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Principle & application of energy storage based on 2D material: Evidence from graphene

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Abstract. The development of new energy and related industries has raised higher requirements for energy storage devices. Graphene, a 2-D carbon material with a single atomic layer thickness, possesses excellent mechanical properties, thermal conductivity, SSA, optical transparency, and rapid electron migration, among other unique physical and chemical properties. The addition of graphene is predicted to enhance the rate performance, durability and energy density of electrochemical energy storage devices. This study summarizes the recent research in the production and application of graphene in electrochemical energy storage devices, primarily focusing on supercapacitors and the positive and negative electrode of lithium-ion batteries. The main roles of graphene include serving as an ultrathin support and buffering material, an active substance, and a conductive material. In addition, the limitations of graphene due to its production technologies and the potential brought by its super flexibility and lightweight properties are discussed. Finally, a brief outlook in the field of graphene is provided.

Keywords: graphene, energy storage, supercapacitors, lithium-ion batteries.

1. Introduction

The advancement and application of sustainable energy resources is a promising method to alleviate the energy crisis and address the environmental pollution caused by traditional fossil fuels. The readily available renewable energy resources are mostly wind energy and solar energy and the technologies for energy conversion has made massive progress. However, different from the stable energy resources used by most of China's thermal-power generation, these type of energy resources are intermittent, and their fluctuations are unstable in time and space, making continuous extraction challenging. Therefore, the development of efficient and cheap energy storage technologies is particularly significant. Electrochemical energy storage devices (ESSD), which can efficiently store fossil fuels and renewable energy sources and release clean energy when used, is utilized more than before [1]. They have the ability to convert and store energy, making them suitable for various applications with specific requirements. Two-dimensional materials, such as layered lithium metal oxides (LiMO2) and graphene [2], exhibit superior performance compared to other materials used in electrochemical energy storage. In recent years, research related to electrochemical energy storage has concentrated on the unique properties and preparation of nanomaterials. For two-dimensional materials, this involves manufacturing nanosheets by either exfoliating bulk layered materials or synthesizing them directly [3, 4]. These nanosheets typically possess excellent conductivity and exhibits reversible ion intercalation while maintaining minimal alterations to its structure.

This paper summarizes the applications of two-dimensional materials in energy storage, with graphene as examples. It discusses their preparation methods, basic properties, and explores the principles of energy storage using these materials. It provides an overview of the current market of graphene-based materials in energy storage and identifies their existing defects and causes. Based on this analysis, it offers prospects for future research and application in this field.

2. Basic description and preparation of graphene

The new 2-D graphene was first prepared by the GEIM research team in 2004. by mechanical exfoliation. The internal lattice structure of graphene forms an ortho-hexagonal honeycomb pattern. There are partial π bonds and σ bonds between carbon atoms that are close to each other in the hexagonal lattice structure of graphene. The π bonds in graphene are formed by the hybridization of 2pz orbitals perpendicular to the plane of layer. They play a crucial role in partially separating graphene layers. The σ bonds are formed by the hybridization of sp^2 orbitals and the bond length is approximately 1.42Å. It has higher energy compared to the sp^3 hybridized C-C bonds in diamond-like structures. This enables graphene to possess exceptional mechanical properties, such as a strength about 100 times that of steel. Additionally, because the π bonds are in a partially filled state, the electron binding around the π bonds decreases, leading to increased electron activity and exceptional electrical properties in graphene. Due to its unique structures, graphene exhibits high specific surface area (SSA) of $2.6\times10^3\ m^2 \cdot g^{-1}$, high conductivity ($10^6\ S \cdot m^{-1}$), high electron mobility ($1.5\times10^4\ cm^2 \cdot V^{-1} \cdot s^{-1}$), high transparency, and excellent mechanical properties [5, 6]. According to the synthesis mechanism of graphene, the preparation methods can be classified into two categories, i.e., bottom-up and top-down. Bottom-up methods are growing graphene continuously by depositing carbon atoms on a substrate, such as chemical vapor deposition (CVD) [7]. Top-down methods involves applying external forces or techniques to break the van der Waals forces between graphite layer sheets. Top-down methods include mechanical exfoliation, Hummers method, electrochemical exfoliation, etc.

