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Mini Review

Past, Present and Future of Carbon Nanotubes and Graphene based Electrode Materials for Energy Storage Batteries

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Electrochemical energy storage materials are one of the keys to the development and performance improvement of electrochemical energy storage devices. Carbon materials have played an extremely important role in various electrochemical energy storage systems; in particular, the recent emergence of various types of new carbon materials has brought new impetus to the development of electrochemical energy storage. This article reviews the progress in the research on carbon materials, especially carbon nanotubes and graphene, in lithium-ion/sodium-ion batteries, supercapacitors, lithium-sulfur batteries, and flexible electrochemical energy storage.

Keywords: Carbon materials; Electrochemistry; Energy storage; Catalysis; Lithium sulfur; Oxygen reduction

1. INTRODUCTION

The world is currently facing severe environmental and energy challenges. The continuous consumption of traditional energy sources, such as coal and oil, and the deteriorating environment have seriously affected the daily lives of human beings and the normal development of society. Therefore, the development of more efficient and environmentally friendly energy equipment has attracted increasing attention.

At present, high-performance electrode materials have become a hot spot in the field of materials and electrochemical energy storage applications. For future battery systems, such as lithium-sulfur batteries and flexible batteries, the research regarding electrode materials has great scientific significance and application potential and has received extensive attention [1–5]. However, electrochemical energy storage systems are very complex, and many thermodynamic and kinetic behaviours (including chemical, physical, and mechanical behaviours) occur simultaneously at different scales in the electrochemical process. These behaviours are closely related to the structure and properties of the electrode materials. However, due to the constraints of research methods, people do not have a deep understanding of these behaviours [6–9]. Although the research on materials and devices used for electrochemical energy storage has made great progress, no fundamental breakthrough has been made to date. Current electrochemical energy storage materials are insufficient to meet the requirements of new electronic devices in the future.

Since carbon nanotubes (CNTs) were reported by Iijima in 1991 [10], this one-dimensional nano-sized tubular carbon material has been shown to confer unique mechanical, electrical, thermal and optical properties to electrode materials, medicines, hydrogen storage devices and catalysts that have been widely used in many fields [11–21]. The field of lithium-ion batteries is one of the most promising potential applications of carbon nanotubes. First, carbon nanotubes themselves are an excellent anode material for lithium-ion batteries; second, carbon nanotubes, especially the directionally grown three-dimensional carbon nanotube arrays prepared using chemical vapour deposition technology, have excellent mechanical strength, and because of their unique ballistic electron conduction effects and anti-electromigration abilities, their conductivity can be as high as 10^5 S/m [22–24]. Adding CNTs as a three-dimensional conductive structure or conductive additive to other electrode materials can not only improve the electron and ion transport capabilities of the composite electrode but also significantly enhance the mechanical properties of the electrode [25,26].

Graphene is a new member of the carbon material family. Graphene is a single-layer, sheet-like structural material that is composed of carbon atoms with sp^2 hybrid orbitals and is only one atomic layer thick [27]. Similar to carbon nanotubes, graphene is widely used in the field of energy storage batteries due to its many advantages: (1) graphene has a very high specific surface area, with a theoretical value as high as 2600 m^2/g [28], which gives graphene-based composite electrodes good electrolyte compatibility; (2) the electrical conductivity of graphene far exceeds that of other carbon materials [29], so composite electrode materials with graphene as the conductive structure can exhibit excellent rate performance; and (3) a large number of functional groups and defect sites on graphene derivatives, such as graphene oxide (GO) and reduced graphene oxide (RGO), can be used as growth sites for various metals and metal oxide nanoparticles [30–33]. This composite structure composed of a graphene matrix can effectively suppress the agglomeration phenomenon of nano-electrode materials during charge and discharge and the substantial volume change of electrodes, thereby enhancing the capacity retention rate and cycle stability of electrode materials [34–42].

