Applications of graphene-based composites in the anode of lithium-ion batteries

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Limited by the disadvantages of low theoretical capacity, sluggish lithium ion deintercalation kinetics as well as inferior energy density, traditional graphite anode material has failed to meet the ever-increasing specific energy demand for lithium-ion battery technologies. Therefore, constructing high-efficiency and stable anodes is of great significance for the practical application of lithium-ion batteries. In response, graphene-based composite anodes have recently achieved much-enhanced electrochemical performance due to their unique two-dimensional cellular lattice structure, excellent electrical conductivity, high specific surface area and superior physicochemical stability. In this review, we start with the geometric and electronic properties of graphene, and then summarize the recent progresses of graphene preparation in terms of both methods and characteristics. Subsequently, we focus on the applications of various graphene based lithium-ion battery anodes and their inherent structure-activity relationships. Finally, the challenges and advisory guidelines for graphene composites are discussed. This review aims to provide a fresh perspective on structure optimization and performance modulation of graphene-based composites as lithium-ion battery anodes.

KEYWORDS

lithium-ion battery, graphene, anode, energy storage, composite

Introduction

With the continuous progress of science and technology, sustainable development is the current goal pursued by human society, and the environment and energy have become the eternal theme of sustainable development. Within the next 30 years, human demand for energy will increase by at least 40% (Evers and Nazar, 2013). The demand for fossil energy is increasing, but its current reserves are not promising (Martins et al., 2019; Liu et al., 2021). On the one hand, the volatile prices of fossil energy products place a burden on consumers (Johnsson et al., 2018). Furthermore, emissions from fossil energy combustion cause significant damage to the ozone layer (Destek and Sinha, 2020). In 2015, the signing of the Paris Agreement signaled that all of humanity was seeking a way to combat climate change by changing forms of energy production (Sudhakar et al., 2019). Together, these concerns have led to the gradual introduction of renewable energy into the

public consciousness. Therefore, the field of energy storage is receiving increasingly widespread attention. It is worth noting that electrochemical energy storage devices can effectively store excess fossil energy or renewable energy and provide clean energy. Among different kinds of electrochemical energy storage devices, lithium-ion batteries have been considered as one of the most promising energy storage technologies due to its high power density and energy density. The lithium-ion battery is essentially a battery with a concentration difference, where the cathode and anode materials have different electrochemical potentials and separated by a membrane. Li^+ moves in the electrolyte from the electrode with the higher chemical potential to the electrode with the lower potential, and the charge compensating electrons can only move through the external circuit, thus creating a current for output use. Lithium-ion batteries are widely used, but they still cannot meet the increasing demands for energy density and power density in the fields of electric vehicles and large-scale energy storage. In fact, it is the electrode materials, including the cathode and anode materials that determine the electrochemical performance of lithium-ion batteries. Therefore, obtaining optimized electrodes has become a hot issue in the research of lithium-ion batteries. In particular, for anode materials, widely studied materials include carbon-based materials such as graphite, hard carbon, and soft carbon, and non-carbon-based materials such as alloys, lithium titanate, and nitrides. Among them, carbon-based anodes are considered to be the most promising. This is mainly because the lithiation/delithiation reaction of carbon materials is quite reversible, and the carbon-based materials have the advantages of high capacity and low lithiation potential, showing good application potential. However, traditional carbon materials, like graphite materials, cannot simultaneously meet the stringent requirements such as light weight, high electrical conductivity, high specific surface area, tunable surface wettability and excellent chemical properties (Choi et al., 2012; Xiong et al., 2015). Therefore, great efforts have been made to find and design new carbon based electrode materials in lithium-ion batteries.

Graphene is a two-dimensional lamellar material with a honeycomb lattice structure and consisting of sp^2-bonded monolayers of carbon atoms. When these carbon atoms are stacked and curled with each other, they can exhibit various molecular structures, which can be 0-dimensional fullerene spherical molecules, 1-dimensional carbon nanotubes, 2-dimensional graphene, or 3-dimensional graphite (Geim and Novoselov, 2007; Farjadian et al., 2020). Graphene has unique structural characteristics, including excellent flexibility, outstanding electrical and thermal conductivity and solar radiation absorption, high charge mobility ($2 \times 105 \, cm^2/Vs.$), high specific surface area, high specific capacity (theoretical value of 744 mAh g^{-1}) and specific capacitance (550 F g^{-1}) (Oye et al., 2013; Lawal, 2019; Wang et al., 2019; Tsang et al., 2020; Yu et al., 2020; Olabi et al., 2021). Therefore, these merits make graphene

