

Research progress of carbon-based anode materials for lithium-ion batteries

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Abstract. Lithium-ion batteries have received widespread attention for their high operating voltage, excellent energy density, long cycle life, low self-discharge rate, and environmental friendly characteristics. Currently, carbon-based anode materials are one of the most widely used choices for commercial applications. However, graphitic carbon materials suffer from low theoretical capacity, insufficient initial Coulombic efficiency, poor multiplicative performance, and graphite flake layer detachment due to interaction with electrolyte, and these defects limit their application scope. Although amorphous carbon materials perform better in terms of cycling and multiplicity performance, their large irreversible capacity is also a drawback that cannot be ignored. Therefore, the search for anode materials with better electrochemical performance has become one of the hotspots in current research. This paper summarizes the classification of carbon-based anode materials for lithium-ion batteries in detail, and reviews the recent research progress on the modification of carbon-based anode materials for lithium-ion batteries, including activated porosity, heterogeneous atom doping, and composite materials, etc., and looks forward to its future development direction.

Keywords: Lithium-ion, Battery, Anode Materials.

1. Introduction

Over the past centuries, the main source of energy has been fossil fuels, which not only run out, but also lead to many environmental problems, which in turn affect the health of the average person. Therefore, considering all the ongoing problems, researchers have turned to new sources of energy. Lithium-ion batteries (LIBs) are favored worldwide for their high battery capacity and power, energy density, low pollution, low self-discharge, and are widely used in portable electronic devices, electric vehicles, energy storage systems, aerospace field, and medical devices. Conventional graphite anode materials are unable to meet the growing demand due to their low theoretical specific capacity of 372 mAh g^{-1} . In this case, there is an urgent need for a new type of anode material with high capacity, long-term stability, and affordability. The selection and application of electrode materials have been the subject of discussion and research as people have higher requirements for various performances of LIBs such as energy density, battery life and cycle safety, etc[1].

Currently, common anode materials mainly include silicon-based materials, carbon-based materials, and alloy-based materials. Silicon has a theoretical embedded lithium capacity of up to 4200 mAh g^{-1} , which is much higher than the graphite anode commercially available recently, and has become the focus of current research. However, when silicon is used as the negative electrode of lithium batteries, serious volume expansion occurs during charging and discharging, and at the same time, silicon is a semiconductor with poor electrical conductivity, leading to a sharp decline in cycling capacity as well as poor electrochemical performance. Alloy anode materials are alloys that can react with lithium at room temperature, including metals and their alloys, intermetallic compounds and composite materials, such as Sn, Si, Al, Sb and so on. The charge-discharge reaction is essentially a reaction mechanism of alloying and anti-alloying. According to the existing reports, the research of transformed anode materials mainly includes oxides and sulfides of dozens of transition metal elements, such as Co, Ni, Mn, Fe, Ti and so on. The alloyed anode has a moderate embedded lithium voltage, which helps to inhibit the generation of lithium dendrites, and thus improves the overall safety of the battery; however, the alloyed anode undergoes significant volume expansion during the cycling process, which is prone to trigger the deactivation of active material particles by pulverization, poor electrical conductivity, and frequent rupture of SEIs, which fatally affects the cycling stability

of the anode[2]. This paper mainly focuses on LIBs carbon-based anode materials to review their research progress. Among them, carbon-based materials have high development potential due to their abundant reserves and cheap prices, their rich and diverse types as well as their stable electrochemical reaction properties. Therefore, improving the performance of carbon-based anode materials will be the key to improve the overall performance of LIBs.

Carbon-based materials are mainly divided into amorphous carbon materials and graphitic carbon materials, of which amorphous carbon materials include: hard carbon (HC), soft carbon (SC); graphitic carbon materials include: natural graphite (NG), artificial graphite (AG), and graphitized carbon (e.g., carbon fiber (CF), intermediate phase carbon microspheres (MCMB)). Carbon-based anode materials are usually made from carbon materials such as graphite or amorphous carbon, and have the advantages of high specific capacity, excellent cycling stability, lower cost and environmental friendliness.

At present, the capacity of traditional carbon-based materials cannot satisfy large-scale energy storage applications, and further improvement of energy density and extension of cycle life are needed, and the capacity of LIBs can be enhanced by various modification methods. The following three modification techniques are mainly studied at present:

(1) Preparation of composite carbon materials. Because the simple graphite negative electrode and electrolyte compatibility is poor, electrolyte molecules are easy to embed, resulting in graphite lamellae peeling off in the charging and discharging process, or a larger atomic volume in the charging and discharging process is easy to make the graphite volume expansion, the degree of ordering is reduced; and graphite's low high-current charging and discharging ability leads to poor power performance. Usually composite with MCMB, amorphous carbon, carbon nanofibers, lithium titanate, tin oxide, bismuth alloy and so on[3]. Taking amorphous carbon as an example, Liu et al [4] used natural graphite (NG) as the substrate and acetylene as the carbon source to achieve uniform coating of pristine NG under fluidized conditions by fluidized bed CVD process, and obtained modified natural graphite (MNG) with core-shell structure, and the first discharge capacity of MNG spheres decreased to 389 mAh g⁻¹ compared with that of NG (410 mAh g⁻¹), but the first discharge capacity retention rate was 84.0 % after 41 cycles, and the stability was significantly improved. However, the retention rate of the first discharge capacity after 41 cycles was 84.0 %, which significantly improved the stability.

(2) Heteroatom doping. By doping a small amount of other elements or compounds into the carbon material, the energy band structure of the carbon material can be changed to make it have good electrical conductivity, change the pore structure of the carbon matrix, increase the active sites, and reduce the Li⁺ diffusion resistance. Common doping elements are N, O, B, P. Elemental doping is a common and proven modification method. For example, Monje et al [5] used 3-(aminopropyl) triethoxysilane (APTES) and low-cost, environmentally friendly sodium citrate and glycerol to prepare nitrogen-doped C/SiOC materials in situ, showing two times higher delithiation capacity values than those reported for graphite, with a first cycle charging capacity of 367 mAh g⁻¹ and an initial coulombic efficiency (approx. 55 %) with 98% recovery capacity maintained over 1000 cycles at 1.6 A g⁻¹. Excellent electrochemical performance was maintained.

