

Carbon-based Anode Nanomaterials for Lithium-Ion Battery

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Abstract. In consideration of environmental protection, more and more countries in the world put the issue of sustainable development on the agenda while lithium-ion battery (LIB) plays a crucial part in this process. In addition, carbon based nanomaterials are characterized as diverse types of materials that are produced in a variety of characteristics. Due to the large specific surface area, great electronic and mechanical qualities, variable chemical functionality as well as wide potential window they own, carbon nanomaterials have been studied and developed as anode materials for LIB to enhance its performance. In this paper, the basic structure, main properties together with the synthesis methods that are related to carbon nanomaterials including CNTs, graphene and CNSs are presented. In addition, these potential candidate materials for anode materials of LIBs are also summarized and discussed. The main functions and the importance of synergy between active electrode species and carbon nanomaterials are emphasized.

Keywords: Nanotechnology, carbon, anode materials, LIB.

1. Introduction

Nowadays, LIB is developing rapidly to meet people's expectations of reducing environmental pollution and create a sustainable society. At present, the main development direction of LIB is to improve the anode materials thus enhance the battery capacity, efficiency and other performance. Many discovered materials such as metal alloys have been used as LIB anode. However, those materials have shortages like low specific capacity, poor conductivity, and low ion transport rate. Since nanotechnology can promote the development of existing technology and even produce innovation, it has been widely used as electrode material for preparing anode of LIB battery. The combination of carbon and nanotechnology has had a profound impact on the beginning of a new era of batteries. Carbon nanomaterials have great potential in improving LIB performance due to their unique nanostructure, excellent charge transfer, high specific surface area, low mass density and adjustable chemical function and morphology. Therefore, one of the potential materials to solve the existing problems of LIB is the advanced nanotechnology of the rich carbonaceous materials on the earth. Because they can provide a large number of lithium ion storage points and fast ion diffusion channels, Carbon nanomaterials is superior to conventional carbon materials such as graphite electrode in LIB performance. In addition, effective structural modification can provide carbon nanoparticles with better electrochemical performance.

In this paper, the structure and possible LIB applications of carbon nanomaterials are discussed. Advantages as well as disadvantages of each advanced carbon nanomaterials are introduced. In order to manufacture LIB with better performance, the production potential of various composite anode materials based on carbon nanomaterials was also emphasized.

2. Carbon-based Anode Nanomaterials

Carbon nanomaterials are sp² conjugated carbon-based materials with nanometer size. Because of their unique nanostructure and excellent chemical and physical properties, carbon nanomaterials have received considerable attention. They can be divided into three categories according to their dimensions. Carbon nanotubes, graphene and carbon nanospheres are their representative materials. Depend on their shape and structure, carbon nanomaterials' properties can be controlled by corresponding synthesis methods. The results reveal the properties of carbon nanomaterials in different dimensions.

2.1. 1D material - Carbon nanotube

2.1.1. Basic structure & main property

CNT is a 1D structural material with tubular shape and it has two types: single-walled carbon nanotubes (SWCNT), and multi-walled carbon nanotubes (MWCNT). In SWCNT, every carbon atom is covalently bonded with other three adjacent carbon atoms via sp^2 molecular orbital and thus form a hexagonal lattice. And a delocalized π -band is created when the fourth valence electron in the p_z orbital hybridizes with all the others.

The structure of CNT makes it have unique conductive characteristics. Some conductive properties show relatively high conductivity, and can be adjusted to the properties of conductors or semiconductors. The band gap of semiconductor CNT ranges from 1.80eV to 0.18eV [1]. In addition, CNT also has excellent thermal conductivity. There are reports show that the thermal conduction property of CNT is at least five times larger than that of silver, which has the highest thermal conductivity among metal. However, the atomic arrangement, tube structure, structural defects as well as impurities can affect thermal characteristics of CNT [2]. In addition, CNT also has outstanding mechanical properties. The CNT modified by heteroatoms doping, donors or acceptors to generate holes and electrons can change the charge distribution on it, and improving its performance in many aspects. Therefore, CNT is considered as one of the candidate materials for LIB.

