

Preparation of Fluorinated Graphite and Its Application Research in Lithium Primary Batteries

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Abstract: Fluorinated graphite is an important functional material, and its preparation methods mainly include direct synthesis, catalytic synthesis, synthesis in a vertical vibrating reactor, and electrolysis. The direct synthesis method involves heating solid carbon and gaseous fluorine within a certain temperature range, but it has safety hazards and low yield issues. The catalytic synthesis method involves adding trace amounts of metal fluorides as catalysts to the reaction system of graphite and fluorine, which can enhance the conductivity. Fluorinated graphite also exhibits good hydrophobic and oleophobic properties, as well as high-temperature solid lubrication properties, making it suitable for a wide range of applications. Fluorinated graphite holds great promise for application in lithium primary batteries, particularly as a high-energy battery active material. However, the degree of fluorination of fluorinated graphite is closely related to the battery's energy density and electrical conductivity. Researchers have modified fluorinated graphite through methods such as conductive layer coating and material nanosizing to improve battery power characteristics.

Keywords: fluorinated graphite; lithium primary batteries; cathode; fluorine; energy

1. INTRODUCTION

Fluorinated graphite, also known as fluorinated carbon, is a new type of high-tech, high-performance, and high-efficiency carbon/graphite material internationally. Fluorinated graphite obtained through the direct reaction of fluorine with graphite carbon exhibits two structures: poly (monofluorocarbon) $(CF)_n$ and poly (monofluorodicarbon) $(C_2F)_n$, and appears as a gray-white solid powder. Due to covalent bonds, fluorinated graphite is a special interlayer compound of graphite, exhibiting excellent surface energy properties, lubrication performance, electrochemical properties, chemical properties, and insulating properties [1]. Its superior performance makes it widely applicable in functional materials and electrochemical fields. Fluorinated graphite has extremely low surface energy and interlayer energy but high electrical activity, making it an excellent electrode material and a good lubricant. It maintains good lubrication performance even under high temperature, high pressure, and higher speed conditions, giving it a significant advantage over previous solid lubricants such as graphite and molybdenum disulfide in terms of resistance to environmental influence. Additionally, fluorinated graphite has high heat storage capacity and is also an excellent thermal insulation material. German chemist Ruff et al. conducted research on fluorinated graphite as early as 1934. By controlling combustion and explosion reactions, Ruff synthesized a gray hydrophobic substance $(CF_{0.92})_n$ from graphite, thus opening the prelude to the study of fluorinated graphite [2]. In 1947, G. Rudorff et al. synthesized $CF_{0.676}$ to $CF_{0.988}$ within a temperature range of $410^\circ C$ to $550^\circ C$ by strictly controlling the reaction temperature. As the fluorine content in the product increased, its color gradually lightened from gray to white [3]. By 1963, Watanabe Shinjun discovered that fluorinated graphite, with an interlayer energy much lower than that of graphite and unchanged by ambient atmosphere, could be used as a solid lubricant. Subsequently, he also found that fluorinated graphite is an ideal positive electrode active material for high-energy density lithium batteries. The unique properties and outstanding performance

of fluorinated graphite have attracted close attention from researchers in various fields. In the 1980s, Fujimoto et al. [4] prepared fluorinated graphite by reacting AlF_3 and MgF_2 with fluorine and graphite at low temperatures and studied the fiber intercalation compounds of fluorinated graphite. This article reviews the preparation methods of fluorinated graphite and its application in lithium primary batteries.

2. PREPARATION METHOD

The non-conductive interlayer compound of graphite formed by the direct reaction of carbon with fluorine is known as fluorinated graphite, with fluorine atoms acting as the interlayer species. Fluorinated graphite can be represented as $(CF_x)_n$, where x is a variable value. As far as the currently known fluorinated graphites are concerned, there are three compounds: $(CF)_n$, $(C_2F)_n$, and $(C_4F)_n$. Currently, the synthesis methods of fluorinated graphite mainly include gas-phase method, solid-phase method, electrolytic synthesis method, etc.