Mechanical exfoliation utilizes mechanical force to disperse and peel the graphite layers, transforming them into single-layer or few-layer graphene. Mechanical exfoliation techniques include ball milling exfoliation and high-shear exfoliation methods. In high-shear exfoliation graphene layers are obtained by shearing the graphite layers under high shear forces. In the process of ball milling exfoliation, graphite particles are ground together with milling media, gradually dispersing into graphene layers after breaking the van der Waals forces. Novoselov et al. first used the adhesive force of tape to repeatedly peel graphite layer by layer and obtained graphene by removing excess material from the surface of the graphite layers using organic solvents such as acetone [8]. Although the products are of high quality, it is time-consuming, labor-intensive, and has limited yield. Alternatively, the ball milling exfoliation method for preparing graphene utilizes the impact and grinding between high-speed rotating balls and graphite. Graphene is obtained under various mechanical forces such as vibration and shearing force to strip off the graphite layers. The graphene prepared by this method has advantages such as relatively complete structure, fewer layers, and high thermal and electrical conductivity. The main factors affecting the preparation of graphene include the type of graphite, the ratio of balls to solvent, ball milling speed, and milling additives. Among them, the type of milling additive Exerts a significant influence on the quality of graphene prepared by mechanical methods. Common milling additives include choline chloride, ammonium carbonate, and hexadecyltrimethylammonium bromide [9-11].

The liquid phase exfoliation method refers to a method of preparing graphene by placing graphite directly in deionized water or organic solvents, and subjecting it to high temperature, ultrasound, airflow, and other conditions to achieve the exfoliation of graphite. Among the process parameters for preparing graphene, the type of organic solvent has an important impact on the quality of the graphene. Commonly used organic solvents include N-methyl-2-pyrrolidone, sodium deoxycholate, alkaline lignin, etc. [12, 13].

During the process of CVD, a carbon-containing substance is first gasified and undergoes a chemical reaction under specific conditions. The resulting reaction products are then deposited onto a substrate surface to form graphene. During the CVD process of graphene preparation, factors such as the ambient atmosphere and catalyst could significantly influence the performance of the synthesized graphene. CVD allows for the production of graphene with excellent physical properties and high repeatability, making it suitable for industrial-scale production. However, there are drawbacks to using CVD for graphene film fabrication, including higher production costs, longer deposition time, inability to reuse the metal substrate, and susceptibility of the graphene film to damage during the transfer process.

3. Devices

3.1. Supercapacitors

With the continuous progress and advancement in science and technology, there is an increasing energy storage devices requirement with regard to capacity density, power density, stability, and lifespan. Supercapacitors have achieved a prominence for their high energy storage and utilization efficiency. Compared to traditional capacitors or other energy storage devices, supercapacitors have larger energy storage capacity, higher energy and power density, and characteristics such as fast charging and discharging. The electrode material in capacitors is vital to determine their performance. Currently used electrode materials include MnO_2 [14], carbon nanotubes [15], etc. MnO_2 electrodes possess high specific capacitance, low cost, abundant reserves, and environmental friendliness. However, the low electronic conductivity of MnO_2 leads to reduced capacitance under high current density charge-discharge conditions, and the dissolution of manganese results in cycling instability, limiting its further development. Carbon nanotubes are characterized by large SSA and high conductivity, exhibiting good power density and reversibility as capacitor materials, albeit relatively lower energy density. Graphene, with its unique two-dimensional structure, high SAA of 2,630 $m^2 \cdot g^{-1}$, and excellent conductivity, is an ideal electrode material for capacitors.