2. CARBON MATERIALS OVERVIEW

The development of carbon materials continues to expand new fields and provides new directions to science and research. From the fullerenes and carbon nanotubes discovered in the last century to the recent emergence of graphene and graphyne, researchers and industry departments have been paying close attention to carbon materials, forming a continuous hot spot [43–46]. The element carbon exists widely in nature and has the characteristics of diversity and specificity of constituent materials. As a simple substance, the atoms of carbon can form solids with completely different structures and properties by three hybridization methods: sp^1, sp^2, and sp^3. The carbonaceous materials composed of sp^2 hybridized carbon atoms are the most diverse, and the new carbon materials are basically sp^2 hybridized [47–52].

A sp^2 hybridized carbon material is composed of graphite flakes or graphite crystallites. The sp^2 hybridized carbon atoms form a single layer of carbon atoms with a six-membered ring as the basic unit. The sheets are directly bent and joined together to form one-dimensional carbon nanotubes. Single-layer or few-layer stacks form two-dimensional graphene, while multi-layer stacks form three-dimensional graphite crystals (Figure 1). Each carbon nanomaterial also has many different structures. For example, carbon nanotubes are divided into single-wall carbon nanotubes and multi-wall carbon nanotubes. Carbon nanotubes are made of single-layer and multi-layer graphene coiled hollow tubular carbon materials. When a certain number of five-membered carbon rings exist in the graphite sheet, the graphite sheet will bend. When the number of five-membered rings is large, a closed carbon structure may be formed. If there are 12 five-membered rings, zero-dimensional fullerene nanospheres will be formed.

The nano-scale micro-conducting network constructed by various sp^2 hybrid carbon materials can be used as the active site of electrochemical reactions [53–58]. In addition, the network can efficiently transfer mass and conduct electricity. This is a key component to achieving high-efficiency electrochemical energy storage, and the resulting macroscopic material has a large specific surface area and excellent electrochemical stability and mechanical properties. Moreover, carbon materials are abundant and inexpensive, and they have become an important electrochemical energy storage material. Therefore, since the emergence and development of lithium-ion batteries in the last century, carbon materials (artificial graphite/natural graphite) as negative electrode materials have formed a complete industry [59–61]. With the further development of the electrochemical energy storage industry, carbon materials, especially new nano-carbon materials with excellent performance, will play a more extensive and important role.

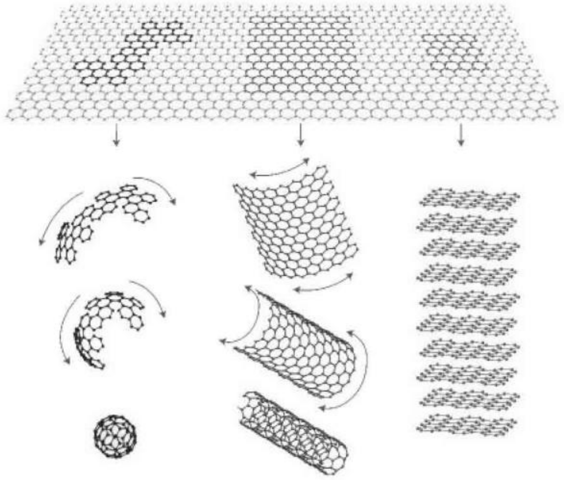

Figure 1. The formations of different carbon materials from graphene building blocks reported by Dubey and Guruviah [54]. Copyright has been obtained by Springer.

Carbon materials can effectively construct a three-dimensional conductive network and form a stable microscopic electron and ion transport interface, optimizing the kinetic characteristics of electrode reactions [62]. In addition, the pores in the network are conducive to the rapid diffusion of ions, promote the ion diffusion of electrode materials, and improve the utilization of electrode materials. The large specific surface area of the material can effectively fix, disperse and load the active material as well as prevent the agglomeration and loss of the electrode material [63–65]. The large pore volume and rich pore structure of carbon materials can form an electric double layer to contribute capacity and can also effectively buffer the stress generated by the volume change of the electrode material in the electrochemical reaction. Carbon materials can be used as active materials, such as negative electrodes in lithium-ion batteries and electrode materials in supercapacitors [66]. Abundant functional groups can form on the surface of carbon materials. In addition to contributing capacity, carbon materials can also become nucleation sites for active materials, which can be fixed on the surface of carbon materials to form active centres for electrocatalytic reactions [67–70]. Carbon materials, especially nano-carbon materials, have good flexibility, which is conducive to the construction of carbon-based flexible electrodes for flexible electrochemical energy storage devices. The rational design and adjustment of the morphology, dimensions, size, pore structure and surface chemistry of the carbon material in the composite material can improve the dynamic characteristics and structural stability of the electrode material and ultimately significantly improve the capacity, rate, performance, and cycle stability of the electrochemical energy storage device [71–74].