(3) Carbon material activation. It mainly includes physical activation method, chemical activation method, template activation method, etc. During the activation process, the pore structure and defective sites of carbon materials will be further expanded and increased, which improves the surface area and adsorption capacity of activated carbon materials. In conclusion, the mechanism of activated carbon materials is mainly through the interaction of various roles such as ablation, gas desorption, chemical reaction and physical adsorption to form materials with higher surface area, more pore structure and more abundant functional groups [6].

In order to improve the electrochemical performance and reduce the application cost of carbon-based anode materials, the current research in the industry focuses on in-depth exploration of the Li⁺ embedding/de-embedding mechanism, electrochemical behavior, thermodynamic properties, kinetic behavior, stability behavior, and interfacial reaction of anode materials, and to improve the

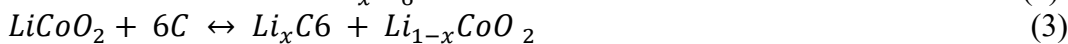
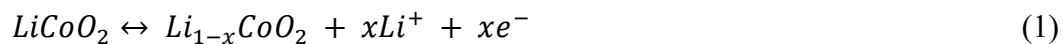
performance through the doping modification of the material elements, nanostructuring, and electrode activation, as well as reduce the cost, to optimize the overall performance and prolong the service life of the The overall performance and service life of the battery can be optimized. In this paper, the feasibility of the application and modification of carbon-based materials for energy storage in LIBs is investigated, the constitutive relationship and mechanism are analyzed, the energy storage effect of different carbon-based materials is analyzed, and finally, the outlook of promoting the practical application of carbon-based anode in LIBs is proposed.

2. Principles and Classification of Carbon Materials in LIBs

2.1 Principles of LIBs

LIBs are secondary batteries (rechargeable batteries) in which Li^+ is embedded and de-embedded back and forth between the two electrodes during the charging and discharging process: during charging, Li^+ is de-embedded from the positive electrode, and passes through the electrolyte to be embedded in the negative electrode, which is in a lithium-rich state; and the opposite is true during discharging, and Fig.1.(a) demonstrates its dynamic process[7].

Currently, most commercially available cathode materials for LIBs are layered LiMO_2 ($\text{M} = \text{Co}, \text{Ni}, \text{Mn}$) and LiFeO_4 . In the case of lithium cobalt-acid batteries, for example, the electrode reaction equation is as follows:



Battery performance depends on the Li^+ transport efficiency in the electrolyte. When the flow of Li^+ released by the positive electrode material is greater than that received by the negative electrode material, the limitation of the transport efficiency of the negative electrode material leads to the continuous deposition of Li^+ on the surface of the negative electrode and the formation of intercalation compounds. Due to the repulsive effect between Li^+ , they are unable to aggregate and arrange themselves on the graphite layer, but instead occupy neighboring or more distant lattice sites. When Li^+ reaches the maximum theoretical filling, six graphite lattices correspond to one Li^+ , the chemical formula is LiC_6 , and the theoretical specific capacity is 372 mAh g^{-1} [8].

2.2 Graphite-based materials

Carbon-based anode materials include graphite-based, non-graphite-based and nanostructured carbon-based anode materials. Graphite-based materials can be classified into natural graphite (NG), artificial graphite (AG), graphitized carbon (nanostructured carbon) (Fig.1.(b)).

Natural graphite has many favorable properties, such as high reversible capacity, large reserves, low cost, low potential with a smooth curve, first week Coulombic efficiency of 90 % to 93 % in suitable electrolytes, reversible capacity up to $340\text{-}370 \text{ mAh g}^{-1}$, and especially low cost, which can be used as an anode material for LIBs. Although natural graphite has these favorable conditions, the regular layered structure of natural graphite leads to its high anisotropy, the phenomenon of delayed Li^+ embedding and insufficient contact between graphite particles and the collector, which is also the main reason for the low multiplication performance of natural graphite; moreover, natural graphite's outer surface reactivity of the particles is uneven, and the grain size is large, so that the surface crystalline structure is easy to be destroyed during the charge and discharge process. In addition, the surface SEI film coverage is not uniform, resulting in low initial Coulombic efficiency and poor multiplication performance, which limits its practical application [9].

The production of synthetic graphite relies on graphite powder, petroleum-based or coal-based precursors as raw materials. Auxiliary materials such as polymers, conductive agents and binders are added to enhance the material properties. After mechanical milling, high temperature or chemical treatment, high electrode density and high capacity per unit volume of manufactured graphite can be obtained [10]. Compared with natural graphite, synthetic graphite has superior cycling properties and

low expansion coefficient due to smaller internal voids. However, its internal movement distance becomes longer and low velocity characteristics can occur. In order to improve this problem, activation is often used to generate Li^+ insertable holes in the graphite layer, which improves the Li^+ diffusion rate. Overall, the performance of artificial graphite as an anode material is superior to that of natural graphite and is an important choice in the field of LIBs.

Nanostructured graphitic carbon is an important class of carbon materials with excellent chemical stability, large specific surface area, high thermal and electrical conductivity. Nanostructured graphitic carbon, such as carbon nanotubes, provides a large number of Li^+ storage sites that buffer the volume change during charging and discharging, and has good cycling performance. Although valuable in applications such as batteries, they still suffer from low first-time coulombic efficiency, high reaction potentials, high cost, and complex preparation. Therefore, the development of cheaper, scalable and sustainable production routes for nanostructured graphitic carbon is a current research priority [11].

