Preparation of Graphene and its application in lithium batteries

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Abstract: The dual-carbon nanomaterial graphene has attracted the attention of scientific researchers all over the world because of its excellent properties and structure. Among them, graphene as anode material for lithium battery is a hot topic. In this study, the properties of graphene, the preparation method of graphene, the application prospect of modern graphene and the existing preparation methods are discussed.

1. INTRODUCTION

The rapid development of science and technology in recent years has led to the emergence of electronic products such as mobile phones and computers and new energy vehicles. It is not difficult to find that these products are powered by electric energy. This requires a stronger energy supply device to support the energy loss caused by its more functions, with the expectation of longer working hours.

Lithium batteries as a capacity supply device have higher capacity and higher circulation efficiency than traditional lead acid batteries and zinc manganese batteries. Therefore, in recent years, lithium battery has also become a major hot topic of research. Based on the excellent performance of lithium batteries, we can regard them as the ideal energy supply device for future electronic equipment (as shown as how lithium works). The key factor of the performance of lithium battery is the power storage capacity of its anode material, now lithium batteries usually use the metal anode. Metal negative electrode will appear some irreversible phenomena such as electrochemical dissolution reactivity, which limits its performance as a battery negative electrode. So we hope to find a better quality negative electrode material.
the field of vision of researchers because of their excellent electrochemical properties. Researchers apply different carbon materials to the negative electrode of lithium battery, hoping to get more efficient lithium battery. Graphite is a more negative electrode material, but with further research, graphene has greater potential than graphite because of its better performance. Graphene is a new type of two-dimensional material with the thinnest thickness, the highest strength and the best thermal conductivity. It has great potential in many fields, such as intelligent equipment, aerospace, energy storage and environmental control, and is an important strategic new material. As an incompetent semiconductor material, graphene has the advantages of high conductivity and stable specific capacity chemical properties. At the same time, graphene, compared with other carbon-based materials, can absorb more lithium ions and perform better in mechanical strength, charge mobility, conductivity and so on.

Therefore, graphene is ideal as a graphite negative electrode material. With the increasing demand for graphene, seeking an efficient, environmentally friendly, and large-scale graphene preparation method is particularly important. However, the traditional redox preparation method with complex process, poor environmental protection and poor conductivity performance is not an ideal preparation method. In recent years, one of the hot research directions of the preparation of graphene has also produced a lot of literature and data. It can be said that when the application research and preparation of graphene research breakthrough, we have the opportunity to get more excellent performance of lithium batteries. There is no doubt that this has a very important role in promoting the current development trend.

Properties of graphene

Graphene is a two-dimensional crystal with a single atomic layer connected by carbon atoms in a sp² hybrid carbon atoms are arranged into honeycomb structural units. This structure is important for graphene as a composite. graphene can react with active metals, graphene can be oxidized by oxidizing acids in air. The structure of graphene is very stable, and the connection between the internal carbon atoms is very flexible. When the external force is applied, the surface of the carbon atom will bend, thus avoiding the rearrangement of the carbon atoms. At the same time, the stable lattice structure makes the thermal conductivity of graphene very excellent. Thanks to this structure, the electrons inside graphene are less affected when they receive interference. The remaining π bonds form large π bonds with each carbon atom in addition to σ bonds used to connect other carbon atoms, and electrons can move freely in this region. Therefore, graphene material has good electrical conductivity, which provides a theoretical basis for its application on negative electrode of lithium battery.

2. Preparation of graphene

2.1 Micro-machine stripping method

Graphene prepared by the Geim Institute of Manchester University in 2004 was using the adhesive force of the tape, the flake graphite was stripped layer by layer and placed on the crystal surface to obtain graphene. Although the cost of this approach is minimal, its production can’t meet large-scale production demand.

2.2 Chemical Vapor Deposition CVD Method

Chemical vapor deposition is the application of two or more gaseous raw materials into a reaction chamber, allowing them to react chemically to form new materials and deposit them on the wafer surface. As follows: the hydrocarbon methane, ethanol and so on are passed into the Cu, Ni surface at high temperature, and several layers and monolayer graphene can be formed during cooling. It is found that other metals can also be well prepared for graphene. (As platinum, iridium, etc). The method is also considered to be the most potential method. The advantage of this method is that it can be produced on a large scale, and the required reaction conditions are low and easy to separate, which is beneficial to the subsequent processing. But it is undeniable that it also has some problems. One is
that the yield of graphene will be affected by the conductivity of the metal substrate. Second, although graphene with high quality can be obtained, its cost is high and the process is complex, so there will be challenges in large-scale industrial production.

2.3 Graphite oxide reduction method
Because of its simple operation and low preparation cost, large-scale production is considered one of the best methods for preparing graphene. The preparation of graphene is divided into three steps: oxidation, stripping, and reduction.