3. ANODES FOR LITHIUM ION BATTERIES

Because carbon nanotubes have excellent electrical conductivity and can effectively construct a perfect electronic conduction network, they can be combined with lithium-ion battery electrode materials as conductive structures to obtain composite electrode materials with good electrochemical performance [75,76]. The compositing method for carbon nanotubes and electrode materials is flexible, and the composite electrode materials in which carbon nanotubes are evenly distributed can be obtained by the gel-sol method, hydrothermal method, chemical deposition method, vapour deposition method and physical grinding [77–80]. In the report by Xia et al. [81], a $LiMn_2O_4$/CNTs composite structure was obtained by a one-step hydrothermal treatment. $LiMn_2O_4$ nanoparticles with a uniform particle size can be evenly loaded on carbon nanotubes to form a good conductive contact. The prepared electrode can be cycled stably for more than 1000 cycles at a rate of 10 C. Ko et al. [82] closely grew CuO nanoparticles on CNTs by chemical deposition. The prepared electrode was cycled at 0.1 C for 100 cycles, and the capacity was almost without any attenuation. This result occurred due to the strong binding force between CuO and CNTs prepared by the deposition method, which can not only improve the electrical conductivity of the composite itself but also enhance its structural stability.

Compounding carbon nanotubes as a conductive structure with electrode active materials has been shown to effectively improve the electrochemical performance of the prepared composite electrodes [83–85]. However, the new high-energy-density lithium ion electrode materials that are currently research hotspots, especially negative electrode active materials, such as MnO_2, Fe_2O_3, Fe_3O_4,

SnO_2, Mn_3O_4, and Co_3O_4, are generally ubiquitous, with low bulk conductivity and large volume changes during charging and discharging, and are easily synthesized nanoparticles. The inherent defect of reunion. Therefore, in order to further improve the rate performance and cycle life of such materials, it is necessary to develop new composite forms with carbon nanotubes. Recent studies have found that three-dimensional composite electrode materials with the following unique advantages can be obtained by the composite growth of electrode materials on vertically oriented carbon nanotube arrays prepared by chemical vapour deposition techniques [86–88]. The carbon nanotube array can provide a more direct and unobstructed electronic conduction path, thereby enhancing the rate performance of the composite electrode. The flexible carbon nanotube array is extremely elastic, which can effectively relieve the volume change of the electrode material and inhibit the agglomeration of nanoparticles, thereby improving the cycle stability of the electrode structure [89–91]. This method eliminates the need for additional conductive additives and binders and can greatly increase the energy density of the entire battery. Furthermore, this method avoids the occurrence of electrode cracking and current collector peeling caused by the evaporation of the solvent during the drying process of the electrode slurry.

Reddy et al. [92] directed the growth of carbon nanotubes inside MnO_2 nanotubes by chemical vapour deposition and obtained a coaxial tubular MnO_2/CNTs composite tubular structure with controllable wall thickness and tube length. The elastic nanotube film can be directly prepared as an electrode without adding a conductive agent or binder. With 50 mA/g current charge and discharge, the first discharge capacity reached 2170 mAh/g. After 15 cycles, the reversible capacity remained above 500 mAh/g. The pure MnO_2 electrode capacity is only approximately 100 mAh/g. Obviously, the composite tubular structure of MnO_2/CNTs greatly improves the cycling stability of the electrode. The porous structure facilitates the immersion of the electrolyte and promotes the contact between the electrolyte and the electrode material. The inner core of elastic CNTs improves the conductivity of the material and effectively relieves the volume expansion of the electrode.