2.1 high-temperature synthesis method

The high-temperature synthesis method is a direct synthesis method for fluorinated graphite, also known as the gas-phase synthesis method. In this process, graphite is directly reacted with fluorine gas at temperatures above $600^\circ C$. The graphite is first activated by grinding it into a powder, then placed in a reactor with dry nitrogen for several hours to remove volatile impurities. Finally, fluorine gas is introduced for the reaction, with the temperature typically controlled between $624^\circ C$ and $630^\circ C$. The composition of the resulting fluorinated graphite is determined by the type of graphite raw material and the reaction temperature, meaning that the C/F ratio in the molecular structure of fluorinated graphite is dependent on the reaction temperature, which in turn determines the properties of the final fluorinated graphite [5]. The decomposition temperature of fluorinated graphite in fluorine is lower than the reaction temperature for the reaction between graphite and fluorine, but the decomposition temperature of fluorinated graphite in the sample is higher than the reaction temperature

(650°C). Therefore, at such high temperatures, when the pressure of fluorine reaches a certain limit, the reaction may decompose and even explode. As a result, the high-temperature synthesis method is not a safe synthesis method.

2.2 Low-Temperature Synthesis Method

The low-temperature synthesis method is also a direct synthesis method for fluorinated graphite, which is a safe, efficient, and continuous production method. It involves first reacting graphite with a pentahalide, followed by reacting the resulting graphite interlayer compound with elemental fluorine at low temperatures, resulting in a product with a C/F ratio of no less than 1 in the final molecule. The pentahalide used in the reactants refers to oxides, chlorides, bromides, or iodides of antimony and arsenic, with pentachloride antimony being the most commonly used. Since the boiling point of pentachloride antimony is 92°C, condensation can be used to collect the vapor of pentachloride antimony for reactions conducted at temperatures higher than its boiling point [6].

2.3 Catalytic Synthesis Method

If trace amounts of metal fluorides, such as LiF, MgF₂, AlF₃, or CuF₂, are added to the reaction system of graphite and fluorine in the high-temperature synthesis method, fluorinated graphite can be successfully produced even at temperatures below 300°C, with these metal fluorides acting as catalysts. The fluorinated graphite produced by the catalytic synthesis method contains trace amounts of metal fluorides, which significantly improve the electrical conductivity of the fluorinated graphite. The production equipment used in the catalytic synthesis method is the same as that used in the direct synthesis method, but there are higher requirements for the purity of the raw materials. Specifically, the carbon content of natural graphite must be above 99.4%, and the purity of gaseous fluorine must be between 99.4% and 99.9%, with the nitrogen content in fluorine not exceeding 0.30% to 0.6% and the HF gas content not exceeding 0.01%. The purity requirements for metal fluorides used as catalysts, such as CuF₂ and AlF₃, need to be greater than 98% [7].

2.4 Electrolytic Synthesis Method

This method involves electrolyzing graphite and hydrofluoric acid to generate fluorinated graphite through an electrochemical reaction. Since hydrofluoric acid continuously circulates between the anode and cathode, fluorinated graphite can be synthesized continuously. The entire synthesis process can be controlled by adjusting the concentration of the reaction solution, the reaction temperature, or by using conductive additives.

3. Application of Fluorinated Graphite in Lithium Primary Batteries

Fluorinated graphite has a wide range of applications due to its extremely low surface energy, high electrode activity, and other properties. It exhibits excellent performance in various fields such as lubrication, anti-fouling, nuclear reactions, and battery reactions. For instance, it can be used as a waterproof material, mold release agent, solid lubricant, and to manufacture various composite materials. Among these, the most important application is fluorinated graphite as a cathode material for primary batteries. Due to the physicochemical properties of fluorine and lithium, batteries combining them possess the highest energy. However, using fluorine as an anode active material is excessively dangerous and presents a difficult technical challenge. With the emergence of fluorinated graphite, which has excellent thermal and chemical stability, the production of lithium/fluorinated

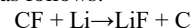
graphite batteries has become the optimal choice. Lithium/fluorinated graphite batteries have a stable voltage and high specific capacity, resulting in nearly 100% battery utilization. Therefore, fluorinated graphite as a battery cathode material is also a current research hotspot.

Table 1 Comparison of several different types of lithium primary batteries (LIBs).

