

Research Progress of Cathode Materials for Graphene-based Fuel Cells

Zejun Zhang

Qingdao No.67 High School of Shandong Province, Qingdao, China

Abstract: Graphite is the most widely used cathode material for commercial lithium-ion batteries at present, and the increasing market demand puts forward higher requirements for lithium storage performance of graphite cathode materials. Graphene is a kind of cathode material with great development potential, and its lithium storage performance is influenced by many factors such as structural characteristics, oxygen-containing functional groups and impurity atoms, which leads to complex lithium storage behavior and mechanism. When the polymer with lithium storage activity is compounded with graphene as cathode material, the lithium storage performance is affected by the reversibility of polymer redox and the composite structure. In this article, the working principle of Li-ion and the lithium intercalation mechanism of graphite are introduced, and the research status and progress of graphite cathode materials in surface modification and structural regulation in recent years are emphatically reviewed.

Keywords: Li-ion, Graphene, Cathode material, Research progress.

1. Introduction

At present, the energy structure is dominated by fossil energy such as oil, coal and natural gas, which have greatly promoted the industrialization process and the progress of human society. However, the pollution gas produced by its consumption will cause global warming, lead to the greenhouse effect, and lead to many disasters such as the continuous disappearance of glaciers and frozen soil, rising sea level and frequent extreme weather [1]. At present, the trend of energy development is changing, from developing new energy sources such as solar energy, hydro energy and wind energy to developing materials and devices based on electrochemical energy storage [2]. There are many kinds of electrochemical energy storage devices, such as Li-ion, electrochemical capacitors and fuel cells. Among them, lithium-ion batteries have the advantages of high energy density, high working voltage, low self-discharge rate, long cycle life and environmental friendliness, and have been widely used in mobile electronic equipment, electric vehicles, medical equipment and aerospace and other fields [3]. Carbon materials are mostly block and powder carbon materials. As the cathode of lithium-ion batteries, binders and conductive agents need to be loaded on the surface of metal current collectors through coating process for application [4]. Therefore, the development of self-supporting carbon-based cathode without conductive agent and binder can not only improve the energy density of electrode materials, but also simplify the electrode preparation process. Surface modification of electrode materials, reducing the side reaction between electrode materials and electrolyte and increasing the conductivity of electrode materials are the main methods to prolong the cycle life of batteries and improve the rate performance [5].

Graphene has attracted extensive attention for its unique properties since it came out. It has many excellent properties, such as good conductivity, high Young's modulus and huge surface area [6]. Graphite has good conductivity and lithium ion intercalation/deintercalation performance, and it is the cathode material with the highest proportion and the widest

commercialization degree in commercial Li-ion [7]. As a cathode material of Li-ion, it also shows excellent electrochemical performance, which has higher specific capacity and better cycle performance compared with ordinary carbon-based materials [8]. Lithium-ion batteries can store and convert discontinuous and unstable solar energy, wind energy and ocean energy, and supply power to the grid [9]. Therefore, it is of great significance to study the energy storage technology represented by Li-ion to get rid of the dependence on petrochemical energy and promote the large-scale use of new energy. Graphene composites, as cathode materials, generally show better performance than a single raw material electrode. This is because the introduction of graphene can effectively alleviate the serious volume expansion of cathode materials during lithium intercalation and prolong the service life of electrodes. In this article, the working principle of Li-ion and the lithium intercalation mechanism of graphite are introduced, and the research status and progress of graphite cathode materials in surface modification and structural regulation in recent years are emphatically reviewed.

2. Lithium Storage Performance of Graphene

As one of the commonly used cathode materials, the modification of carbon materials has always been a hot research topic. People introduce different metal elements and dope them in order to obtain cathode materials with high specific capacity. The structure of graphene is shown in Figure 1.