2.1.2. Methods of synthesis

To prepare CNT, various methods have been developed. Three main CNT synthesis techniques have recently been developed, all of which rely heavily on gas-phase plasma processes. Arc discharge and laser ablation were two earlier common high-temperature methods. However, high-temperature technologies are currently being replaced by low-temperature processes like chemical vapor deposition (CVD) techniques. In addition, CVD allows precise control of the synthesis parameters of CNT like length, diameter, purity, orientation etc.

CVD is widely used in the synthesis of CNT and has reached the industrial production level. In addition, CVD has been considered as the most common method to produce heteroatom-doped CNTs. Among various CVD technologies, catalytic chemical vapor deposition (CCVD) is one of the most commonly used methods of CNT synthesis [3]. During the process of CCVD, the catalyst is first deposited on the substrate, and then nucleated by chemical etching or thermal annealing. After that, a tubular reactor where the substrate is placed in is heated to 650-1200°C to gasify the incoming hydrocarbon. The compound of formed hydrocarbon gas as well as buffer gas flows to the surface of catalyst to make CNT grow on the catalyst. As shown in Fig. 1, CNT is able to grow on the top or bottom of catalyst particles. In this method, CNT could grow on a pre-designed substrate to form the desired structure.

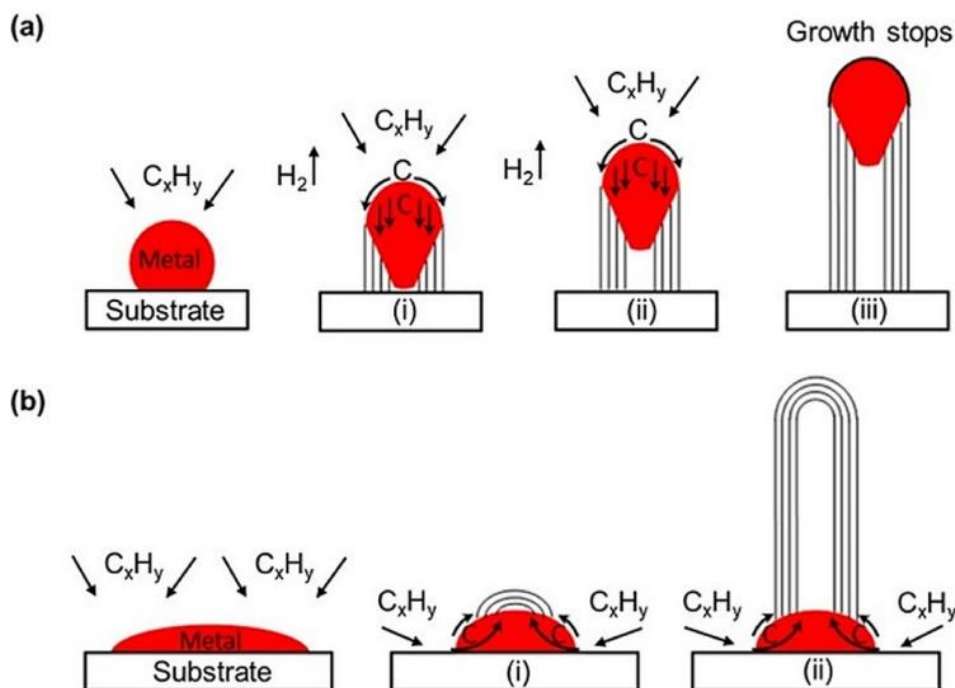


Figure 1. Different model of CNT growing a) Top-growth and b) Bottom-growth [4]

2.1.3. CNT basal anode

Compared with graphite (320 mAh g^{-1}), SWCNT ($300\text{--}600 \text{ mAh g}^{-1}$) has a larger specific capacity. Through mechanical and chemical treatment of structural defects of SWCNT, the reversible capacity of LIB can be increased to 1000 mAh g^{-1} [5]. Due to the multi-layer structure of MWCNT, Li ions have additional connection positions for embedding on the interior or exterior of the hollow tube body by defects or the ends on its walls. However, although CNTs have shown excellent performance in LIB anode applications, there are still some disadvantages, such as high irreversible capacity as well as the lack of stable voltage due to uneven structural parameters such as diameter and number of layers. Therefore, directly using pure CNT as LIB anode material is difficult. However, composite materials can improve the performance of CNT through synergistic effect between hybrid materials and the hollow structure of CNT.