Graphite (Gr) exhibits high sensitivity to electrolytes and poor compatibility with solvents due to its high crystallinity and layered structure. In addition, graphite's performance is limited by its low high-current charging and discharging capability, which affects its power performance and makes it difficult to achieve high energy and power densities when used as an anode material. In order to improve the electrochemical performance and stability of graphite-based negative electrodes, they are usually modified by heteroatom (boron, sulfur, nitrogen, phosphorus, etc.) doping, surface activation, and polymer pyrolytic carbon coating in practical applications.

2.3 Non-graphite materials

The ability of hard carbon (HC) to maintain its disordered structure, low crystallinity and large layer spacing (Fig.1.(c)) even after high temperature graphitization allows hard carbon to accommodate sodium (Na^+) and potassium (K^+) ions with larger ionic radii. The abundance of surface defects and heteroatoms in the hard carbon material helps to activate more potential active sites, facilitating rapid ion transport within the material and solving the metal deposition problem, thus showing excellent lithium intercalation potential and superior multiplication rate performance [12]. Issatayev et al [13] obtained NHC/3LiF by ball-milling date palm kernels treated at 800 °C under N_2 atmosphere to hard carbon (NHC) and mixing it with 3 % LiF, and the charging/discharging capacity was 597/976 mAh g^{-1} with an initial coulombic efficiency (ICE) of 61 %, respectively, in the first 0.1C cycle; after 100 cycles, NHC/3LiF could still maintain a specific capacity of 279.25 mAh g^{-1} . 3LiF still maintains a specific capacity of 279.25 mAh g^{-1} after 100 cycles. It is true that defects, heteroatoms, and functional groups provide sufficient lithium storage sites; however, they lead to significant irreversible capacity loss during the initial cycling period and result in lower initial coulombic efficiency (ICE), among other problems [14].

Soft carbon refers to carbon that can be transformed into graphitic structure after high-temperature treatment (more than 2800 °C), and its disordered structure can be eliminated relatively easily, which is also known as readily graphitizable carbon, and its internal microstructure consists of randomly oriented Gr nanocrystals containing 3 - 4 graphitic layers with a more ordered structure and a narrower spacing between layers. This unique microstructure provides multiple paths for Li^+ migration, which in turn provides a characteristic skewed capacity distribution for SC. Compared to hard carbon materials, soft carbon materials show superiority in terms of orderliness, defect and heteroatom content, and electrical conductivity. Cao et al [15] mixed powdered mesophase bitumen and nano CaCO_3 at a weight ratio of 1 : 3.5 and kept the mixture under nitrogen at 800 °C for 2 h. Waiting for the MSC material, the charge/discharge of the MSC electrode was measured for the initial cycle at a constant current density of 30 mA g^{-1} with a reversible capacity of 331 mAh g^{-1} , however, the first time coulombic efficiency of the MSC (45%) was low; about 200 mAh g^{-1} could be maintained after 200 cycles by electrostatic charge/discharge cycling at 50 mA g^{-1} . After treatment, the soft carbon material was also able to exhibit good electrochemical performance.

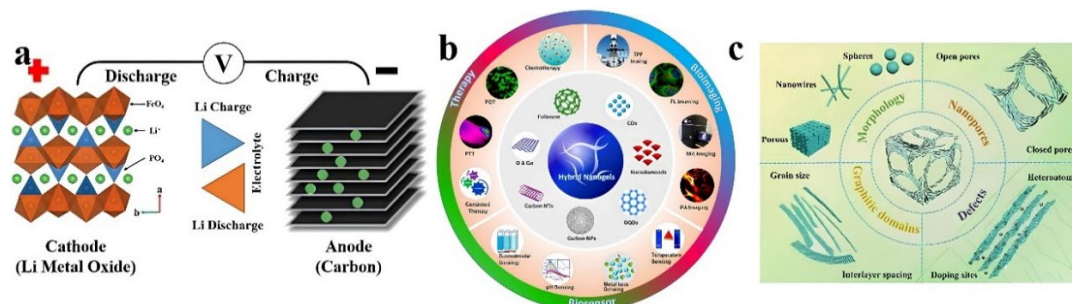


Fig. 1. (a) Schematic diagram of the working principle of lithium-ion batteries, (b) Classification of graphite based carbon materials, (c) Structural characteristics of hard carbon materials.

3. Modification method

3.1 Revitalization stoma

Carbon materials come from a wide range of sources, and are prepared by high-temperature carbonization and activation using various plants, animal dung, animal bones, agricultural and forestry wastes and other carbon-rich materials in nature as precursors. The activation process is a key step in the preparation of organic carbon anode materials, during which the pore structure of the carbon material is formed and the specific surface area increases, which can provide more charge storage sites and is conducive to improving its electrochemical performance. The activation methods are mainly divided into physical activation method and chemical activation method, on the basis of which, template activation method and so on are derived. Porous carbon materials have the advantages of large specific surface area (SSA) and stable chemical structure, which are widely used in the fields of adsorption, phase separation, catalysis and energy storage, etc.

3.1.1 Physical activation method

The physical activation method consists of two steps, carbonization and activation, in which the carbon-rich raw material is firstly heated and treated under the protection of inert gas, and then reamed with water vapor, CO₂, air, flue gas, etc., at about 900°C. The activation process is carried out in an oxidizing gas medium [16].

Park et al [17] prepared graphene oxide (G-O) by the modified Hummers method and reduced G-O with hypophosphorous acid (H₃PO₂) and iodine (I₂), and freeze-dried it to obtain reduced graphene oxide (RG-O). RG-O was heated to 900 °C under N₂ atmosphere, and then stabilized by injecting steam and activating the RG-O samples, and the porous material obtained was denoted by sRG-O (Fig.2.(a)). sRG-O surface area and pore volume were estimated to be 1917 m² g⁻¹ and 11.01 cm³ g⁻¹, respectively. (The surface area and pore volume of sRG-O were estimated to be 1917 m² g⁻¹ and 11.01 cm³ g⁻¹, respectively. 3-D steam-activated macroporous structures provide a large activation surface area, easy access to active sites, and rapid charge and mass transfer; it was also found that mixing one-dimensional carbon nanotubes (CNTs) into the 3-D graphene structure not only greatly improves the stability of the structure but also the stability of the structure. greatly improves the stability of the structure, but also improves the rate and cycling performance.