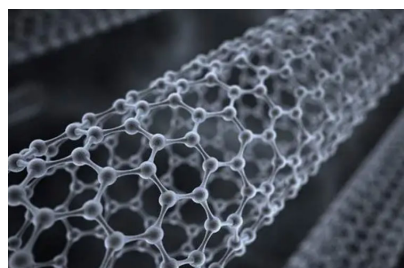
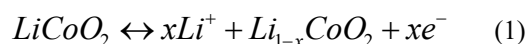


Figure 1. Schematic diagram of graphene structure

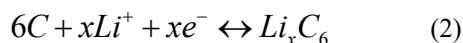
Li-ion is a kind of lithium-ion concentration battery, which is mainly composed of cathode, cathode, diaphragm and electrolyte. During charging, lithium ions emerge from the lattice of cathode LiCoO_2 , diffuse into the electrolyte, and gradually insert into the graphite cathode layer through the diaphragm. At the same time, in order to maintain the balance of charge, the cathode will release the same amount of electrons to flow to the graphite cathode through the external circuit, forming a complete loop. Graphene can produce synergistic effect with some substances to achieve higher specific capacity and better cycle performance than the original electrode. The addition of some elements can prevent the deactivation of graphene surface. Therefore, graphene-based composites are excellent cathode materials for Li-ion.

During discharge, lithium ions will come out from the interlayer of graphite at the negative electrode, return through the electrolyte and be embedded in the lattice of LiCoO_2 , and electrons will be transmitted to the positive electrode by the external circuit, thus completing a charge-discharge cycle.

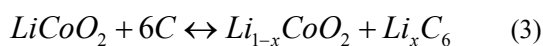
Positive reaction:



Negative reaction:



Total battery reaction:



3. Electrochemical Mechanism of Li-ion and Lithium Intercalation Mechanism of Graphite

The application of graphene in cathode materials of Li-ion has been extensively studied in recent two years. For example, lithium iron phosphate (LiFePO_4) cathode material with olivine structure has the advantages of rich source of raw materials, low price, environmental friendliness, high specific capacity and stable circulation, but its wide application is limited to a certain extent by its low ion mobility and electronic conductivity. Graphene is composed of a single layer of carbon atoms arranged closely and has unique lithium storage properties. Li^+ can not only be stored on both sides of graphene lamellae to form LiC_3 compounds, but also can be stored in the edges and holes of graphene lamellae. The theoretical specific capacity is more than twice that of traditional graphite materials [10]. The size of graphene is micro-nano scale, and the diffusion path of Li^+ is short, which is conducive to the diffusion and transmission of Li^+ . Therefore, graphene cathode materials have good electron and ion transmission channels, which is helpful to improve the power performance of Li-ion.

As a member of carbon materials, graphene has attracted the attention of researchers due to its unique structure, high specific surface area and specific electronic conduction mode. Shen et al. prepared high-quality graphene flakes by rapid thermal expansion of graphite oxide powder in nitrogen atmosphere. Under the condition of current density of 100mA/g, its reversible capacity is 852mAh/g after 50 cycles; When the current density is increased to 500mA/g, its

reversible capacity can still reach 725mAh/g [11]. Jing et al. prepared LiFePO_4 /graphene composite by hydrothermal method, and found that LiFePO_4 can attach to the surface of graphene, and the specific capacity of LiFePO_4 /graphene reached 162.5mAh \cdot g⁻¹ at 0.1 °C [12]. Xu et al. prepared graphene flakes by oxidation and rapid expansion of graphite under microwave conditions. Its initial discharge capacity is 565mAh/g, and after 60 cycles, its specific capacity is 425mAh/g, showing good cycle performance [13]. Jiang et al. found that the surface wrinkles of graphene can effectively wrap it on the surface of LiCoO_2 particles to form a conductive interface with surface contact, which is conducive to improving the electrochemical reaction activity, discharge specific capacity and high-rate cycling performance of LiCoO_2 [14].

The specific discharge capacity of LiCoO_2 /graphene at 20 °C reaches 132.1 mAh \cdot g⁻¹. After being compounded with LiMn_2O_4 , graphene can effectively improve the cyclic stability of LiMn_2O_4 as electrode material while improving its ionic and electronic conductivity [15]. Xu et al. prepared graphene by H_2 thermal reduction of graphite oxide at 300 °C, and used this graphene as cathode material. At the current density of 50mA/g, its discharge capacity is 1545mAh/g, and the coulomb efficiency is more than 96% [16]. It can be seen that the reversible capacity of graphene prepared by either method is much higher than that of graphite cathode, and its cycle performance is also better than that of graphite cathode. People not only prepared layered graphene, but also used chemical reduction method to reduce graphene oxide at 100 °C to obtain multilayer graphene composed of microspheres. As a cathode material, its specific capacity is nearly twice higher than that of ordinary multilayer graphene, and it shows good cycle performance and high power charge and discharge performance [17]. Jia et al. studied $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ coated with graphene oxide as cathode material of Li-ion. The composite material has excellent cycle life and magnification performance [18].