One effective way to enhance CNT anode materials is heteroatom doping. By doping with heteroatom, excellent electrochemical performance of CNT has been obtained due to the synergistic effect, which leads to the rapid conductive rate of electrons or Li ions. Besides, CNT may be utilized to build novel CNT/metal nanoparticle composites by acting as a support material, the composite benefits from the high Li capacity of metal nanoparticles. Metal nanoparticles deposited on the internal or external area of the support material. They do not prevent Li ions from inserting into CNT, because they can combine with Li to form alloy. T. Hou et al. prepared the LIB anode material of MWCNT and ZnS nanoparticles (CC-ZnS/CNT) by covalent coupling technology (Fig. 2 (a)) [6]. Fig. 2 (b-c) show that the material has excellent rate capacity and excellent capacitance (1110 mAh g^{-1}) at 0.1 Ag^{-1} , and its coulombic efficiency is about 60%. Since MWCNT and ZnS nanoparticles have a strong covalent coupling, CC-ZnS/CNT has good long-term cycle stability, and can still provide 333 mAh g^{-1} reversible capacity after 4000 cycles at 2 Ag^{-1} (Fig. 2 (d)). This strategy offers a new direction for the application of CNT in LIB negative electrode materials. Its most significant advantage is to allow the negative electrode materials to use the high Li capacity of metal to avoid electrode breakage.

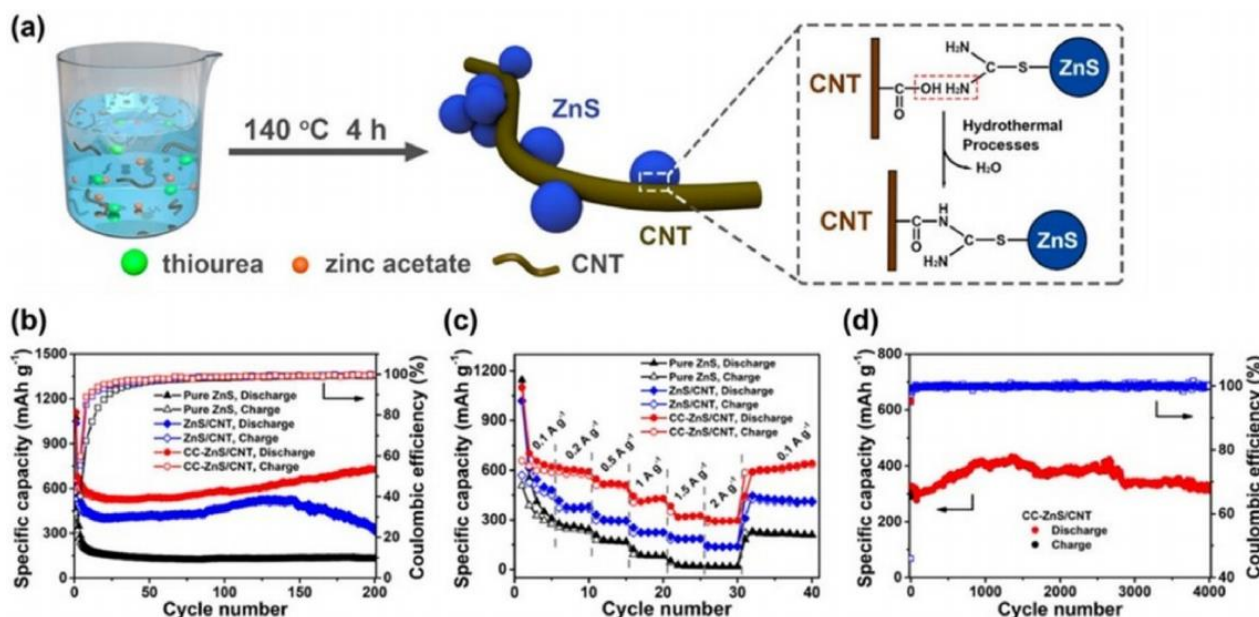


Figure 2. a) CC-ZnS/CNT synthesis illustration. b) CC-ZnS/CNT, ZnS/CNT, and pure ZnS cycling performance. c) CC-ZnS/CNT, ZnS/CNT, and pure ZnS rate capability at different current densities. d) long-term effectiveness of CC-ZnS/CNT [6]