and its composites demonstrate great potential in a wide range of applications, such as catalysis, catalyst carriers, CO_2 capture and other energy conversion and storage devices (Sahoo et al., 2012; Taheri Najafabadi, 2015; Georgakilas et al., 2016; Devrim et al., 2018; Palacios et al., 2019). In particular, when it is applied to the anode material of lithium-ion battery, it can provide abundant lithium ion de/intercalation sites, enhance the wettability of electrolyte, establish a fast charge transport channel, and effectively compound the volume expansion of the second phase, thereby expressing excellent charge-discharge capacity, rate performance and cycle stability. In this review, the synthesis strategies of graphene and the associated structures and properties are discussed firstly. Subsequently, the application of graphene composites is mainly summarized. Finally, we present the challenges and future perspectives for graphene composites materials. This review aims to provide a new perspective on optimizing the performance of graphene composites for lithium-ion battery anode applications.

Preparation of graphene

Current graphene preparation methods are broadly divided into two categories, including top-down top layer exfoliation and bottom-up bottom layer growth. One is the use of physicochemical methods to weaken the Van der Waals forces between graphite layers and exfoliate to obtain a single layer or few layers of graphene, such as mechanical exfoliation, liquid phase exfoliation, redox exfoliation, electrochemical exfoliation, supercritical fluid exfoliation, etc. One is the synthesis of graphene flake layers through chemical reactions, such as chemical vapour deposition, epitaxial growth and organic synthesis.

Mechanical exfoliation method

In 1999, Rodney S Ruoff et al. demonstrated the use of oxygen plasma to ion etch highly oriented pyrolytic graphite to obtain uniformly sized "graphite islands", which were then manipulated with the tip of an atomic force microscope to exfoliate monolayers of graphene, and this was the beginning of the mechanical exfoliation method (Lu et al., 1999). In 2008, King et al. achieved large-scale exfoliation of graphene with the help of a method that uses ultrasonic waves to disperse graphite in an aqueous surfactant solution (Lotya et al., 2009). Due to the Coulombic forces repelling each other between the surfactant coatings, the exfoliated flakes can be stabilised by a relatively large potential barrier to prevent re-agglomeration.

The mechanical exfoliation method is simple to operate, does not destroy the molecular structure, and produces graphene of relatively high quality, but the yield is low, which is not suitable for large-scale preparation, and is currently only in the laboratory stage.

Liquid phase exfoliation

In 2008, by using a solvent whose surface energy matches that of graphene, and balancing the energy required to exfoliate graphene with the solvent-graphene interaction, Yenny Hernandez et al. demonstrated graphene dispersions up to $0.01 \, mg \, ml^{-1}$, which was produced by the dispersion and exfoliation of graphite in N-methyl-pyrrolidone (Hernandez et al., 2008). In 2020, Yang et al. developed a two-step method combining resonant ball milling with hydrothermal treatment to prepare few-layer graphene in high yields (Yang et al., 2020). During resonant ball milling, Fe_3O_4 nanoparticles are used to promote the fragmentation and delamination of graphite layers. During hydrothermal treatment, shear force driven by Brownian motion of molecules at high temperature and pressure is used to enhance the exfoliation of the ball-milled product. The final exfoliation efficiency can reach 92%.

Redox method

The redox method has roughly three steps. First, The graphite is oxidized in the presence of a strong acid or strong oxidizing agent, which destroys its π-electron conjugate structure, creating defects in the graphene plane and introducing a large number of oxygen-containing groups between its layers (Zou et al., 2020). Then, the graphite oxide is exfoliated to graphene oxide under the action of ultrasonic waves. Finally, a reducing agent is used to remove the oxygen-containing functional groups from the graphene oxide surface, mostly by treating the graphite oxide at high temperatures using inert gases and exfoliating the graphene flakes by pressure to obtain the reduced graphene oxide (Du et al., 2019).

Redox method is inexpensive and can be mass-produced, but their own structure is destroyed during the oxidation process, while there is the problem of incomplete reduction, resulting in more defects in the obtained graphene, which is not conducive to practical applications.