Fe_3O_4 is an inexpensive and environmentally friendly anode material for high-capacity lithium-ion batteries. Wu et al. [93] produced a nano-scale Fe_3O_4 particle layer on a directionally grown carbon nanotube array by magnetron sputtering. Due to the good contact with the three-dimensional array of highly conductive carbon nanotubes, the first discharge capacity of the prepared Fe_3O_4 particles reached 1814 mAh/g at a cycle current of 0.1 A/g, and it still maintained a reversible capacity of up to 1670 mAh/g after 100 cycles. Even if the carbon nanotubes in the composite are included in the mass of the active material, their reversible capacity (836 mAh/g) after 100 cycles is much higher than the theoretical capacity of the graphite anode.

With the continuous development of mild-condition, low-cost and large-volume graphene preparation technology, graphene-based composite lithium-ion battery materials have been widely studied. There are usually two methods for preparing graphene-based composite materials. One method is to deposit the prepared active electrode material directly on the graphene or graphene oxide substrate by physical mixing [94–97]. The advantage of this method is that the structure and morphology of the active material prepared in advance can be controlled by a mature synthesis process. However, the uniform mixing of the material with the graphene substrate depends on its ability to disperse in the graphene solution. The other method is to grow the active electrode material in situ on a graphene or graphene oxide substrate. This method is unique because the active material can be generated more closely and uniformly on the two-dimensional level of graphene [98–101]. The graphene sheet structure can inhibit the agglomeration of particles during the high-temperature synthesis of the material, thereby forming a sandwich composite material with a uniform and stable structure and chemical properties, but the requirements for the preparation process are relatively high.

Xue et al. [102] designed a double-layer protective structure to improve the rate and cycle performance of germanium (Ge) anodes. First, the pyrolysis of oleamine coats the carbon layer (Ge@C) over the Ge nanoparticles. Then, the Ge nanoparticles coated with the carbon layer and the reduced graphene oxide (RGO) were evenly mixed in an ethanol solution to obtain a Ge@C/RGO composite electrode material coated with RGO and carbon double layers. By uniformly dispersing Ge nanoparticles in the RGO coating layer, the conductivity of the electrode and the buffer capacity for volume expansion are improved. After 50 cycles of charge and discharge, the reversible capacity of the Ge@C/RGO composite electrode was 940 mAh/g after 50 cycles. The reversible capacity of Ge@C without graphene recombination is only 490 mAh/g.

Wang et al. [103] prepared the Mn_3O_4/RGO composite anode material using a two-step method. The first step is to uniformly grow low-crystallinity Mn_3O_4 precursor particles on graphene oxide (GO). The second step is to reduce the GO to RGO by obtaining Mn_3O_4 particles with a uniform particle size and good crystallinity through a hydrothermal reaction. The composite structure of Mn_3O_4/RGO. When charging and discharging at a current of 40 mA/g, a reversible capacity of up to 900 mAh/g, which is close to the theoretical value (936 mAh/g), was obtained in the first 5 cycles. By increasing the current to 400 mA/g, a reversible capacity of approximately 780 mAh/g can still be obtained after 15 cycles. As a comparison, when pure Mn_3O_4 synthesized by the same method was used as the electrode material, the charge and discharge at a current of 40 mA/g decreased the capacity to approximately 115 mAh/g after only 10 cycles. By depositing a highly insulating electrode material on a graphene substrate with high conductivity, the electrochemical lithium storage performance of the material can be significantly improved.

4. CATHODES FOR LITHIUM ION BATTERIES

As allotropes of graphite, carbon nanotubes and graphene have proved to be very promising anode active materials for lithium ion batteries. The stable cycling capacity of carbon nanotubes with different shapes can reach 300~600 mAh/g. Graphene has an extremely high specific surface area, excellent electrical conductivity and a unique lithium storage mechanism. Lithium ions can be stored not only on both sides of the graphene sheet but also on the edge and defect positions of the graphene sheet, thereby obtaining a higher lithium storage capacity [104–107]. In addition, compared with the shortcomings of traditional graphite electrodes that are easy to pulverize and break during a long charge and discharge cycle, carbon nanotubes and graphene can exhibit more stable cycle performance due to their excellent mechanical strength and structural toughness [108–110].