In recent years, people have tried to build CNT with core@shell structure to produce LIB anode with good performance. CNT with the structure of core@shell can have metal nanoparticles inside or metal coating deposition on its outer surface. By combining the benefits of the CNT@metal materials together with the core@shell structure, such as increasing in the capacity of Li of metal alloy materials and preventing the metal anode material from being crushed of the CNT support matrix, people can produce the expected LIB anode. Additionally, because to its large theoretical capacity (4200 mAhg⁻¹) and low charge/discharge potential, the application of Si in LIB anode materials has raise wide attention. However, since the serious change in volume of Si during the charging/discharging process and the instability of the solid electrolyte interface (SEI), its application is limited. J, Fu et al. reported a ultra-thin Si/CNT LIB anode that can be applied to LIB anode was prepared by electrodepositing Si thin layer on CNT [7]. Si/CNT composites exhibit excellent volume capacity ($\sim 1400 \text{mAhcm}^{-3}$) at high current density (200mAhg⁻¹). The anode material with increased mechanical strength through CNT network can stabilize the conductive network of Si to improve cycle performance and prevent Si from cracking on Si@C-CNT anode. In addition, CNT improves the conductivity of the electrode while inhibiting the change in volume of Si. Therefore, the Si@C-CNT anode maintains 70% high capacity after 40 cycles, showing excellent cycle stability. In addition, when cyclic voltammetry curve is arranged from 0.02 to 2V and the scanning speed is 0.05mV/s, the addition of CNT leads to the transfer of SEI formation. And Si@C Compared with 0.32 V, its SEI formation transferred to 0.6 V.

2.2. 2D material - Graphene

2.2.1. Basic structure and main property

Graphene is the thinnest two-dimensional carbon structure, which refers to a single atomic layer of graphite. Huge specific surface area (2630 m²g⁻¹), significant thermal conductivity (about 5000Wm⁻¹K⁻¹) and large Young's modulus (about 1.0 TPa) are the main properties of graphene, and its structure determines all the above properties [8]. In graphene, the three adjacent carbon atoms are connected by the sp² hybrid orbital, which makes them to form a hexagonal lattice on the two-dimensional plane and strong σ bonds between the carbon atoms. The π bonds on each carbon atom together form the delocalized electrons network while σ bonds together form the basic structure of graphene.

The quantity of carbon layers that make up the material determines the final form of a product. Graphene can be typically classified through the number of its layers. There are also graphene derivatives like reduced graphene oxide (rGO) and graphene oxide (GO). One of graphene's most important properties is the electrical structure of it, which significantly impact on electronic conductivity within it. Comparing single-layer (SLG) or bi-layer (BLG) to metals and semiconductors, certain special properties are offered. Low temperature ambipolar properties of SLG allow the charge carriers to switch between electrons and holes. SLG is now appropriate for use in electronic storage applications due to its distinctive characteristics. On the contrary, few-layer (FLG, 3-5 layers) or multilayer graphene (MLG, 3-10 layers) do not exhibit semiconductor properties. They have more significantly metallic structure as more layers are added. As a result of its excellent ability to be functionalized by various covalent and non-covalent modifications, FLG has a surface area that is quite high and nearly identical to that of SLG [9]. This allows it to be soluble in a variety of solvents. Due to its good electrochemical properties, FLG has also been successfully applied to LIB anode materials.

2.2.2. Methods of synthesis

Synthesis method of graphene in the early days is mechanical exfoliation of graphite. However, in recent years, researchers have been trying to improve or propose methods of producing graphene. There are two types of methods in graphene synthesis: top-down methods and bottom-up methods. Top-down synthesis method is used to produce graphene from graphite materials, including exfoliation, unzipping of CNT etc. The bottom-up method is to decompose the organic precursor molecules, and then place the decomposition products in appropriate positions to produce graphene. In recent years, researchers have made significant progress in bottom-up synthesis methods such as solution plasma process (SPP) and chemical vapor deposition (CVD).

