

Application of Nano-Carbon Materials in Battery Electrode

Fangzhou Pan *

School of Materials Science and Engineering, Hunan University, Changsha, China

* Corresponding author: 15030720539@xs.hnit.edu.cn

Abstract. As it is the trend is for new energy sources to replace old fossil fuels, people begin to choose new energy instead fossil energy, and fossil energy is widely used in household mobility scooters. One of the most obvious signs of this is the entry of different new energy vehicles into the public eye. However, the range of new energy vehicles is still not as good as that of traditional cars. Many studies have begun to focus on improving the batteries of new energy vehicles. Some batteries in the traditional sense, such as lead-acid batteries, and ordinary lithium batteries are unable to achieve the capacity needed on a daily basis. Recent research has shown that carbon nanomaterial batteries have performance that far exceeds that of conventional battery materials. This paper summarises the application of new materials-carbon nanomaterials in battery electrodes. Because of the many advantages of nanomaterials, such as good electrical conductivity, good expansion resistance, good ion storage ability and so on, the application of four common carbon nanomaterials in electric vehicle battery electrodes was discussed.

Keywords: Carbon-based electrode, fullerene, graphene, nanotubes, nanofiber.

1. Introduction

Humans first obtained energy conversion through the burning of biomass such as fireweed and twigs. However, with the massive use of fossil fuels, global environmental as well as ecological problems have become particularly problematic. Finding new sources of energy that can replace traditional energy sources has become an urgent priority [1-3]. Many papers and researches on sustainability, climate change, alternative energy, green chemistry, and engineering have emerged [4]. Lithium-ion batteries have many excellent electrical properties, include high energy density, extensive operating temperature range, extended cycle life, and high charging efficiency. Early on, Whittingham developed lithium metal batteries using lithium metal and titanium sulphide as electrodes [5]. Significant safety concerns, but coping mechanisms offer new ideas. Then based on that research, Goodenough tried using lithium cobaltate instead of titanium sulfide to power the battery. Yoshino used the carbonaceous material petroleum coke as a negative electrode instead of lithium metal, reducing battery safety risks and improving high safety of lithium- ion batteries. From petroleum coke, to the emergence of graphite electrode, and to the popularization of commercial mineral ink, carbon materials account for a large proportion in the research of lithium-ion batteries. With the continuous improvement of the performance requirements of lithium-ion batteries, the traditional carbon materials cannot meet people's needs gradually, and people urgently need better performance alternative materials. Research has revealed that carbon nanomaterials have excellent electrical properties such as lithium storage. Therefore, four common carbon nanomaterials have come into the limelight [6,7]. Nano-carbon materials are rich, and their meta-chemical properties make them the main factor in the application and research of lithium-ion batteries [8-11]. According to the literature search results from 2016 to 2020, research papers on fullerenes, carbon nanotubes, graphene, and porous carbon account for up to 61.5% of all carbon materials.

2. Nano-Carbon Materials

2.1. Fullerene

The shape of the hollow fullerene molecule, which is entirely made of carbon, might be spherical, ellipsoidal, cylindrical, or tubular. Fullerenes are structurally comparable to graphite, which is made

up many levels' graphene stacked in Circles with six members. Lithium ions (Li^+) can be embedded between C_{60} molecules to form Li_xC_{60} , where each C_{60} molecule can be stored at most 12 lithium ions, with theoretical the ability of lithium to 446 mAh/g. However, due to the singlecrystal properties of fullerenes, the actual charging capacity is only 90 mAh/g, and the reversibility of lithium storage is poor. Therefore, pure fullerene is not an ideal electrode material for lithium storage. In order to obtain high performance fullerene-based anode materials, most studies have further modified C_{60} , such as doping, hybridization and derivatization [12]. For example, using C_{60} as the precursor, in ammonia atmosphere, through KOH activation, the original C_{60} molecule is converted into a material containing a large amount of pyrrole and pyridine nitrogen, which has many defects [13]. Electrochemical tests show that this N-doped C_{60} sample product has a substantial reversible capacity and excellent amplification performance. a significant current density of 5A/g, it still has an ability of 600mAh/g. Guan et al. used zeolite imidazolite frame-8 (ZIF-8) as a precursor to investigate the effects of the C_{60} in situ after embedding carbide into nitrogen doped porous carbon materials. As the anode material of the C_{60} N-MPC lithium-ion battery, it has a reversible capacity of 1351 mA h/g at 0.1 A/g and 10 A/g. These are mixed complex fullerene-based materials, and the original spherical junctions of fullerenes during the doping process. When the structure is destroyed, the excellent conductivity and redox activity of fullerene cannot be obtained. Fullerenes are only used as raw materials, so the study of doped fullerene-based electrode materials is relatively limited. How to ensure the unique properties of fullerene doping modification is still a major challenge.