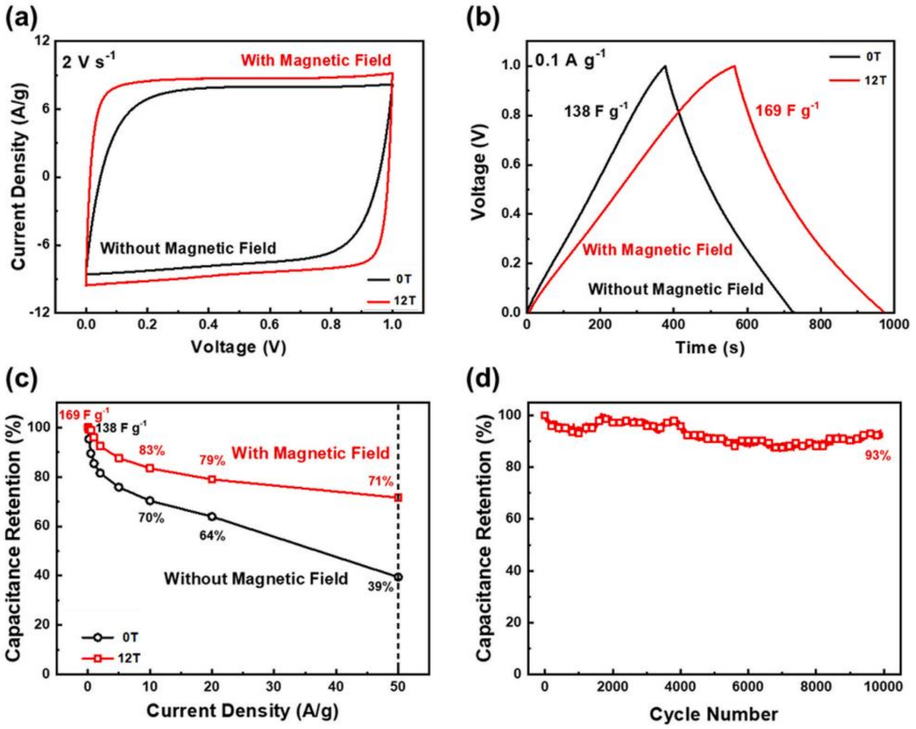

Figure 1. Experiment results of graphene's characteristic curves (a) CV curves at fast voltage sweep rate of $2\ V \cdot s^{-1}$, (b) GCD curves at constant current density of $0.1\ A \cdot g^{-1}$, (c) Rate performance at various current densities from $0.1A \cdot g^{-1}$ to $50A \cdot g^{-1}$ and (d) Cycling performance of supercapacitor with graphene /PEDOT/PSS composite electrodes prepared with the aid of magnetic field [16].

Stoller et al. used chemical modification method to prepare functionalized graphene and used it to fabricate capacitors [17]. The specific capacitance of the capacitor in aqueous electrolyte was 135 $F \cdot g^{-1}$. With the aim of a further improvement of the graphene supercapacitors' performance, researchers conducted extensive research on improving the dispersibility and structural orderliness of graphene, as well as introducing pseudocapacitance, and have achieved good research results. Lin et al. used PEDOT/PSS as a binder to prepare graphene/PEDOT/PSS composite films under a strong magnetic field of 12 T [16]. Research has found that through magnetic field treatment, the structural orderliness of graphene can be increased, and the ion transport rate can be improved, thereby improving the performance of the capacitor. The performance test results of the capacitor are illustrated in Figure 1. From Figure 1(a), it is noticeable that the CV curve of the capacitor composed of magnetically treated graphene is rectangular, resulting in faster electrochemical response. In addition, from Figures 1(b) and 1(c), it can be seen that the capacitor assembled with magnetically treated graphene has a specific capacitance of 169 $F \cdot g^{-1}$ at a current density of 0.1 $A \cdot g^{-1}$, and maintains about 70% capacitance at a current density of 50 $A \cdot g^{-1}$. Conversely, the capacity of the capacitor assembled with untreated graphene is only 138 $F \cdot g^{-1}$, and it only maintains 39% capacitance at a current density of 50 $A \cdot g^{-1}$. Figure 1(d) shows the cycling performance of the capacitor in a 1M sulfuric acid electrolyte at a current density of 0.5$A \cdot g^{-1}$. After 10000 cycles, it retains 93% of the initial specific capacitance, indicating good cycling stability of the capacitor.

In terms of introducing pseudocapacitance, the main approach is to modify the graphene electrode with small molecules or construct asymmetric capacitors. By utilizing the chemical transformations that occur during the working and recharging processes of the capacitor, the capacity of pseudocapacitance can be increased, thus achieving the goal of improving the capacitance. Zhou et al. prepared graphene-based fibers by modifying them with naphthoquinone and reducing them with a mixture of nickel hydroxide and cobalt and used the prepared materials as electrodes to construct symmetric capacitors [18]. The capacitor constructed with NCHrGO/CF as the electrode displayed a high specific capacitance of 763.0 $F \cdot g^{-1}$ at a current density of 0.70 $A \cdot g^{-1}$, maintaining 87% of its initial capacitance after 10,000 cycles. In addition, they also constructed an asymmetric supercapacitor using NQ/graphene/CF and nickel, achieving a maximum power density of 1642.1 $W \cdot kg^{-1}$ and a maximum energy density of 50.7 $W \cdot h \cdot kg^{-1}$ under a working voltage window of 2V. Asymmetric supercapacitors combine the advantages of capacitors and batteries, significantly improving capacitor performance, and are an important research direction for enhancing supercapacitor performance.

