity of CNSs can be decreased by impurities such as amorphous carbon, metal catalyst byproducts, or other pollutants. To clean CNSs, techniques like acid treatment, filtering, centrifugation, or ultrasonication are required. The performance of CNS applications can also be impacted by their morphology. By changing the synthesis parameters, such as the carbon supply, solvent type, temperature, pressure, or time, one may modify the morphology of CNSs. CNSs' porosity, surface area, packing density, and contact area with the electrolyte can all be influenced by their shape. By adding more lithium storage sites or enhancing their compatibility with other materials, modifications to CNSs can improve their application performance. The modification methods of CNSs include doping with heteroatoms (such as N, B, or S), coating with metal oxides (such as TiO₂, SnO₂, or Fe₃O₄), or compositing with other carbon materials (such as graphene or CNTs). The reported capacities of CNSs as negative electrode materials for LIBs vary from 200 to 1000 mAh g⁻¹ depending on the structure, purity, morphology, and modification of CNSs. The highest capacity of CNSs reported so far is 1018 mAh g⁻¹ achieved by N-doped hollow CNSs coated with SnO₂ nanoparticles.

3.3.2. Nanoporous Carbons. Nanoporous carbons (NPCs) are porous materials that are composed of carbon atoms with different hybridizations and arrangements. NPCs have a pore size of less than 100 nm and a surface area of up to 3000 m² g⁻¹. NPCs have many advantages for LIBs, such as high specific surface area, high electrical conductivity, high mechanical strength, and good chemical stability [12]. NPCs can provide abundant lithium storage sites on their pore walls and surfaces, as well as in their pore spaces. Additionally, NPCs can buffer the volume shift that occurs during lithiation and delithiation as well as the movement of electrons and ions in the electrode. Hard template, soft template, and template-free approaches are all used in the synthesis of NPCs. The hard template approach is the most popular of these techniques since it is scalable, reproducible, and easy to regulate. Hard templates, such as silica, alumina, or zeolites, are impregnated with carbon precursors, such as resins, polymers, or sugars, which are then carbonized at high temperatures (600-1200 °C) in an inert atmosphere before being removed by acid treatment or calcination.

The structure, purity, shape, and alteration of NPCs, as well as their use as negative electrode materials for LIBs, all affect how well they function in applications. Due to their bigger pore volume and reduced tortuosity, NPCs with larger pore sizes often have higher capacities than NPCs with smaller pore sizes. However, because of their thinner pore walls and bigger empty areas, NPCs with higher pore sizes have worse structural stability and conductivity than NPCs with smaller pore sizes. To balance capacity and stability, it is crucial to optimize the pore size distribution of NPCs. Another crucial element that influences NPCs' application performance is their cleanliness. The presence of impurities such as amorphous carbon, metal catalyst residues, or other contaminants can reduce the specific surface area, electrical conductivity, and lithium storage capacity of NPCs. Therefore, it is necessary to purify NPCs by using methods such as acid treatment, filtration, centrifugation, or ultrasonication. The morphology of NPCs can also influence their application performance. The morphology of NPCs can be controlled by adjusting the synthesis parameters such as the carbon source, template type, impregnation ratio, temperature, or time. The morphology of NPCs can affect their porosity, surface area, packing density, and contact area with the electrolyte [13]. The modification of NPCs can enhance their application performance by introducing new lithium storage sites or improving their compatibility with other

materials. The modification methods of NPCs include doping with heteroatoms (such as N, B, or S), coating with metal oxides (such as TiO_2 , SnO_2 , or Fe_3O_4), or compositing with other carbon materials (such as graphene or CNTs). The reported capacities of NPCs as negative electrode materials for LIBs vary from 300 to 900 mAh g^{-1} depending on the structure, purity, morphology, and modification of NPCs. The highest capacity of NPCs reported so far is 912 mAh g^{-1} achieved by N-doped NPCs coated with SnO_2 nanoparticles.

4. Conclusions

Carbon nanomaterials are well suited for LIBs due to their several benefits, including their plentiful lithium storage sites, high specific surface area, high electrical conductivity, high mechanical strength, strong chemical stability, and superior electron and ion transport capabilities. Additionally, carbon nanomaterials can buffer the volume shift that occurs during lithiation and delithiation, which enhances LIBs' cycle and rate performance.

However, there are certain faults and difficulties with carbon nanomaterials as well, including limited capacity, poor dispersion, irreversible aggregation, structural deterioration, and safety concerns. Therefore, to improve the electrochemical performance of carbon nanomaterials, it is required to optimize their structure, purity, shape, and modification.

The future development of carbon nanomaterials for LIBs should focus on the following aspects: (1) exploring new carbon sources and synthesis methods to obtain high-quality and low-cost carbon nanomaterials; (2) designing novel structures and morphologies of carbon nanomaterials to increase their surface area, porosity, and lithium storage capacity; (3) modifying carbon nanomaterials with heteroatoms, metal oxides, or other carbon materials to improve their conductivity, stability, and compatibility; (4) integrating carbon nanomaterials with other advanced materials to form hybrid or composite electrodes with synergistic effects; (5) investigating the mechanisms and kinetics of lithium storage in carbon nanomaterials to reveal their intrinsic properties and optimize their performance.

Carbon nanomaterials are promising candidates to replace or improve graphite as negative electrode materials for LIBs. With the continuous development of science and technology, carbon nanomaterials will play a more important role in the field of energy storage.

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