The method of oxidation process can be divided into three methods: Hummers, Brodietz and Staudenmaier. Compared with the three methods, the Hummers method has a high security. The layer structure of Staudenmaier method graphite oxide will be greatly destroyed. Therefore, The mainstream preparation of graphene is the improved Hummers method. There are two mainstream methods: thermal expansion stripping and ultrasonic dispersion. Thermal expansion separation is the GO decomposition when heat treatment produces carbon dioxide and water vapor, the interlayer pressure using the velocity difference between the released and generating gas, then, the stripping of graphene oxide. Ultrasonic dispersion is a high pressure impact GO layer with closed bubbles formed using GO water dispersion under ultrasonic radiation, Then the stripping of graphene oxide. There are now three main methods for reducing graphene oxide. The first category is the direct reduction of graphene oxide. The second category is the solid phase thermal reduction using a short time of high temperature reduction GO, but the product of this method is solid graphene and more difficult to integrate into other polar or non-polar solutions is detrimental to further utilization. The third category is the catalytic reduction method, namely, under high temperature or light conditions, Mixed the catalyst into graphene oxide induced its reduction. Common methods are also microwave reduction method, electrochemical reduction method, solvent thermal reduction method, etc.

2.4 Graphite intercalation:
The formation of new compound [2] is inserted by atoms, molecules, ions, etc. of non-carbon materials between the layers using natural graphite. Thus reducing the interlayer action of graphite, graphene sheets can be obtained more conveniently by corresponding operation. Although this method is convenient, there are also shortcomings, that is, the perfect intercalation can’t be guaranteed during operation, which will affect the stripping.

2.5 surface epitaxial growth method:
When the temperature of heating graphite by electron beam bombardment is in vacuum environment. The removal of oxygen is at 1000°C. the temperature increase to 1450°C after 20 min, and cause the epitaxial growth of graphene in ultra-vacuum state. During this period, we can observe the growth of graphene by low energy diffraction. The cost of the method is high, the preparation procedure is more complex, and the large-scale preparation can’t be carried out.

2.6 electrochemical method:
Electrochemical method is a common method to prepare graphene. With the strengthening of research, an ideal method for the preparation of graphene has emerged, that is, graphene is used as anode. It is stripped by electrochemical method. It is found that the properties of graphene are affected by electrolyte. However, the method has advantages in cost, low cost and no environmental pollution in preparation stage. It can be said that at this stage, this is the most likely to achieve industrial production of graphene preparation method.

3. Application of graphene in lithium batteries
The large specific surface area and excellent conductivity of graphene make it an ideal lithium ion anode material. Now, The types of materials used in lithium ion anode are natural graphite, artificial graphite, mesophase carbon microspheres, etc. The cost of these materials accounts for about 15% of
the core cost. The reason why graphite materials are used in lithium battery anode, Thanks to the structure of graphite, it has high conductivity, stability, lithium ion deintercalation and other excellent properties. The theoretical specific capacity is about 372 mAh/g [3]. Graphite when we look at graphene with the same structure as graphene, it will be found that while retaining the excellent properties of graphite, Graphene can realize lithium intercalation at both ends of the lamellar. This means that graphene has a higher theoretical capacity. Theoretical capacity of graphene is 740mAh/g, about twice as much as graphite. There is no doubt that graphene as a negative electrode material can be used to obtain better performance lithium batteries.

Except for the high theoretical capacity, graphene as a matrix material also has excellent performance allowing it to play an active role in the composite electrode material. For example, in lithium sulfur batteries, although sulfur is low and high capacity with little environmental pollution, its poor conductivity and the defects in the volume change during discharge limit its application in batteries. When we apply graphene to lithium sulfur batteries, let graphene play the role of the skeleton while using its higher specific surface area to store sulfur [4], it can greatly improve the defects. Lithium sulfur batteries have been developed for decades since the late 1960 s and have made great progress. The following figure shows a configuration comparison between LIBs and LSBs.

![Configuration comparison between LIBs and LSBs](image)

**Figure 2. Configuration comparison between LIBs and LSBs [1]**

4. Conclusion

Although the mechanical stripping method first discovered is simple in operation and low in cost, it can’t be put into large-scale use and can’t meet the demand. High quality graphene can be prepared by chemical vapor precipitation CVD method, but its production mode is not suitable for large-scale industrial production, so it can’t meet the needs of industrialization. The surface epitaxial growth method also faces this problem. At present, redox method and CVD gas precipitation method are the most potential and valuable methods. How to prepare graphene efficiently is the research direction that should be focused on at present. In application, graphene has a better effect than graphite in lithium storage due to its unique structure. This is also the lithium battery that we hope to use graphene to replace graphite. At the same time, the two-dimensional structure of graphene also allows it to be used as a substrate for composites. Many studies are carried out around graphene matrix composites, which is also a hot research direction.

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