Exfoliation is the earliest method in graphene production, but it is also difficult to realize massive manufacture. In addition, CVD can produce high-quality graphene through a single-step, and this method is suitable for massive manufacture [10]. The CVD method of graphene synthesis is similar to that of CNT. During the procedure, biomass or hydrocarbon gases are first broken down in order to make graphene layer grow on metal catalyst at high temperatures (650-1000°C). The metal catalyst's hot surface causes the dissociation of the carbon precursor to form free hydrogen and carbon atoms. Diffusion of the carbon atom across the surface makes it to deposit on the metal catalyst once reaching the carbon solubility limit, where a graphene layer is formed. The two most popular catalysts for thermal CVD-based graphene synthesis are Cu and Ni. However, its disadvantages including high cost and the need for additional purification to get rid of catalyst residue and producing other substrates instead of graphene.

2.2.3. Graphene basal anode

The theoretically highest capacity of Li storage of graphene sheet is 1488 mAh g⁻¹ with a thickness of 0.7 nm according to the density of state calculation. Although graphene has excellent conductivity, the few defects on the surface of graphene substrate are the only way for lithium diffusion in some cases, which will limit the diffusion of Li and reduce the conductivity. However, graphene with more defects can enhance the conductivity to solve this problem, such as GO and rGO. D. Pan et al. discussed the impact of disordering on the electrochemical performance of graphene-based materials as LIB anode [11]. The images of rGO ultra-thin nanosheets with a domain size of 5 nm are shown in Fig. 3(a-b). The formation of irreversible SEI on carbonaceous materials is depicted in Fig. 3(c-1). Fig. 3 (c-2) demonstrates the reversible lithium ion storage mechanism in graphene defects and edges, demonstrating how the amount of defects affects a material's capacity. Lithium stored in the area within graphene layers is shown in Fig. 3(c-3) According to the electrochemical data in Fig. 3(d)-(f), disordered graphene rGO can improve the LIB's cycle stability and capacity. Higher levels of disorder in the samples increase their capacity. This discovery shows that lithium is mainly in the defects of graphene anode materials.