LIBs	Li/SO ₂	Li/MnO ₂	Li/SOCl ₂	Li/CF _x
Theoretical Energy Densit (Wh/Kg)	1170	1005	1470	2180
Operating Temperature Range /°C	-20~60	-20~60	-40~55	-40~170
Life/Years	5~10	10~20	10	15

From the comparison of various primary batteries presented in Table 1, it can be understood that lithium/fluorinated carbon batteries have the highest theoretical specific energy among disposable batteries. Furthermore, lithium/fluorinated carbon batteries also possess advantages such as high mass and volumetric specific energies, as well as a long storage life, similar to other lithium solid-state batteries. In addition, lithium/fluorinated carbon batteries have the advantage of over 90%, or even 100%, utilization of the cathode active material, and they ensure safety even in cases of misuse such as short circuits, collisions, crushing, or high temperatures. Fluorinated graphite lithium batteries use metallic lithium as the anode and fluorinated graphite as the cathode material, and they possess the highest theoretical specific energy (approximately 2180 Wh/kg) [8]. Coupled with their superior performance compared to other primary batteries, fluorinated graphite lithium batteries can meet the application requirements of high-end civilian instruments, military equipment, and aerospace backup power supplies, making them a key focus of current research and development.

In lithium/fluorinated carbon batteries, metallic lithium is used as the anode, and fluorinated carbon (CF)_n is used as the cathode. When n=1 in fluorinated carbon (CF)_n, the battery discharge process is as follows:



The discharge mechanism is as follows: When the battery begins to discharge, the active material at the cathode, fluorinated graphite, transitions from being an initial poor conductor to conductive carbon. This conductive carbon, which has an amorphous microporous structure, gradually deposits onto the surface of the lithium battery's cathode. This increases the battery's conductivity and reduces its internal resistance. Therefore, when the battery starts to discharge, there is initially a slight increase in voltage, followed by a stable voltage platform, which leads to an increase in the utilization rate of the cathode material. Simultaneously, as amorphous conductive carbon forms at the cathode, the anode is oxidized into LiF crystals. As the battery discharge reaction progresses, these LiF crystals slowly fill the micropores of the conductive carbon. This results in a swelling phenomenon in the fluorinated graphite at the cathode after the discharge is complete [9]. Figure 1 illustrates the structural principle of the lithium/fluorinated carbon battery.

Although lithium/fluorinated carbon batteries possess many excellent properties that are difficult for similar batteries to match, they also face some challenges. Currently, the main method for synthesizing fluorinated graphite both domestically and internationally involves reacting flake graphite powder with fluorine gas under high temperatures and specific process conditions. The high fluorine content results in poor conductivity, which in turn affects the battery's discharge performance at high rates. In addition, the use of fluorine gas in the production process of fluorinated graphite

imposes stringent requirements on the production conditions and equipment, leading to high costs for lithium/fluorinated carbon batteries. Furthermore, when the battery is discharged at high rates, the internal resistance of the battery increases, ultimately causing severe electrode aging. Therefore, despite the high specific energy of lithium/fluorinated carbon batteries, their inability to be used for long periods at high rates prevents this advantage from being fully realized. For example, when the discharge rate is 2C, the average voltage of a fluorinated carbon coin battery is approximately 1.6 V to 1.8 V, with a specific capacity of around 300 mAh/g to 500 mAh/g. Therefore, additional treatments are required to improve the performance of lithium/fluorinated carbon batteries.

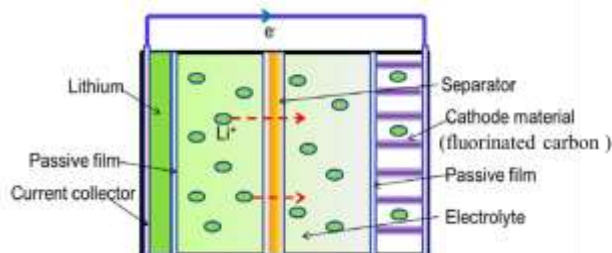


Figure 1. Schematic diagram of the lithium/fluorinated carbon battery structure.

4. CONCLUSION

In lithium primary batteries, fluorinated graphite, as a high-energy battery active material, boasts advantages such as ultra-high energy density, long storage life, and low self-discharge. It has been widely applied in crucial fields like aerospace and deep-sea exploration. However, its degree of fluorination is closely related to the battery's energy density and conductivity, necessitating modifications through techniques such as conductive layer coating and material nanoscaling to enhance the battery's power characteristics. In recent years, researchers have further improved the rate performance and energy density of lithium primary batteries by introducing new electrolyte additives, such as boron trifluoride gas.

5. ACKNOWLEDGMENTS

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