Assuming that lithium ions can be diffused and stored stably on the inner and outer surfaces of single-walled carbon nanotubes or even in the gaps of multiple closely packed carbon nanotubes, the theoretical lithium storage capacity can be as high as 1116 mAh/g [111]. To convert such a substantial theoretical capacity into a practical and stable reversible capacity, some studies have used methods such as optimizing the preparation method and electrode structure of carbon nanotubes and mechanical and chemical post-treatment methods to increase the conductivity of carbon nanotubes. The number of defective bits increase with reversible lithium insertion. Through the heteroatom doping method, a large number of defect sites be introduced on the carbon nanotubes. In addition, because the dopant nitrogen atom has a lone pair of electrons, it can provide additional electrons and electron carriers for the electron conduction band. For example, Shin et al. [112] prepared nitrogen-doped multi-walled carbon nanotubes with multiple defect sites by plasma-enhanced vapour deposition and attached nickel oxide to them to enhance lithium storage performance. The defect sites formed on the walls of the multi-walled carbon nanotubes by nitrogen doping not only have a strong lithium storage capacity but also facilitate the transfer of electrons and lithium ions between the multi-walls, thereby improving the efficiency of lithium storage.

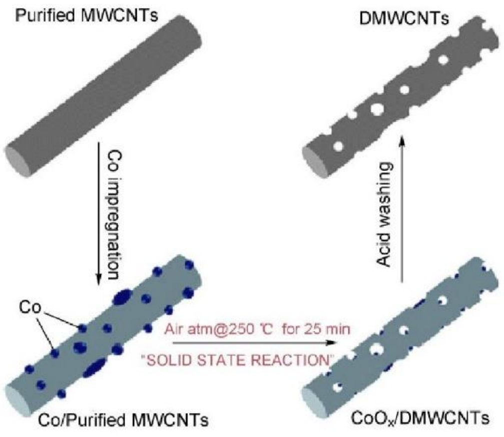

Figure 2. Schematic procedure for drilling MWCNTs reported by Oktaviano et al [113]. Copyright has been obtained by Royal Society of Chemistry.

Although carbon nanotubes have greater advantages over traditional graphite materials in lithium storage capacity, they have two drawbacks that affect their commercial application. First, the irreversible capacity of carbon nanotubes in the first cycle is larger. This large capacity is because the lithium ions embedded in the carbon nanotubes during the first discharge process cannot be completely removed in the subsequent charging process and become "dead lithium" without electrochemical activity. Second, the carbon nanotubes have a large voltage change range during the discharge process and cannot form a stable discharge platform, so they cannot meet the requirements of electronic devices for a stable power supply voltage. In the report of Oktaviano et al. [113], porous carbon nanotubes covered with mesopores with a diameters of 4 nm were obtained by embedding cobalt oxide as a pore-forming template on the wall of acidified and purified multi-walled carbon nanotubes (Figure 2). Because of the pore structure, lithium ions are easily inserted into and removed from the inner wall of the carbon nanotubes. Therefore, compared with the untreated carbon nanotubes, the porous carbon nanotubes have significantly improved coulombic efficiency and reversible capacity. The first cycle Coulomb efficiency increased from 34% to 40%. When charging and discharging with a current of 25 mA/g, the reversible capacity is 625 mAh/g after 20 cycles, while the capacity of untreated carbon nanotubes is only 421 mAh/g.

Graphene materials can be divided into graphene, reduced graphene oxide, and graphene oxide materials according to the degree of functionalization. Although these materials have many differences in physical and chemical properties, they show much higher capacity performances than traditional graphite when used as negative electrode active materials for lithium ion batteries [114–116]. Graphene materials with high functional group contents or more defect sites include graphene oxide and incompletely reduced graphene oxide. These graphene materials contain more lithium ion intercalation sites, so they can exhibit a higher initial capacity [117,118]. However, due to the low conductivity of the material body, the cycle stability and rate performance are often limited.

Compared with graphene oxide, graphene oxide with a higher degree of reduction or graphene prepared by vapour deposition have more complete lamellar planar conductive structures, so it has a stronger cycle at a higher charge and discharge rate stability. For example, Lian et al. [119] used a thermal expansion method to strip and reduce graphene oxide to prepare graphene nanosheets with high specific surface area and high conductivity. Electrochemical performance tests show that this material has good reversibility; the reversible capacity in the first week is close to 1200 mAh/g, and the capacity remains at 848 mAh/g after 40 weeks of cycling.