2.2. Carbon nanotube

In general, the capacity of nanotubes of carbon when used as anode substance for Li-ion batteries. The quantity depends greatly on their structure and morphology (range 300-1500 mA·h/g). The carbon's capacity nanotubes are determined by their diameter, length, and surface defects. Through oxidation of acid and ball milling and post-processing of cutting with metal oxide showed the highest reversible capacity of electrode materials. It can reach 1116mAh/g [14]. However, because carbon nanotubes have large knot's structure defects and high voltage hysteresis, single wall carbon nanotubes as electrode materials to achieving high coulombic efficiency remains challenging [15]. To get better electrical properties that combine carbon nanotubes with activity to form composite structure is a promising approach. In composite materials, carbon nanotubes can form a stable interpenetrating conductive network, thereby shortening the lithium diffusion distance and realizing fast charge speed transmission. It has a higher theoretical capacity of metal oxide and carbon nanotubes. The combination significantly improves its electrochemical performance. If carbon nanotubes were doped with Fe_2O_3 , the composites are integrated together and formed into 3D network junctions by cold spraying. Lithium storage capacity is equal to 100 mA/g current volume 1598 mA·h/g. With a density of current of 1000 mA/g, 1000 passes are made after the charge-discharge cycle, the retention rate of the structure's capacity is still 88%. The tube acts as the conductive skeleton of MoS_2 and uses TiO_2 as the surface coating of MoS_2 . A multifunctional carbon nanotube was prepared, 1000 mA/g and 2000 mA/g after 1000 rotates at current density. The multifunctional carbon nanotube/ MoS_2 composite has been developed excellent long cycle performance (528.5mAh/g and 455.2m h/g). The above results show that carbon nanotubes can accelerate the transport of Li ions and that the utilisation of highly reactive materials increases.

2.3. Graphene

Graphene has many similarities in structure and properties to carbon nanotubes, including a large specific surface area, abundant electronic states, and good mechanical properties It can be used instead of carbon nanotubes in many fields and has a huge application prospect [16]. In energy storage applications. atomically thick graphite with two-dimensional planar geometry. The sheet is better at transporting electrons than carbon nanotubes, so it is a more efficient electrode. Many researchers believe that using graphene, which has metal-grade conductivity, large surface area (theoretical benefit 2 630 m²/ g) can adsorb lithium atoms. The exposed side (i.e., forming the expected double

particular ability to 744 mA·h/g Li_2C_6) of the ultimate carbon material can be developed by simply replacing the traditional graphite anode. At the time, this goal was not achieved using pure graphene materials. Indeed, even for graphene's lithium storage mechanism (or its lithium storage location), it is true that both are controversial in theory. One idea is that a single layer of graphene lets lithium ions get through and stored by adsorption, this contrasts sharply with the graphite's piecewise intercalation method. Some studies have shown that lithium in monolayer graphene exists on both sides of the graphene sheet, giving an estimated maximum specific capacity of 744 mA h/g Li_2C_6 stoichiometric ratio, which is about twice the specific capacity of a commercial graphite anode. Additionally, it has been claimed that the covalent link between adjacent lithium atoms allows for the trapping of Li ions in the benzene ring., the principle is derived from the stoichiometric ratio of LiC_2 , which has a particular capability of 1116 mA h/g [17]. The argument is that because lithium atoms are embedded only between graphene layers or sandwiched between the bottom. It is simple to adsorb Li onto a single graphene layer. Ji et al. Synthesized graphene by high-temperature exchange chemical vapor deposition to produce a high quality self-supporting double layer graphene foam carbon material with lithium storage. Cheng carried out systematic and comprehensive characterization and analysis, and they concluded: the storage behavior of lithium in ink is comparable to that of graphite, which goes through many stages of intercalation. Controversially, Kuhne et al. used in situ low-pressure transmission electron microscopy to observe reversible intercalation of lithium in bilayer graphene, and they found lithium ions in bilayer. The space presents a tightly packed sequence of layers, which means a double layer of graphene. Lithium-ion storage capacity is much higher than LiC_6 . In order to further investigate lithium ions in diffusion laws in graphene materials, Lee et al. Used chemical vapour deposition (CVD) to obtain monolayer graphene with a perfect base surface and rich edges was prepared. By comparing the two structural types of graphene, defects were found to promote the expansion of lithium ions perpendicular to the graphene basal plane. The defect sites favoured the adsorption of lithium ions, while the vacant sites hindered the aggregation of lithium ions. They also worked through density functional theory (DFT) to prove that lithium ion may use double vacancy or high order defect as transport. Although graphene has excellent electrical conductivity, high mechanical strength, high electrical charge mobility and large specific surface area, the coulombic efficiency is low. It is difficult to be used as anode material directly because of its poor performance. However, with carbon sodium, graphene can also be combined with activity to form hybrid structures to prepare electrode materials with excellent properties [18].