The cryogenic process is a novel material processing technology, but it is currently less used in carbon negative electrode materials for LIBs. Li et al [18] experimental anode carbon material was obtained by activating hemp stems with a mixing temperature of 500°C. The dried activated carbon was then placed in a cryostat and gradually cooled to -185°C and held for 2 h (Fig. 2.(b)). Then, it was returned to room temperature to obtain the experimental cryogenic carbon material (CAC). The specific surface area of the CAC was 1728 m² g⁻¹ with an average adsorption pore size of 3.547 nm, respectively. The first discharge specific capacity and charging specific capacity of the CAC-500 were 2469.7 mAh g⁻¹ and 1168.1 mAh g⁻¹, respectively. The relatively poor Coulombic efficiency (only about 36%) in the first cycle was related to its large specific surface area, which consumed a large amount of Li⁺ to produce SEI film; however, the discharge curves almost overlapped in the

subsequent 100 cycles (Fig. 3.(c)), which indicated the excellent stability of CAC. The porous carbon electrode produced by the physical activation method has a microporous structure, which restricts the penetration of the electrolyte and has a low surface utilization rate.

3.1.2 Chemical activation method

In the chemical activation process, the specific surface area and pore volume of the biocarbon materials were improved by adding chemical activators (KOH, NaOH, H_3PO_4 and K_2SO_4 , etc.) during calcination and etching the carbon skeleton at high temperatures, which is usually controlled to be activated at a specific temperature, and the residual activators and impurities generated during activation were washed to remove them after the activation process [19]. Chemical activation can better control the pore size distribution and obtain a higher specific surface area than physical activation, which is conducive to increasing the functional groups on the surface of the material, which not only improves the wettability to the electrolyte and reduces the diffusion resistance between the electrode and the electrolyte, but also the functional groups on the surface undergo a rapid Faraday reaction with the electrolyte ions, which increases the extra pseudocapacitance and is conducive to improving the electrochemical performance of the carbon material. Wei et al [20] prepped pig bone samples in a muffle furnace at 450 °C and activated them by impregnating a crucible with KOH reagent in a weight ratio of 1:1 inside a corundum tube under flowing N_2 and heated to 850 °C. The porous carbon prepared from pig bone has a hierarchical pore structure and highly mesoporous/macroporous nature with a surface area and pore volume of 2157 $m^2 g^{-1}$ and 2.26 $cm^3 g^{-1}$, respectively. Elizabeth et al [21] used shrimp shells as the raw material, pre-carbonized and then leached out the acidic impurities in the raw material with NaOH activator to form a porous structure (Fig.3.(d)). The specific surface area of the PSC was 336 $m^2 g^{-1}$, and the main sizes of the pore size of the PSC were in the range of 2~10 nm. Its cycling stability is far beyond that of pure carbon samples, and the cycling lifetime can reach 200 times ($J=0.1 A g^{-1}$). Hanhart et al [22] utilized coffee grounds as a raw material, which was first fully impregnated with the activator iron chloride hexahydrate ($FeCl_3 \cdot 6H_2O$), then graphitized at high temperatures, and the samples were obtained by acid etching (Fig.3.(e)). Removal of activator particles by acid etching creates mesopores in the material. The maximum reversible capacity value is up to 240 mAh g^{-1} . Due to the serious environmental pollution and high cost of activators such as KOH and NaOH, there is a need for high quality activators that are more promising, economical and readily available.

3.1.3 Template activation method

The template activation method usually takes the inorganic material with very small space (nano-scale) as the template, introduces organic polymer into it and then carbonizes it, and then removes the inorganic template (strong acid washing and solubilizing) to obtain the porous material with similar spatial structure with the template. The activated carbon prepared by the template activation method is generally mesoporous activated carbon, and has the advantages of high selective adsorption activity and narrow pore distribution. The template method has great advantages in controlling the size of the material and has great application prospects. Gao et al [23] proposed a new method using oyster shells as template and activator precursor. A sample of asphalt-oyster shell sandwich structure was prepared (Fig.3.(f)). HPC was acid-impregnated with 10 % HCl solution and dried to obtain HPC, which has a high specific surface area (920 $m^2 g^{-1}$), a pore size mainly distributed between 0.7 ~ 6.5 nm and a reasonable interconnecting pore structure, and exhibits a high reversible capacity (1251 mAh g^{-1} at 0.1 A g^{-1}) and a long cycling stability (9.5 mAh g^{-1} after 450 cycles at 1.0 A g^{-1}) when used as an inverse electrode material for LIBs.) and long cycle stability (94 % capacitance after 450 cycles at 1.0 A g^{-1}). Huang et al [24] designed and fabricated an ultra-thick (900 μm) LCO cathode by means of a directed ice template (DIT), which has a coral-like structure containing well-aligned pores (widths ranging from 1.2 to 7.5 μm) in the direction through the electrode thickness (the kinetic direction that facilitates the Li^+ transport during charging and discharging), with a porosity of about 45%, which gives the DIT electrode a high capacity retention rate.