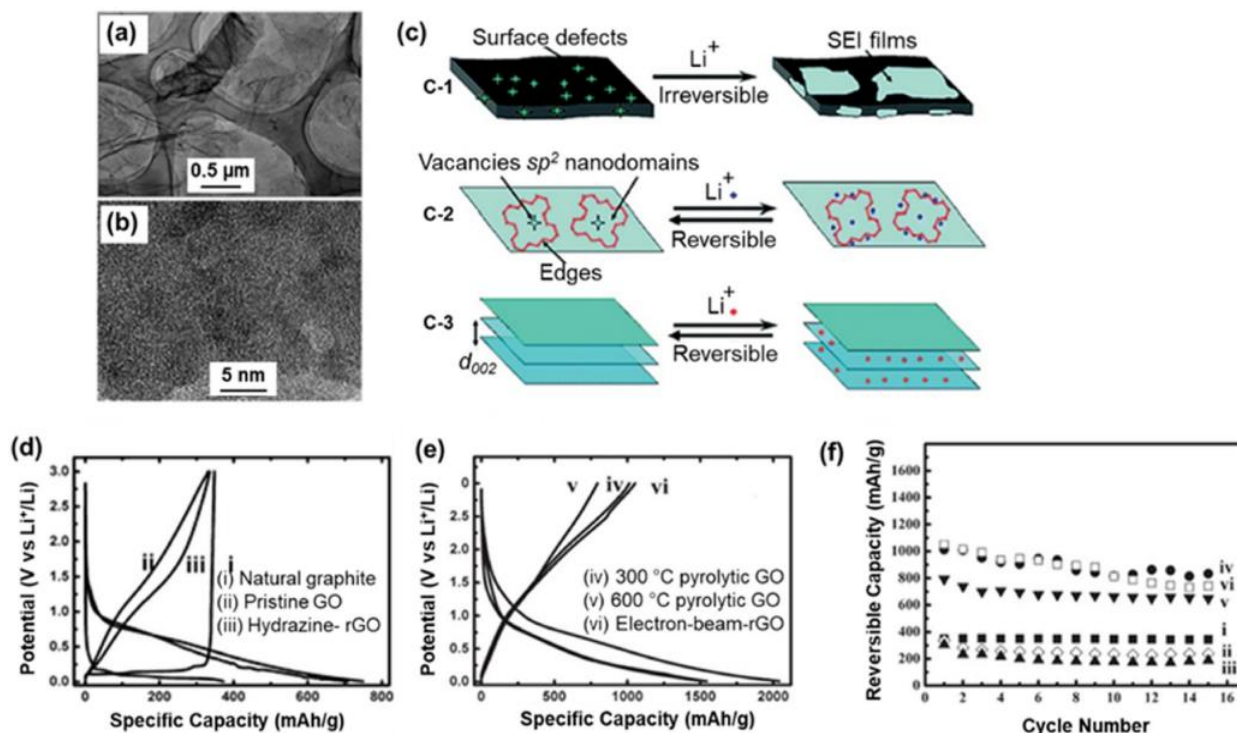


Figure 3. a) The TEM image of rGO. b) The HRTEM image of rGO. c) Reversible Li storage, irreversible SEI formation, reversible Li storage at edge sites. d)-f) rGO anode performance in LIB test [11]

Heteroatom doping is another effective method to adjust the chemical, physical and electrical properties of graphene. The charge transfer ability of graphene can be changed by changing the parameters like type and concentration of dopants. Heteroatom doped graphene can improve the electrode properties such as lithium storage capacity, charge/discharge capacity during the first cycle and cycle performance by enhancing the transport between active sites and Li. C. Ma et al. discussed the Li storage capacity at graphene nitrogen doped graphene, pyridine nitrogen doped graphene and pyrrole nitrogen doped graphene, as shown in Fig. 4 (a) [12]. The hybrid peak in pyridine and graphitic nitrogen doped graphene is shown in Fig. 4 (b). Compared with graphitic N-doped structure, which does not have higher hybrid peak, it is significantly increased in pyridine N-doped graphene. Binding energy of Li and pyridine N-doped graphene (1.37eV) is also higher than that of Li and graphite nitrogen doped graphene (0.95eV). When 9 Li atoms are embedded, the pyridine nitrogen doped structure provides the highest Li atom adsorption voltage among the others, as shown in Fig. 4(c). In addition, the reversible capacity of pyridine nitrogen doped structure (1262 mAhg^{-1}) is also higher than that of graphite N-doped (1087 mAhg^{-1}) and pyrrole N-doped (1198 mAhg^{-1}) graphene. Therefore, pyridine N-doped graphene is most suitable for lithium storage.