4. Application of Graphene in Cathode Materials of Li-ion

At present, many scholars have studied the lithium storage properties of graphene. Guan et al. reported that graphene was used as cathode material for Li-ion. The reversible specific capacity of graphene electrode was 550mAh/g, which was higher than the theoretical value of natural graphite. The reason was that Li^+ was stored on both sides of graphene, increasing the lithium storage capacity [19]. Li et al. reduced graphite oxide at different temperatures, prepared graphene with different number of layers, and studied the electrochemical properties of the product [20]. Graphene with less than 5 layers obtained by reduction at 300 °C has good lithium storage performance and cycle stability. It is charged and discharged at 0~3V with a current of 50mA/g, and the reversible specific capacity of the first cycle is 944mAh/g [21]. The effective combination between nano-particles and graphene can effectively prevent the lamination/agglomeration between graphene sheets, which is conducive to the intercalation and desorption of lithium ions. At the same time, the combination of two-dimensional layered graphene and nano-particles can produce a large number of pore/hole structures, which can alleviate/reduce the volume expansion and contraction of the electrode material during the lithium ion intercalation process, thus

improving the cycle performance and structural stability of the battery.

Due to the chemical inertness of graphene, the effective composite of graphene and active material of electrode material is mostly weak physical interaction, and the structural stability of composite material is poor, which seriously affects its practical application. Bai et al. prepared graphene with controllable number of layers by controlling graphite oxide [22]. With the increase of the number of graphene sheets, the first irreversible specific capacity gradually decreases, and the cycle stability also decreases, with the specific capacity decreasing from 1175mAh/g to 845mAh/g [23]. The electrochemical performance of graphene is good, but the capacity of graphene electrode decreases rapidly after a period of charging and discharging, which may be related to the arrangement of graphene layers [24]. The honeycomb structure of graphene material shortens the transmission path of Li^+ , and the layered structure increases the lithium storage capacity of the material, so it has good electrochemical performance. Although graphene has a high specific capacity, if graphene is used as cathode material of Li-ion alone, problems such as large irreversible specific capacity and voltage hysteresis need to be solved. It is a research direction to use graphene, metal oxide and silicon as cathode materials for Li-ion.

5. Conclusion

Graphene has a large specific surface area and good electrical properties, and has great potential as an electrode material for Li-ion. Adjusting the arrangement of graphene on the current collector to form good electron and ion transport channels can further improve the performance of graphene electrode materials. In order to realize the marketization of graphene and its polymer composites as soon as possible, it is urgent to explore and solve the scientific problems faced by the composites in the process of molecular structure, functional design and construction. For graphene-based composites, the introduction of graphene can improve their specific capacity and cycle performance to some extent, which makes them have better electrochemical performance as cathode materials of Li-ion. Graphene can prevent the agglomeration of nanoparticles in composites, alleviate the volume effect during charging and discharging, and prolong the cycle life of materials; Nano-particles can increase the lithium intercalation and deintercalation ability of materials through chemical reaction with Li^+ ; The adhesion of particles on graphene surface can reduce the energy loss of materials reacting with electrolytes in the process of forming SEI film, which is of great significance to practical production. The combination of graphene and cathode material of Li-ion can increase the specific surface area of electrode material and improve the conductivity, thus increasing the effective capacity of the material.