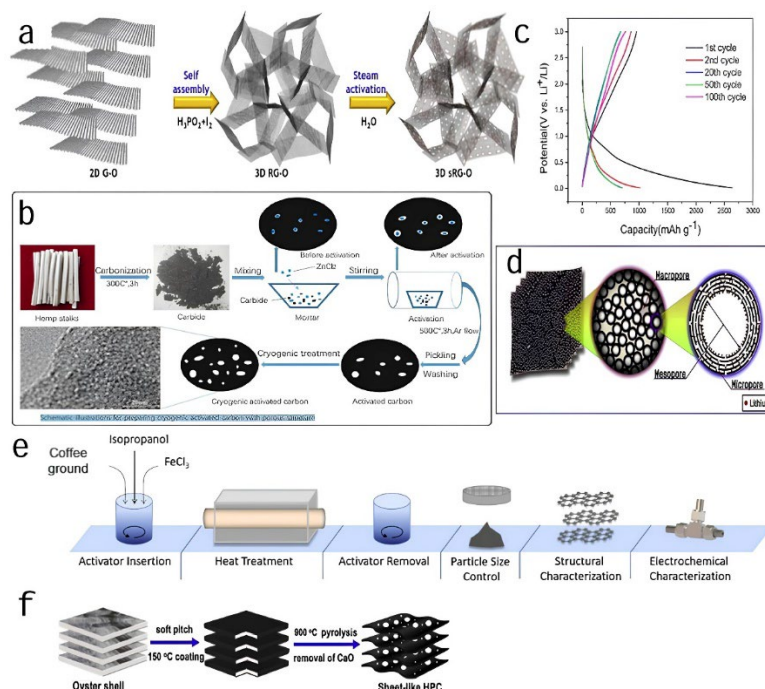


Fig.2.(a) Synthesis of 3D sRG-0 heterostructure. (b) Schematic illustrations for preparing cryogenic activated carbon with porous structure. (c) Charge-discharge voltage curves of CAC-500. (d) Mechanism of Li^+ insertion in PSC. (e) Overview of carbon material synthesis, processing and evaluation in this work. (f) Schematic illustration of synthesis of HPC with oyster shell as both the template and activation agent and soft pitch as the carbon source. (g) DIT process. (h) Representations of stacked 2D image slices after segmentation and 3D rendering of electrode structures made by DIT.

3.2 Heteroatom doping

The construction of porous structure has a significant effect on improving the lithium storage performance of graphite anode. However, introducing a porous structure by enlarging the graphite layer usually introduces a large number of defective structures in the graphite layer, leading to a large amount of irreversible Li^+ storage, which affects the energy storage performance of the material. Therefore, heterogeneous atomic doping is widely regarded as one of the effective and inexpensive means to enhance the electrochemical performance of carbon materials. By introducing different atomic elements, not only the electronegativity of the material can be enhanced, but also the spacing between carbon layers can be increased. In addition, heterogeneous atom doping introduces a large number of defects and active sites, which reduces the energy barrier of the chemical reaction and achieves efficient adsorption of Li^+ . This approach helps to improve the high power charging and discharging capability of the battery. Common doping elements include nitrogen (N), oxygen (O), boron (B), and phosphorus (P). Differences in the distribution and concentration of these elements in carbon materials can significantly affect the performance of the battery.

Doping techniques can be categorized into two main types: (1) Post-processing methods: Hard carbon containing almost no hetero-elements is converted into carbon materials doped with hetero-elements through the interaction of the precursor with a source of heteroatoms. (2) In-situ doping: a method that utilizes the heteroatoms contained in the precursor itself and introduces the heteroatoms directly during the preparation process. As an example of post-treatment method, Gomez et al [25] ball milled and mixed the precursor olivine with urea powder and heated it up to 900 °C to obtain nitrogen doped carbon material (Fig.4.(a)). The energy efficiency of the nitrogen-doped carbon samples remained almost constant with the increase of the charge/discharge specific current until 1860 mAh g^{-1} . However, the cumulative irreversible capacity of the samples over 100 cycles ranged from 500 to 900 mAh g^{-1} , and these materials are more suitable for high-energy applications. However,

the large irreversibility of the storage reaction is still a major drawback and requires continuous improvement. As an example of in situ doping method Guan et al [26] added natural silk to FeCl_3 solution and mixed it and heated it in tube furnace at lower temperature to obtain semi-graphitized sample SGNC (Fig.4.(b)). The prepared SGNC sample has a helical layered structure. The helical structure and high specific surface area allow the electrolyte to access the surface of the active material, thus minimizing the diffusion path of ions. The coupled N-doping and nanopore defects in the helical semi-graphitic carbon can significantly improve the binding and charge transfer capacity for Li^+ , thus enhancing the charge transport kinetics and hence the multiplicative capacity of SGNC. The reversible capacity of SGNC increased steadily over 800 cycles ($431 \text{ mAh g}^{-1} \sim 974 \text{ mAh g}^{-1}$), and this gradual increase in the capacity over the course of the cycling process can be attributed to the fact that graphite nanosheets are gradually activated during the initial cycling, and the number of defects increases as the reaction proceeds, thus providing more active sites for Li^+ storage. Although single-element doped hard carbon materials can improve the electrochemical performance of LIBs to a certain extent, multi-element co-doping can further enhance the electrical conductivity of the electrode materials due to their different structures and bonding modes as compared to multi-element doped hard carbon materials. Liang et al [27] prepared N, O, P ternary doped coal-based layered porous carbon networks (N/O/P-CCNs) by liquid-phase oxidation combined with self-assembly using coal-based graphite as the raw material and Melamine and Phytic acid as the modifiers. The initial charge-specific capacity of the N/O/P-CCNs was 1079 mAh g^{-1} , which indicated that the multi-element doping synergistic effect is more favorable to improve the storage capacity of Li^+ , the lithium storage mechanism (Fig.4.(c)). The reversible capacity of N/O/P-CCNs negative electrode after 100 cycles (482 mAh g^{-1}), the capacity retention rate is close to 100%. The N/O/P-CCNs negative electrode can be used for the storage of Li^+ , the lithium storage mechanism (Fig.4.(c)), the lithium storage mechanism (Fig.4.(c)). Besides, metal atoms can also be involved in the doping modification.