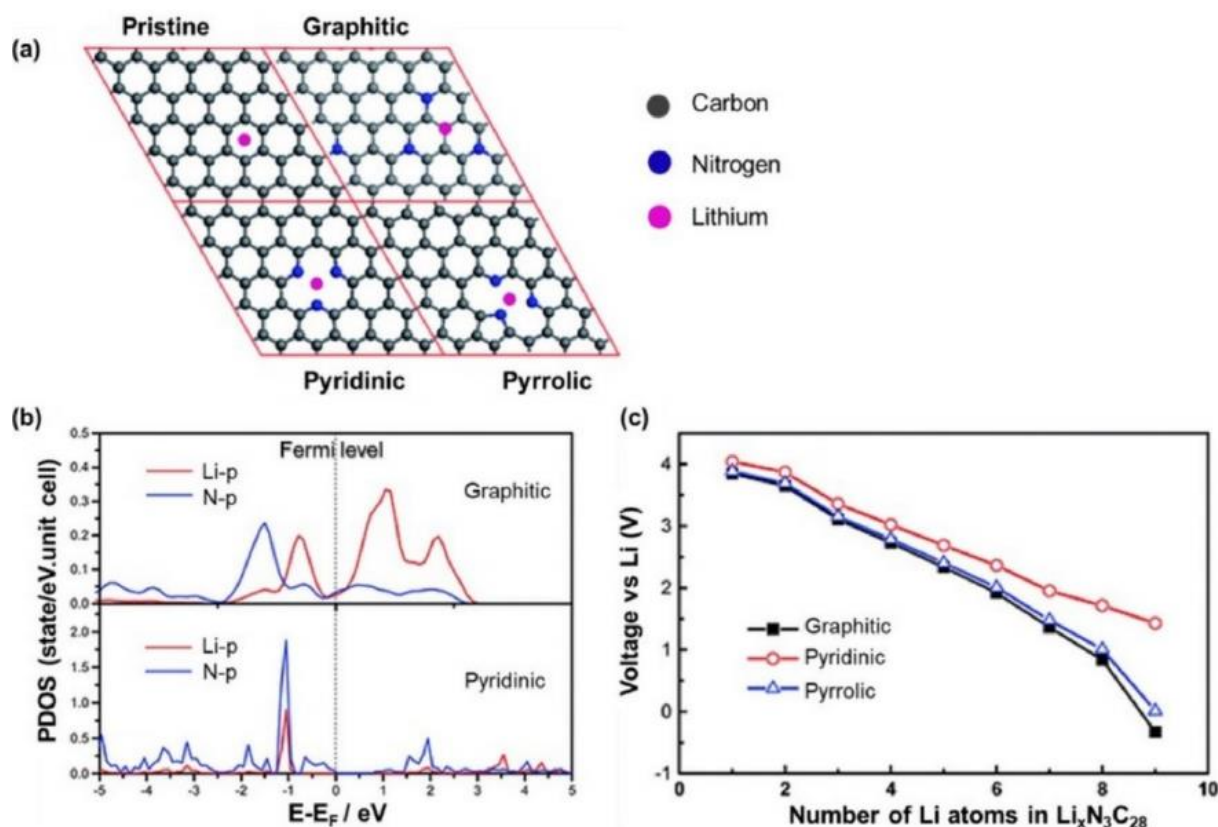


Figure 4. a) The most stable Li atom adsorption locations in different graphene. b) The partial density of states (PDOS) in pyridinic N-doped structure and graphitic N-doped structure c) The voltage distribution of Li embedding in pyridinic, pyrrolic, and graphitic structure [12]

2.3. 3D materials-Carbon nanospheres

2.3.1. Basic structure & main property

Hexagonal, pentagonal and hexagonal carbon structures together form carbon nanospheres (CNSs). In their different arrangement and combination, CNS can take on various forms. According to its structure, CNS can be divided into two types: solid CNS and hollow CNS. These small graphite sheets that form carbon nanospheres can form wave-like structures on its surface. This graphite sheet with wavy structure will produce active unsaturated bonds between fixed atoms with unsaturated valence on the surface of the sphere due to its curvature [13]. It is believed that there are many unsaturated bonds on the surface of these spheres produced by those graphite flakes. These unsaturated bonds can enhance the surface reactivity of CNS and affect its chemical reaction and electronic properties. The high active unsaturated bond on the surface of CNS can not only provide high surface activity, but also easily lead to aggregation between them. CNS often exists in the form of aggregated spheroids rather than isolated spherical molecules. The aggregation of CNS may lead to a smaller active surface area, which will reduce the number of active unsaturated bonds on the surface, leading to a reduction in reactivity. The factors that affect the properties of CNS include the shape and size of the sphere, the degree of aggregation and the doping of heteroatoms. At present, one of the most studied CNS doped with heteroatoms is nitrogen doped carbon nanospheres (NCNS). N-doped hollow CNS' surface has a rough microstructure, which indicates that nitrogen atoms can be dispersed on the whole surface of the sphere. However, due to the difference of atomic properties, the surface of CNS-doped with N may produce defects [14]. In addition, the doping of heteroatoms changes its charge state distribution, making it different from the charge state distribution at nearby locations. By doping nitrogen atoms on the surface, the surface polarity of CNS can be enhanced, its basic surface sites can be changed, and the affinity of electron donors can be improved, so that their performance can be improved when applied to LIB anode materials.

2.3.2. Synthesis methods

CVD is a highly selective direct synthesis technology of CNS, and can produce solid, hollow and composite CNSs of various sizes. Under the carbon precursor and protective atmosphere of the reactor, the carbon precursor continued to deposit and decompose under the action of catalyst, and finally formed CNS aggregates. The catalyst can be used as the nucleus of CNS growth and can also accelerate the decomposition of carbon precursors. The size of the sphere can be adjusted by adjusting specific process parameters like feed rate, pyrolysis temperature and reaction time.