References

- [1] Yuan G, Xiang J, Jin H, et al. Anchoring ZnO Nanoparticles in Nitrogen-Doped Graphene Sheets as a High-Performance Anode Material for Lithium-Ion Batteries[J]. *Materials*, 2018, 11(1):96.
- [2] Aslan E, Aydn Y, Yaa Y. Consideration of graphene material in PCM with aluminum fin structure for improving the battery cooling performance[J]. *International journal of energy research*, 2022(8):46.
- [3] Chang U, Lee J T, Yun J M, et al. In Situ Self-Formed Nanosheet MoS₃/Reduced Graphene Oxide Material Showing Superior Performance as a Lithium-Ion Battery Cathode[J]. *ACS nano*, 2019(2):13.
- [4] Chen L, Yang Z, Qin H, et al. Advanced electrochemical performance of ZnMn₂O₄/N-doped graphene hybrid as cathode material for zinc ion battery[J]. *Journal of power sources*, 2019, 425(JUN.15):162-169.
- [5] Benítez A, Lecce D D, Álvaro Caballero, et al. Lithium sulfur battery exploiting material design and electrolyte chemistry: 3D graphene framework and diglyme solution[J]. *Journal of Power Sources*, 2018, 397(sep.1):102-112.
- [6] Bi X, Li Y, Qiu Z, et al. Fluorinated Graphene Prepared by Direct Fluorination of N, O-Doped Graphene Aerogel at Different Temperatures for Lithium Primary Batteries[J]. *Materials*, 2018, 11(7):1072.
- [7] Zhang L, He Q, Huang S, et al. A novel boron and nitrogen co-doped three-dimensional porous graphene sheet framework as high performance Li-ion battery anode material[J]. *Inorganic Chemistry Communications*, 2018, 96:159-164.
- [8] Li M M, Wang Y, Yang C C, et al. In situ grown Co₃O₄ nanocubes on N-doped graphene as a synergistic hybrid for applications in nickel metal hydride batteries[J]. *International Journal of Hydrogen Energy*, 2018, 43(39):18421-18435.
- [9] Zhong C, Zhang W, Ding G, et al. Three-dimensional graphene networks modified with acetylenic linkages for high-performance optoelectronics and Li-ion battery anode material[J]. *Carbon*, 2019, 154:478-484.
- [10] Assresahegn B D, Ososon B D, D Bélanger. Graphene nanosheets and polyacrylic acid grafted silicon composite anode for lithium ion batteries[J]. *Journal of Power Sources*, 2018, 391:41-50.
- [11] Shen Wenzhuo, Guo Shouwu, et al. Application of graphene in electrode materials of lithium-ion batteries [J]. *Electronic Components and Materials*, 2017, 36(9):4.
- [12] Jing Minghua, Fan Xinzhuang, Liu Jianguo, et al. Electrochemical properties of graphene oxide modified carbon felt as cathode material for vanadium batteries [J]. *Energy Storage Science and Technology*, 2017, 6(2):7.
- [13] [Xu Li, Liu Shuangyu, Xin Chen, et al. Application of 3D graphene electrode materials in lithium-ion batteries [J]. *Smart Grid*, 2017, 5(1):5.
- [14] Jiang Tao. Application of graphene in anode materials of lithium-ion batteries [J]. *Internal Combustion Engine and Accessories*, 2020(6):2.
- [15] Zu Shengzhen. Review on the potential application of graphene composites in anode materials of lithium-ion batteries [J]. *Materials Science*, 2018, 8(3):14.
- [16] Xu Shuaijun, Li Jun, Huang Si, et al. Research progress of graphene-based modified cathode materials for lithium secondary batteries [J]. *New Chemical Materials*, 2017, 45(6):3.
- [17] He Bo, Pan Yufei, Lu Min. Research progress in additive manufacturing of graphene-based energy storage materials [J]. *Materials Guide*, 2017, 031(013):126-130,137.
- [18] Jia Beibei, Zhu Jiliang. Study on electrochemical properties of cathode materials for vanadium sulfide/graphene-based lithium-sulfur batteries [J]. *Materials Science*, 2022, 12(4):10.
- [19] Guan Yibiao, Shen Jinran, Li Kangle, et al. Application of graphene conductive additives in the cathode of lithium-ion batteries [J]. *Energy storage science and technology*, 2020, 9(1):12.
- [20] Li Yue, Yang Bo, Huang Guo. Patent progress of graphene-based cathode materials for lithium-ion batteries [J]. *Battery*, 2020, 50(2):5.

- [21] Liu Shuangyu, Xu Li, Xin Chen, et al. Application of 3D graphene cathode materials in lithium-ion batteries [J]. *Smart Grid*, 2017, 5(3):4.
- [22] Bai Xuejun, Hou Min, Liu Chan, et al. Three-dimensional tin oxide/graphene hydrogel anode material for lithium ion batteries [J]. *Journal of Physical Chemistry*, 2017, 33(2):9.
- [23] Zhu Jianwei, An Yuliang, Yuan Xia, et al. Preparation and properties of anode materials for graphene/lithium titanate composite lithium ion batteries [J]. *Chemistry and Adhesion*, 2018, 40(1):5.
- [24] Deng Lingfeng, Qin Yuchun, Peng Huiyan, et al. Preparation and Characterization of LiFePO₄/ Graphene Composite Cathode Materials by High Temperature Reduction of GO [J]. *Materials Engineering*, 2018, 46(2):7.