5. CONDUCTIVE ADDITIVE FOR LITHIUM ION BATTERY

In the current lithium ion battery system, the lower ion and electronic conductivity of the electrode material body is one of the main factors that limit its rate performance. An excessively high resistance value will cause polarization of the electrode, resulting in a reduction in the utilization rate of the electrode material [120–122]. Carbon materials, such as carbon black and acetylene black, are currently commonly used conductive additives due to their high conductivity and chemical passivity. However, to establish an efficient conductive network, the amount of conductive agent added is often higher. Traditional conductive additives alone cannot provide lithium intercalation and desorption capacity, which leads to a decrease in the specific energy and specific power of the battery [123,124]. In addition, the point-to-point contact between traditional conductive additives and active material particles will cause greater thermal resistance, which will bring certain safety risks. Therefore, it is necessary to develop a new type of conductive additive with a highly efficient conductive network, while reducing the required amount of addition and improving the conductive energy of the overall electrode. Recent studies have found that the one-dimensional fibrous structure of carbon nanotubes and the unique two-dimensional planar structure of graphene can provide a large number of conductive contact sites for electrode active material particles [125,126]. Compared with acetylene black and carbon black, carbon nanotubes and graphene as conductive additives can more effectively reduce the contact resistance between electrode material particles and improve the overall electrode conductivity.

Chan et al. [127] prepared silicon nanowires with an average diameter of 30 nm and a length greater than 10 μm. These authors used conductive carbon black and multi-walled carbon nanotubes as conductive additives to prepare electrode materials and investigated their effects on electrode performance. SEM images show that due to the similar size of carbon black particles and silicon nanowires, a single carbon black particle can only be in contact with a limited number of silicon nanowires and cannot effectively transfer electrons. In contrast, MWCNTs have a larger size and a cross-linked network structure. When used as a conductive additive, MWCNTs can form multi-point contacts with silicon nanowires and improve performance.

Su et al. [128] studied the effects of graphene nanosheets (GNS) and conductive carbon black super-P (SP) as conductive additives on the electrochemical performance of lithium iron phosphate cathode materials. When GNS was used as the conductive additive, the electrode performance was optimal when the GNS content is 2 wt%, far exceeding the electrode containing 20 wt% SP. SEM images show that GNS's unique two-dimensional layered structure can provide a large amount of bonding surface area. GNS can form a point-to-point conductive network with only a small addition, which achieves a far greater conductivity than traditional conductive additive materials. In addition, as a conductive additive, GNS can form close contact with active particles. The soft physical characteristics of GNS can buffer the volume change of the electrode during charge and discharge, thereby improving the cycle stability and service life of the electrode.

6. CONDUCTIVE CARRIER FOR LITHIUM-SULFUR BATTERY

A lithium-sulfur battery is a lithium battery that uses elemental sulfur as the positive electrode and metallic lithium as the negative electrode. Elemental sulfur has an attractive high theoretical specific capacity (1675 mAh/g). In 2009, Nazar et al. [129] used mesoporous carbon CMK-3 with a regular porous structure as a sulfur carrier. By supporting sulfur in the pore structure of carbon materials, its high electrical conductivity and use of porous polysulfide improve the performance of sulfur electrodes. Since then, the use of different carbon materials as a conductive carrier and sulfur compounds has become the main idea of lithium-sulfur batteries. Carbon nanotubes and graphene have also attracted substantial attention from researchers studying lithium-sulfur batteries due to their unique electrical conductivity and structural characteristics.

The synthesis process of the composite structure of sulfur-coated carbon nanotubes is relatively simple, and composite structures with different sulfur loading levels can be obtained by adjusting the use ratio of carbon nanotubes and sulfur. Kaskel et al. [130] prepared multi-walled carbon nanotube arrays grown on nickel foil by vapour deposition and uniformly loaded sulfur on the outside to obtain carbon nanotube/sulfur composites.