2.4. Carbon nanofibre

Carbon nanofibers are characterized as one-dimensional sp^2 hybrid carbon nanostructures, which are beneficial to the electrolyte pathway and high electron conductivity along the longitudinal path of a nanocarbon material. In recent years, several studies have reported the effects of carbon nanofibers on used lithium-ion batteries and demonstrated its excellent lithium storage properties, which shows that carbon nanofibers in lithium-ion battery have an important research significance. Currently, the synthesis of carbon nanofibers, mostly by (1) chemical vapor deposition; (2) electrospinning [19]. Obtained by chemical vapor deposition, carbon nanofibers have higher electrical conductivity, up to $1 \times 10^3 - 1 \times 10^4$ S/cm. However, catalysts and precursor gases are expensive and the growth rate is lower and the preparation cost is higher. Electrostatic spinning method produces carbon nanofibres up to 1000 nm in diameter. The fiber length can reach $1 \times 10^4 \mu\text{m}$. In contrast, most of the sodium carbon fibers produced by chemical vapour deposition are shorter in diameter, around 50-200 nm. Application direction of carbon nanofibers in lithium-ion batteries is like that of carbon nanotubes, but more inclined to flexible lithium-ion battery applications. The composite of carbon nanofibers and other active materials for lithium storage can increase the efficiency. Composite materials used for ion and electron transport have alleviated the product changes of other lithium storage active materials. In recent years, most of these modification methods are integrated. Liu et al. used solvothermal methods to obtain a self-supporting lithium ionization was prepared by combining with

porous nitrogen doped carbon nanofibers [20]. The negative electrode of a sub-cell shows high specific capacity, excellent multiplier performance and cycle stability. At 200 mA/g of current density after 100 cycles, the discharge capacity is 1122 mA h/g. Having an enormous current density of 2 A/g, the capacity exceeds 660 mA h/g after 1000 cycles. Accretion expands to improve cyclic stability, and due to its excellent electrical conductivity, the efficiency of ion transfer between electrodes can be improved. In addition, carbon nanofibers also help form a stable SEI layer, reducing electrolytes during cycling. Due to its surface electricity, carbon nanofibers continually consumed have a huge specific surface area, and the high irreversible capacity is due to the decomposition and formation of the SEI layer. Reasonable structure to balance electron and ion transport enhancement and specific surface area is also helpful. Wang et al. obtained the results of a hydrothermal reaction and a double carbon layer structure is built using the electrospinning method (the inner layer is amorphous carbon, the outer layer is carbon nanofiber), which combines with MoS₂ to achieve high cyclic stability. This unique double carbon layer effectively limits the volume expansion of MoS₂ and the dissolution of polysulfide during the long cycle followed by carbon. The presence of carbon fibres and amorphous carbon leads to an increase in electrical conductivity.

3. Conclusion

Fullerenes, carbon nanotubes, graphene, and nanofiber are selected as representative in this paper, the latest synthesis of carbon nanomaterials and their properties in lithium-ion batteries are discussed in detail. Although this paper will be about nano-carbon materials, which are divided into four typical structures, they are not opposite. Because these nano-carbon materials are regarded as competitors rather than combining them together, they sometimes show beneficial synergy. Therefore, new carbon nanostructures with improved performance can be produced by combining different carbon nanostructures, which is also worth exploring. In recent years, the research of nano-carbon materials has developed rapidly. However, in the future research, nano-carbon materials widely used in lithium-ion batteries will be faced with challenges. (1) Develop new functions. Nano-carbon materials cannot only be used as electrode materials for lithium-ion batteries, but also realize some new functions based on their unique junctions, such as conductive agent, coating, volume buffer, super conductive network matrix, adsorbent, etc. (2) Improve battery performance and safety. The performance of lithium-ion batteries needs to be improved. For example, lithium storage materials such as heteroatom doping can effectively improve the performance of lithium-ion batteries. However, in addition to improving the performance, it is also necessary to ensure the safety of the battery, and the frequent thermal runaway of the battery has caused people to worry about the safety of the lithium-ion battery. Composite materials of carbon nano-materials and some active materials can effectively reduce the volume expansion of lithium batteries (3) Reduce the cost of synthesis. Complex synthesis methods often lead to high costs. In order to bring carbon nanomaterials into the application for batteries, it is necessary to explore low-cost processes that can produce high-performance carbon nanomaterials in large quantities. Chemical vapor deposition is now a proven low-cost synthesis method. Further research can be carried out in the direction of chemical vapor deposition in order to realize the preparation of low-cost and high-quality carbon nano-materials. This method is more suitable for industrial production, and further research can be carried out in the direction of CVD in order to achieve low-cost and high-quality production of carbon nano-materials. Solvothermal method is made by reasonable use of nano-carbon materials to have better energy storage devices, and use these energy storage devices to realize high-voltage discharge, to achieve the goal of low-cost and high-quality preparation of nano-carbon materials, thus forming a virtuous cycle. (4) It is also necessary to understand the dynamics of electrons and ions in carbon nano-material batteries. Analysis and summary, including charge transfer mode, deep storage mechanism and related interface effects, can help better understand the relationship between the geometric mechanism and corresponding electrochemical properties of carbon nanomaterials. Carbon nanomaterials are widely used in the

field of lithium-ion batteries. It is hoped that this review will promote the development of carbon nanomaterials in the application of battery electrodes.

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