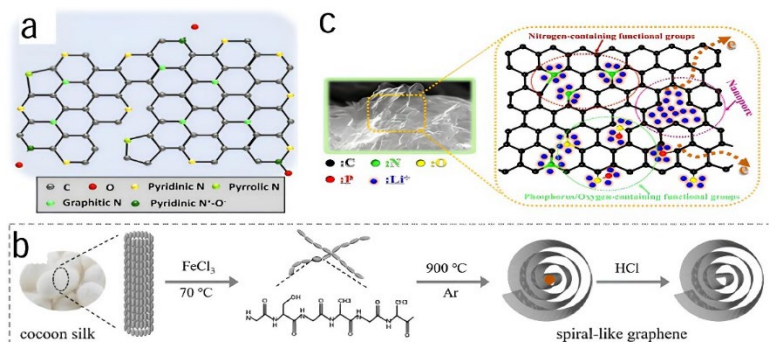


Fig.3.(a) Schematic structure of nitrogen-doped graphene monolayer.(b) Schematic illustration of the preparation process for the SGNC.(c) The schematic diagram of lithium storage mechanism of the N/O/P-CCNs.

3.3 Material composite

Carbon-based anode material is considered an excellent carrier for Li^+ due to its high conductivity, stable structure, and low cost. However, due to its low theoretical capacity (372 mAh g^{-1}) and the graphite flake layer's tendency to dissolve in the electrolyte solution, it fails to meet the market demand. Another example is metal oxides, SiO_2 , Mxene, MOF and other materials, although the theoretical capacity is high, but its lithiation and delithiation process is accompanied by huge volume changes and negative electrode stress, after many cycles will lead to particle fragmentation, generating a thicker SEI film, hindering ion transport, increasing irreversible capacity, and decreasing multiplier performance. In order to overcome the shortcomings of a single material, synthesize the advantages of several different materials, and strengthen the synergistic effect, we have prepared composite structural carbon materials by coating a layer of pyrolytic carbon on the surface of man-made graphite, silicon-based, and metal-oxide matrices, forming a “core-shell structure”[28]. In addition to improving the overall electrochemical performance, the cost is reduced as pyrolyzed

carbon replaces a portion of the base material. The material used for the experiments by Wu et al [29] was CFs reinforced carbon matrix composites with a unique core-shell structure, with carbon fibers (CFs) as the core and chemical vapor deposition pyrolytic carbon (PCs) as the layered shell (Fig. 4.(a)). Li^+ was preferentially adsorbed on the defects, edges, and microporous surfaces and then inserted into the graphite lattice (Fig. 4.(b)). The CFs were cycled at 0.5 C. The capacity retention rate was 80 % after 350 cycles, and the average Coulombic efficiency was as high as 99.7 %; the CFs electrode had a high discharge specific capacity of 235 mAh g^{-1} at 0.1 C, and was maintained at 166 mAh g^{-1} at 2 C, as shown in Fig. 2.(c). The PC layer on the CFs buffered the volume expansion induced by the embedding of Li^+ , covered the interstitial space and the defects, reducing the specific surface area and electrolyte consumption, and realizing the high Coulombic efficiency and good cycling performance of the electrode.

Composite carbon materials with a core-shell structure have been prepared using a layer of amorphous carbon material coated on the surface of a silicon-based anode material (Fig. 2.(e)). Yang et al [30] mixed silica nanopowder, flake graphite and asphalt together for ultrasonication and after drying, heat treatment was applied at 850°C to obtain the composite SGP, which was then ultrasonically mixed with LiF to obtain the experimental sample SGP@LiF (Fig. 2.(d)). The pitch carbon layer formed by asphaltene carbon can buffer the large volume change during charging and discharging and form an electronic network between the active material and the conductive agent to provide sufficient electronic conductivity. The LiF particles are beneficial to the formation of a stable SEI layer and reduce the interfacial side reactions. The initial reversible specific capacity of SGP@LiF was 630 mAh g^{-1} , respectively, and the initial coulombic efficiency reached 83 %; the capacity retention rate of 82.3 % was still maintained after 100 cycles; at current densities of 0.2 - 4 A g^{-1} , it was concluded that SGP@LiF had a high capacity at high current densities, and an excellent capacity recovery ability at low current densities.

Metal oxides (MOs) have received widespread attention due to their high theoretical capacity, low cost, and high density. However, graphitic carbon encapsulated MOs nanoparticles do not have enough cavities to accommodate large volume changes during lithiation/delithiation, which usually leads to the rupture of the carbon coating. In contrast, the void space between shell and shell in the yolk-shell structure can withstand the volume change of the active body core during the lithiation/delithiation process, and the shell plays the role of keeping the crushed core still integrated (Fig. 2.(e)). Due to sufficient internal buffer space, the yolk-shell structure allows for ultra-long lithium storage cycle life, accompanied by high specific capacity and high multiplicity performance [31]. SnO_2 -based materials with a theoretical capacity of 782 mAh g^{-1} have been intensively explored and utilized, and are considered ideal anode materials to replace commercial graphite. Liu et al [32] vacuumed a sealed vessel containing three-dimensional multilevel carbon-based nanocages (hCNC) before filling it with an ethanol solution of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ and subsequent treatment to obtain SnO_2 @hCNC (Fig. 2.(f)). SEI film formation process and tin nanoparticles in the sample. For pristine SnO_2 , the CV curves have two anodic peaks at 0.63 and 1.31 V (while SnO_2 @hCNC drops to 0.52 and 1.25 V, respectively). The lower polarization indicates a better reversible reaction between SnO_2 and Li^+ . At 1 A g^{-1} , SnO_2 @hCNC showed a high initial specific charge capacity of 1018 mAh g^{-1} , which was maintained at 792 mAh g^{-1} after 600 cycles with a capacity retention of 77.8 %.