Although carbon nanotubes are used as the conductive core, coating sulfur on the outside can effectively improve the utilization efficiency and rate performance of the active material of the sulfur electrode, but it does not fundamentally solve the problem of the easy loss of polysulfide. Therefore, Moon et al. [131] chose to deposit sulfur inside the directionally grown carbon nanotubes and deposited a layer of platinum on the open end of the carbon nanotube array to complete the encapsulation of sulfur. Carbon nanotubes can act as a physical barrier, effectively inhibiting the loss of polysulfides.

In addition to combining carbon nanotubes directly with sulfur, other conductive materials, such as polyaniline, polypyrrole, polyacrylonitrile, and porous carbon, can be incorporated into the composite structure to form a carbon nanotube/second conductive material/sulfur composite structure. For example, Wang et al. [132] first added the sulfur-ethylenediamine composite to the multi-walled carbon nanotube solution to obtain a uniform core-shell structure composite of sulfur-coated carbon nanotubes.

Different graphene-based materials can play different roles when used as a conductive support structure in lithium-sulfur batteries. First, graphene-based materials themselves have extremely high electrical conductivity, and the combination of elemental sulfur and sulfur compounds can significantly reduce the electrical impedance of sulfur electrodes, improve the utilization efficiency of active materials, and effectively improve the rate performance. Graphene-based materials have a high specific surface area. By coating sulfur on two adjacent graphene sheets, a large mass of sulfur can be evenly loaded, and the loss of polysulfide can be effectively suppressed. In addition, the unique elastic physical structure of graphene can also provide a buffer space for the substantial volume change in the sulfur electrode during lithium deintercalation, thereby effectively improving the cycle stability of the lithium-sulfur battery.

Ji et al. [133] deposited sulfur in situ on the surface of graphene oxide by a liquid phase reaction. X-ray absorption spectrum test results showed that after co-heating treatment of sulfur and graphene oxide, a new chemical bond can be formed between the two. Through the chemical adsorption of oxygen-containing functional groups on graphene oxide, sulfur can be more tightly and uniformly attached to graphene oxide, thereby helping to suppress the loss of polysulfide and improve the cycle performance.

Graphene oxide-based materials contain a large amount of surface functional groups to form additional chemical adsorption capacity for sulfur, thereby improving the cycle performance of sulfur electrodes. However, due to the poor conductivity of graphene oxide itself, the prepared composite materials often fail to exhibit high rate performance. Therefore, one of the current research directions is the surface chemical modification of graphene. While introducing a pore structure or other functional groups to enhance the physical or chemical adsorption of sulfur, it does not affect the high conductivity of the graphene body, thereby obtaining a lithium-sulfur battery that can be stably cycled at a high rate.

Ding et al. [134] formed a porous structure with an average pore size of 3.8 nm on reduced graphene oxide by an activation treatment with potassium hydroxide solution. A large number of mesopores can not only effectively absorb liquid polysulfide but also act as activation sites for its reaction. Compared with the untreated reduced graphene oxide, the electrode prepared with the chemically treated reduced graphene oxide/sulfur composite structure has significantly improved cycle stability and rate performance.

7. SUMMARY AND OUTLOOK

Energy storage batteries are playing an increasingly important role in daily communication and green travel, which puts forward higher requirements for advanced lithium-ion battery and lithium-sulfur battery electrode preparation technologies. A large number of research results show that nano-carbon materials, represented by carbon nanotubes and graphene, can significantly improve energy storage batteries' performance in different application modes due to their excellent electrical conductivity, good mechanical properties, and unique morphology and structural characteristics. Capacity performance, rate performance and cycle life can be improved. In addition, it should also be recognized that the following problems need to be solved before these materials are more widely and commercially applied. (1) The conductivity of carbon nanotubes and graphene has a decisive influence on the performance of the electrodes used. Therefore, exploring and optimizing new preparation processes and chemical modification methods to ensure high-performance, high-conductivity body materials is essential. (2) Achieving good electrochemical contact with active materials through uniform dispersion is the key to the performance of carbon nanotubes and graphite diluents when used as conductive additives and composite conductive structures. (3) Since carbon nanotubes and graphene can be compounded or composited with other conductive structures, a more perfect conductive structure can be constructed by the synergy of different materials.

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