In addition, CNS can also be produced from polycyclic aromatic hydrocarbon precursors under the induction of Friedel-Craft reaction [15]. This flexible method can be used to create porous polymers with super-crosslinking. It performs Friedel-Crafts alkylation of aromatic monomers in Lewis acid with the help of crosslinking agent. It is reported that after the preparation of monodisperse polystyrene nanospheres with divinylbenzene pre-crosslinking as the precursor, the reaction of polystyrene chain with crosslinking agent CCl_4 was carried out through the direct super-crosslinking process based on Friedel-Crafts reaction under the action of AlCl_3 catalyst, and highly monodisperse microporous CNS with a diameter of 190 nm was synthesized.

2.3.3. CNS basal anode

Because of its large surface area, tunable shape and fast diffusion ability of lithium ion, CNS has high specific capacity as well as strong rate capability, thus it is a potential LIB anode material. The initial reversible capacity of CNS is very high. The battery capacity was about 420mAhg^{-1} at the current density of 60mAhg^{-1} when it was first prepared, and it basically remained stable after cycling. However, CNS still has low energy capacity. By combining with nonmetals, metals, metal oxides or alloys (such as N-CNS), the lithium storage capacity of CNS can be increased. At high rates, N-CNS also works well. Under the current density of 3000mAhg^{-1} , it has a reversible capacity of 200mAhg^{-1} .

The unique structure of hollow CNS has attracted more attention. Since it has a larger surface area comparing with solid CNS, its Li ion diffusion efficiency has been further improved. However, large surface area may lead to the repeating SEI formation, and result in the reduction of cycle stability and the increase of irreversible capacity. Through morphological design, these problems are expected to be solved. R, Zhu et al. proposed a double-shell hollow CNS encapsulated with silicon nanodots (SiNDs@DSHC) [16]. This material can undergo 400 cycles under the current density of 0.3Ag^{-1} , and still has a reversible capacity of 1350mAhg^{-1} . Because of inhibition of the repeating SEI formation, the SiND in the composite has a slighter crushing condition than the large Si particles after multiple lithium/lithium removal cycles. In addition, by forming a chemical reactor to accommodate SiND, the high mesoporous double-layer hollow carbon can stabilize thermodynamics and relieve structural instability of the composite. The production of mesopore in CNS composite helps to alleviate the expansion in volume of electrode as well as the diffusion process of electrolyte to the gap, thus realizing the close contact of SiND

3. Conclusion

This paper investigated and introduced the basic structure and main properties of carbon nanomaterials, together with their synthesis methods and applications in LIB anodes, and discussed the advantages and disadvantages of each carbon nanomaterial as well as the corresponding optimization strategies. According to the classification in this paper, due to its low density, good conductivity and excellent mechanical strength, 1D materials are excellent conductive network and can alleviate the expansion in volume of LIB anode. However, it is difficult to realize its functionalization when acting as LIB cathode. Due to its large surface area, good physical and chemical properties, conductivity and rich surface functionalization, 2D materials with layered conductive structure can effectively alleviate the expansion in volume in LIB system and produce anode materials with large energy capacity. However, when 2D materials and LIB anode are applied,

they need to be agglomerated and packaged, and corresponding additives and adhesives need to be added. For 3D materials, due to its low density, large surface area, high chemical stability as well as layered porous structure, the electrolyte is easy to diffuse electrons and the ion transfer path is short in 3D materials, and no adhesive is required when applied to LIB anode. However, there are still difficulties in the application of 3D materials. After all, it is difficult and expensive to accurately control the 3D structure of materials. Carbon nanomaterials can improve their electrochemical performance through specially designed surface modification. Hybrid materials based on carbon nanomaterials can enhance the performance of carbon nanomaterials and hybrid materials through synergistic effects. Compared with single-component LIB anode materials, the hybrid anode based on carbon nanomaterials significantly improves the battery performance.

Despite the difficulties, researchers around the world are committed to developing advanced carbon nano anode materials to produce LIB with better functions, thus benefiting the whole human society and creating a better future.

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