3.2. Lithium-ion batteries

Lithium-ion battery is widely utilized worldwide due to its high performance. However, their performance still falls short of meeting the requirements of electric vehicles, electronic products, and large-scale energy storage. The market continues to demand lithium-ion batteries of higher energy density, rate capability, and cycling performance. Graphene, with its unique 2-D structure and outstanding electrical, mechanical, and chemical properties, exhibits outstanding conductivity and can alleviate issues such as electrode material volume expansion.

The main cathode materials used in lithium-ion batteries contain $LiFePO_4$, nickel cobalt manganese ternary and $LiCoO_2$. However, these materials have low Li^+ and e^- conductivity, which limits the performance of lithium-ion batteries. Graphene, with its large SSA, excellent conductivity, and superior chemical and mechanical stability, can be added to the positive materialsobviously boosts electrode's stability and conductivity. Researchers studying the influence of different graphene contents on the performance of lithium-ion batteries at low rates have found that the discharge specific capacity initially increases and then decreases as more graphene added. When comparing it with commercial conductive agents, it is found that adding a small amount of graphene can achieve good conductivity and improve battery performance accordingly. Different types of battery preparation processes and the quantities of materials used in them vary, so it is important to consider the issues that may arise during production in the research. In 2010, Yang et al, compared the differences between graphene and Super P conductive agents [19]. The research showed that adding 2 wt% of graphene conductive agent can effectively enhance the energy storage performance of $LiFePO_4$.

With the deepening of research, it has been realized that using graphene alone as a conductive agent does not have consistent performance under high-rate battery charging and discharging. Therefore, the study of the performance changes by compounding graphene with conventional conductive agents as binary conductive agents added to batteries began. In 2016, the research conducted by He et al. indicated that graphene could build a high-efficiency conductive network while serving as a conductive agent in the $LiCoO_2$ lithium-ion battery system [20]. Unlike other nano-scale materials, graphene did not exhibit a rapid decline in discharge specific capacity under high-rate conditions. For example, when 0.2 wt% graphene and 1 wt% carbon black were used as a binary conductive agent, the discharge specific capacity of the $LiCoO_2$ lithium-ion battery system prepared was 146 mAh/g at a 1C rate, with a capacity retention rate of 96.4%. This is because the particle size of the positive electrode materials is larger than that of graphene; graphene is used in a smaller amount and does not completely cover the active material. They achieve a synergistic effect with the carbon added and construct a conductive network.

Graphene can also be added into the negative electrode to enhance electrochemical performance. Conventional lithium-ion batteries use negative electrode materials such as graphite, which have lower specific capacity and energy density and cannot meet the new demands of the market. Currently, research on negative electrode materials mainly focuses on sulfides, transition metal oxides, Sn-based materials and other materials that can promote battery capacity. However, there are issues such as large volume changes and poor conductivity, which limit the performance of lithium-ion batteries. Constructing new composite conductive negative electrode materials with various encapsulation structures is an effective approach to solving this problem.

In 2017, Ci et al. developed a walnut-shaped porous silicon material by combining graphene and silicon [21]. The new material featured a specific capacity of 1258 mAh/g at a current density of 1 A/g. The specific capacities were as high as 2100, 1600, 1500, 1200, and 950 mAh/g corresponding to current densities of 1.0, 2.0, 3.0, 4.0, and 5.0 A/g, respectively. The conductivity of this kind of material was significantly improved through in-situ reduction. During charging and discharging, the metal removal process created a porous silicon structure that provided ample space for volume changes. Furthermore, the shell reduced direct contact surface area between the electrolyte and silicon, providing a high-speed pathway for electron transfer. As a result, the material exhibited excellent capacity retention.

In 2022, Lu et al. from the UCLA synthesized a three-dimensional graphene-CNTs-silicon composite material with excellent mechanical elasticity through spray drying and in-situ CVD synthesis. This in-situ growth method embeds silicon particles into a highly elastic graphene-CNTs spherical framework. The porous structure effectively manages the volume changes of silicon particles, and the continuous graphitized framework ensures exceptional conductivity. The foam-like three-dimensional graphene spherical structure enables mechanical elasticity to withstand mechanical rolling. The CNTs shuttle inside the spheres further enhance conductivity and minimize interface resistance, thus achieving higher rate performance, cycling life (90% capacity retention after 700 cycles at 2 A/g, with a loss of 0.014% per cycle), and mechanical properties (structural stability under 100 MPa pressure) [22].