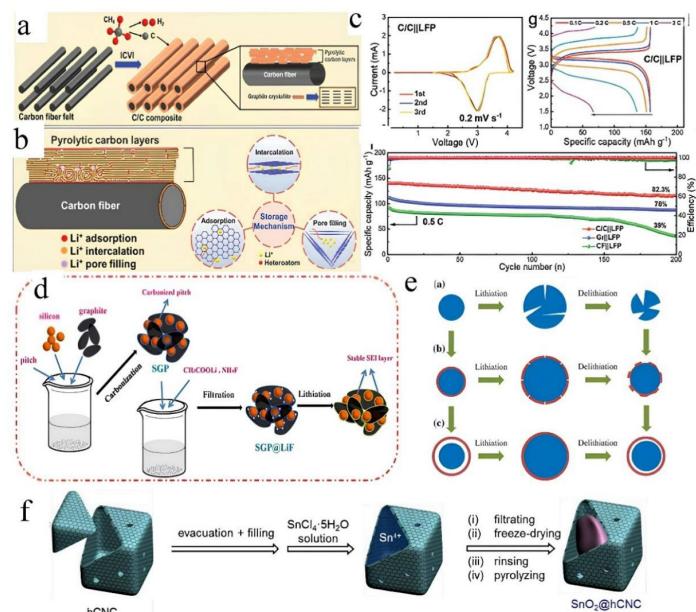


Fig. 4. (a) Schematic illustration for the synthesis of C/C composite employing ICVI technique.(b)Schematics of Li^+ ions storage mechanism in C/C composite.(c) CV curves, GCD profiles, cycling performance at 0.5 C.(d) Schematic illustration of the SCP@LiF synthesis.(e) Uncapsuled, core-shell structure, schematic diagram of yolk shell structure.(f) Schematic illustration of the preparation. Route : the evacuation-filling process.

4. Conclusion

The performance of batteries in energy storage systems is extremely dependent on the electrochemical properties of electrode materials. This review analyzes the insertion/de-embedding mechanism of LIBs and the classification of carbon-based anode materials, which can be broadly classified into graphite-based carbon materials and non-graphite-based carbon materials; the performance of LIBs can be effectively enhanced by modifying the carbon anode materials, such as improving their specific capacitance, first-time coulombic efficiency, charging and discharging efficiencies, multiplicative performance, cycling stability, and prolonging the service life, and so on. The methods and mechanisms of modification mainly include activated porosity, heterogeneous atom doping and material composite.

However, there are still some issues of carbon anode materials that need to be further explored, such as (1) the mechanism of the role of modified doping mode of other carbon materials must be further explored, (2) the value of the prepared carbon materials in the application of other future energy storage devices needs to be further confirmed, and (3) the mechanism of the microscopic reactions occurring at the electrode surface interface needs to be further investigated in depth.

Many breakthroughs have been made in carbon-based anode materials, but they still face challenges such as low theoretical capacity, high irreversible capacity, low energy density, etc., and it is difficult to synthesize carbon materials with the desired structure and morphology at large scale and low cost. Therefore, the main research direction in the future will be to develop carbon-based anode materials with excellent recyclability, high energy capacity, large-scale production and low cost.

References

- [1] R. Clément, K. Hatzell, Y.-K. Sun, Recent Advances in Battery Safety and Recycling. A Virtual Issue, ACS Energy Lett. 8 (2023) 4524–4527.
- [2] X. Yang, Y. Peng, J. Hou, Y. Liu, X. Jian, A review for modified Li composite anode: Principle, preparation and challenge, Nanotechnology Reviews 9 (2020) 1610–1624.