In summary, utilizing the properties of high SSA and excellent conductivity of graphene, when combined with negative electrode materials, it can optimize the infiltration of electrolyte into the negative electrode material, increase its activity and utilization rate and enhance its conductivity. The flexible layers of graphene can mitigate the large volume changes that occur during the intercalation and deintercalation of Li^+ ions in the negative electrode material, stabilizing the structure of the negative electrode and improving the cycling stability of the battery. The three-dimensional hierarchical porous structure framework built by graphene can provide a fast pathway for Li^+ ions and electrons transfer, thereby improving the rate performance of the electrode material. Additionally, graphene possesses good flexibility and mechanical strength, ensuring the stability of the electrode and extending the lifespan of the battery. Due to graphene's high specific surface area, it can be uniformly dispersed on the surface of the negative electrode at the nanoscale, reducing the aggregation of negative sheet, lowering the volumetric expansion rate and enhancing the cycling stability of the negative electrode material.

4. Applications

Rail transportation and city buses are important applications of Supercapacitor in the field of transportation. City buses, subways, and electric tram routes have fixed stops, and frequent start-stop operations during the journey require rapid release and recovery of energy. The frequent braking of traditional fuel vehicles inevitably leads to energy waste. The fast charging and discharging properties fit the requirement well. Using super capacitor modules in the energy storage and power systems of buses can solve these problems.

High-tech devices and instruments associated with aviation have been continuously developed and applied. However, these devices or instruments often need to operate in more demanding working environments, which places higher demands on energy storage systems. These include broader operating temperature ranges, longer lifetimes, and higher power requirements. Aviation equipment also requires safe and reliable energy storage units, and supercapacitors can meet the requirements to some extent depending on its excellent characteristics. The property of instantaneous high-current discharge can provide instant high-power for certain portable electronic devices. They are lightweight and can significantly reduce the weight of carried equipment, while also enhancing the power of vehicles.

With the acceleration of industrial modernization and the increase in production volume, energy waste has also increased. In order to achieve energy conservation, emission reduction, and improve economic efficiency, it is necessary to recycle energy for reuse. In applications where energy is released, such as when a crane lowers heavy objects, a supercapacitor is well suited as an energy recovery device. When a supercapacitor is used as an energy storage system for a crane, the energy released during braking and lowering processes can be effectively recovered, resulting in a fuel savings of 40% for the crane [23].

5. Limitations and prospects

In recent years, graphene-based materials have shown improved electrochemical performance in energy storage and transmission, including longer lifespan and higher energy density, laying the foundation for more efficient electrochemical energy storage devices in the future. Notwithstanding these achievements to date, there are still several unresolved and pressing issues that require attention and resolution. In terms of manufacturing, the biggest challenge lies in how to cost-effectively and efficiently produce graphene materials with the desired defects and surface chemistry to meet specific requirements. Compared to the theoretical research on the properties of graphene, its application in energy storage devices is still in its early stages. For example, the dominant electrode material in the market nowadays is still carbon rather than graphene, mainly because most commercially available graphene products contain metal impurities that don’t reach the standards of high-performance ESSD. Additional, current products of graphene materials can be made feasible by finding electrolyte systems that are less sensitive to metal impurities in graphene. Furthermore, the information era requires for the special features and shapes of products specifically to meet certain applications. Graphene can easily be assembled into various fibre and film materials without losing its excellent properties, providing reliable solutions for future portable and wearable smart devices that require flexibility and foldability.

6. Conclusion

Since the discovery of graphene and graphene oxide, their preparation methods and applications have been continuously developed. Graphene, based on its unique properties, plays an increasingly important role in electrochemical energy storage devices (EESD). In aspect of supercapacitors, graphene's ultrahigh specific surface area facilitates the storage of large amounts of ions. In lithium-ion batteries, its excellent conductivity greatly enhances the conductivity of the positive electrode and the activity level of the negative electrode material. The ultrahigh specific surface area allows for uniform dispersion of the active material, and its excellent flexibility can buffer the volume changes of the active material during charging and discharging processes. In summary, the use of graphene in electrochemical energy storage devices (EESD) can greatly improve their energy density and lifespan. Owing to factors such as the immaturity of graphene preparation technology, its applications in energy storage are still in the research and small-scale trial production stage. Efficient and controllable graphene preparation techniques, as well as the translation from theory to techniques, will be the priority of future exploration in the field of graphene.

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