- [3] K. Nobuhara, H. Nakayama, M. Nose, S. Nakanishi, H. Iba, First-principles study of alkali metal-graphite intercalation compounds, *Journal of Power Sources* 243 (2013) 585–587.
- [4] X. Wu, X. Yang, F. Zhang, L. Cai, L. Zhang, Z. Wen, Carbon-coated isotropic natural graphite spheres as anode material for lithium-ion batteries, *Ceramics International* 43 (2017) 9458–9464.
- [5] I.E. Monje, N. Sanchez-Ramirez, S.H. Santagneli, P.H. Camargo, D. Bélanger, S.B. Schougaard, R.M. Torresi, In situ-formed nitrogen-doped carbon/silicon-based materials as negative electrodes for lithium-ion batteries, *Journal of Electroanalytical Chemistry* 901 (2021) 115732.
- [6] H. Chen, S. He, X. Hou, S. Wang, F. Chen, H. Qin, Y. Xia, G. Zhou, Nano-Si/C microsphere with hollow double spherical interlayer and submicron porous structure to enhance performance for lithium-ion battery anode, *Electrochimica Acta* 312 (2019) 242–250.
- [7] F. Qiao, J. Wang, Y. Zhu, X. Tan, X. Wang, Q. An, Cheese-like porous SnP2O7 composite as a long-life and high-rate anode material for potassium-ion batteries, *Chemical Engineering Journal* 439 (2022) 135777.
- [8] W. Yan, Z. Chen, S. Ma, S. Chen, Y. Lu, M. Wang, L. Chen, Q. Huang, B. Wang, Y. Su, J. Wang, N. Li, F. Wu, Unraveling the relationship between the mineralogical characteristics and lithium storage performance of natural graphite anode materials, *Carbon* 227 (2024) 119270.
- [9] J. Wang, M. Chen, C. Wang, B. Hu, J. Zheng, Amphiphilic carbonaceous material modified graphite as anode material for lithium-ion batteries, *Materials Letters* 64 (2010) 2281–2283.
- [10] S.-M. Lee, D.-S. Kang, J.-S. Roh, Bulk graphite: materials and manufacturing process, *Carbon Letters* 16 (2015) 135–146.
- [11] P. Simon, Y. Gogotsi, Capacitive Energy Storage in Nanostructured Carbon–Electrolyte Systems, *Acc. Chem. Res.* 46 (2013) 1094–1103.
- [12] K. Yu, Y. Wang, X. Wang, W. Liu, J. Liang, C. Liang, Preparation of porous carbon anode materials for lithium-ion battery from rice husk, *Materials Letters* 253 (2019) 405–408.
- [13] B. Cao, H. Liu, B. Xu, Y. Lei, X. Chen, H. Song, Mesoporous soft carbon as an anode material for sodium ion batteries with superior rate and cycling performance, *J. Mater. Chem. A* 4 (2016) 6472–6478.
- [14] X. Ji, Y. Wei, H. Yang, Z. Lu, S. Jin, H. Jin, X. Kong, H. Ji, Extended Plateau Capacity of Hard Carbon Anode for High Energy Lithium-Ion Batteries, *Small* n/a (n.d.) 2402616.
- [15] B. Cao, H. Liu, B. Xu, Y. Lei, X. Chen, H. Song, Mesoporous soft carbon as an anode material for sodium ion batteries with superior rate and cycling performance, *J. Mater. Chem. A* 4 (2016) 6472–6478.
- [16] Synthesis of 2D Co-MOF Nanosheets and Low-Temperature Calcination Activation for Lithium-Ion Batteries, (n.d.).
- [17] S.K. Park, K. Choi, S.-H. Lee, I.-K. Oh, S. Park, H.S. Park, CNT branching of three-dimensional steam-activated graphene hybrid frameworks for excellent rate and cyclic capabilities to store lithium ions, *Carbon* 116 (2017) 500–509.
- [18] Z. Li, Z. Guan, Z. Guan, C. Liang, K. Yu, Effect of Deep Cryogenic Activated Treatment on Hemp Stem-Derived Carbon Used as Anode for Lithium-Ion Batteries, *Nanoscale Res Lett* 15 (2020) 193.
- [19] Z. Zhao, S. Das, G. Xing, P. Fayon, P. Heasman, M. Jay, S. Bailey, C. Lambert, H. Yamada, T. Wakihara, A. Trewin, T. Ben, S. Qiu, V. Valtchev, A 3D Organically Synthesized Porous Carbon Material for Lithium-Ion Batteries, *Angewandte Chemie International Edition* 57 (2018) 11952–11956.
- [20] S. Wei, H. Zhang, Y. Huang, W. Wang, Y. Xia, Z. Yu, Pig bone derived hierarchical porous carbon and its enhanced cycling performance of lithium–sulfur batteries, *Energy Environ. Sci.* 4 (2011) 736.
- [21] I. Elizabeth, B.P. Singh, S. Tripathi, S. Gopukumar, Bio-derived hierarchically macro-meso-micro porous carbon anode for lithium/sodium ion batteries, *Journal of Power Sources* 329 (2016) 412–421.
- [22] V. Hanhart, L. Frankenstein, J. Ramirez-Rico, V. Siozios, M. Winter, A. Gomez-Martin, T. Placke, Insights into the Impact of Activators on the ‘Catalytic’ Graphitization to Design Anode Materials for Lithium Ion Batteries, *ChemElectroChem* 9 (2022) e202200819.
- [23] F. Gao, C. Geng, N. Xiao, J. Qu, J. Qiu, Hierarchical porous carbon sheets derived from biomass containing an activation agent and in-built template for lithium ion batteries, *Carbon* 139 (2018) 1085–1092.

- [24] C. Huang, P.S. Grant, Coral-like directional porosity lithium ion battery cathodes by ice templating, *J. Mater. Chem. A* 6 (2018) 14689–14699.
- [25] A. Gomez-Martin, J. Martinez-Fernandez, M. Rutttert, M. Winter, T. Placke, J. Ramirez-Rico, An electrochemical evaluation of nitrogen-doped carbons as anodes for lithium ion batteries, *Carbon* 164 (2020) 261–271.
- [26] X. Guan, J. Xia, Z. Wei, Y. Xing, J. Guan, S. Yin, H. Zhou, F. Han, S. Zhang, P. Yang, Spiral semi-graphitic nitrogen-doped carbon anode for fast charging lithium-ion batteries, *Carbon* 225 (2024) 119143.
- [27] H. Liang, H. Zeng, B. Xing, L. Feng, Z. Chen, H. Guo, B. Xu, X. Qu, C. Zhang, R. Li, N/O/P ternary-doped coal-based hierarchical porous carbon networks for high lithium-ion storage performance, *Journal of Alloys and Compounds* 968 (2023) 172015.
- [28] X. Shi, S. Liu, B. Tang, X. Lin, A. Li, X. Chen, J. Zhou, Z. Ma, H. Song, SnO₂/TiO₂ nanocomposites embedded in porous carbon as a superior anode material for lithium-ion batteries, *Chemical Engineering Journal* 330 (2017) 453–461.
- [29] H. Wu, L. Wei, W. Li, C. Shi, X. Yao, Q. Fu, H. Li, X. Guo, Highly Conductive Carbon/Carbon Composites as Advanced Multifunctional Anode Materials for Structural Lithium-Ion Batteries, *Advanced Functional Materials* n/a (n.d.) 2403729.
- [30] Y. Yang, Z. Wang, G. Yan, H. Guo, J. Wang, X. Li, Y. Zhou, R. Zhou, Pitch carbon and LiF co-modified Si-based anode material for lithium ion batteries, *Ceramics International* 43 (2017) 8590–8595.
- [31] X. Jia, H. Li, B. Huang, J. Yang, Y. Li, Monodisperse yolk-shell SnO₂/C submicron spheres fabricated through a facile process as an anode material for lithium-ion batteries, *Advanced Powder Technology* 34 (2023) 104056.
- [32] M. Liu, H. Fan, O. Zhuo, J. Chen, Q. Wu, L. Yang, L. Peng, X. Wang, R. Che, Z. Hu, A general strategy to construct yolk-shelled metal oxides inside carbon nanocages for high-stable lithium-ion battery anodes, *Nano Energy* 68 (2020) 104368.