Chemical vapour deposition method

Chemical vapour deposition is a method of growing graphene by cracking carbon precursors at high temperatures, transferring and separating the carbon precursors from the metal substrates. The graphene prepared by this method has high purity and good continuity, but impurities such as carbides and amorphous carbon will be generated during the preparation process. In 2008, the research on chemical vapor deposition using nickel and copper substrates was first reported. The use of metal substrates not only acts as a catalyst, lowering the reaction energy barrier, but also determines the mechanism of graphene deposition (Al Faruque et al., 2021). This method is inexpensive, can produce large areas of graphene and is currently the most promising method. In 2009, Kim et al. used methane as a carbon source to synthesize large graphene films directly on nickel films, proposing two different methods for patterning the films and transferring them to arbitrary substrates (Kim et al., 2009a). The transferred graphene film has a sheet resistance of $\sim 280\Omega \, \square^{-1}$ per square, the light transmittance reaches 80%, and the number of layers can be arbitrarily controlled. In 2010, Bae et al. used a roll-to-roll process to grow 30 inches monolayers of graphene on flexible copper substrates (Bae et al., 2010). The sheet resistance was as low as $\sim 125\Omega \, \square^{-1}$ per square, and the light transmittance reaches 97.4%.

Graphene materials for anodes

The power capability of lithium-ion batteries depends on the rate of migration of lithium ions and electrons through the electrolyte between the two electrodes. Thus, manufacturing high-power lithium-ion batteries is to develop materials with high conductivity for electron and build perfect nanostructures to shorten the diffusion length of lithium ions. Graphene materials have excellent electrical conductivity and high surface area to meet the above requirements (Kim et al., 2009b; Castro Neto et al., 2009; Geim, 2009). At the same time, with all its carbon atoms exposed on the material surface, this structure endows graphene with unique lithium storage properties. Compared to traditional graphite anode materials, graphene not only accelerates lithium ion transport, but also provides more active sites for lithium ions, effectively reducing the energy loss due to the polarisation effect of the battery and improving the battery life (Wang et al., 2010a; Zhou et al., 2011; Li et al., 2012; Petnikota et al., 2015; Li et al., 2016; Zhao et al., 2017).

Graphene as anode

Graphene has a series of excellent properties, but its two-dimensional structure stacked between layers is not ideal for the performance of graphene as an independent electrode. Honma et al. studied the reversible specific capacity of graphene directly used as anode material for lithium-ion batteries. At $50 \, mA \, g^{-1}$ current density, the reversible specific capacity of this graphene can reach $540 \, mAh \, g^{-1}$ in the first cycle, but the reversible specific capacity decays rapidly after multiple cycles. While the reversible specific capacity of graphene obtained by using the thermal expansion method can reach $1,264 \, mAh \, g^{-1}$ in the first cycle at a current density of $100 \, mA \, g^{-1}$, and the capacity decays insignificantly after 40 cycles (Berger et al., 2006; Cheianov et al., 2007; Schedin et al., 2007; Tombros et al., 2007; Yoo et al., 2008).

Graphene-based composites as anodes

Graphene materials are prone to agglomerate when used directly as anode materials for lithium-ion batteries and do not have the advantage of lithium storage. Therefore, graphene-based composites exhibit superior electrochemical performance as anode materials for lithium-ion batteries than single component materials. Graphene can be used to host nanostructures by anchoring nanoparticles to provide support and as a highly conductive substrate (Wang et al., 2009; Yang et al., 2010a; Wang et al., 2010b; Wu et al., 2010; Zhu et al., 2011). In addition, the integration of nanomaterials with graphene layers can help to maintain high surface area by reducing the restacking of graphene sheets. Moreover, the graphene layer can effectively buffer the large volume expansion, shrinkage and aggregation of these active nanoparticles upon lithiation and delithiation. As a result, the graphene-based composites generally demonstrate much enhanced specific capacities, rate capability and cycling performance.

Graphene/transition metal oxide composite as anode

Transition metal oxides are considered promising candidates for large-scale energy storage applications due to their higher capacity than graphite. However, they usually suffer from high volume expansion, poor electrical conductivity, slow charge transfer and ion diffusion kinetics during electrochemical reactions (Wang et al., 2012). A simple and effective way to overcome this obstacle is the synthesis of graphene/metal oxide composites, which can take full advantage of the respective strengths of graphene and metal oxides. So far, a number of graphene/metal oxide composites with different structures have been developed. Notably, the graphene used in the composites is mainly chemically derived graphene with some oxygen-containing functional groups, such as graphene oxide (GO) and reduced graphene oxide (rGO). Yang et al. synthesized rGO encapsulated cobalt oxide nanoparticles by electrostatic forces into core-shell hybrids. This composite structure enables a synergistic effect of both active metal oxide nanoparticles and graphene sheets, thus resulting in improved electrochemical performance with high reversible capacity and stable cycling performance. Specifically, the obtained rGO/Co_3O_4 showed the highest specific capacity compared to mixed rGO/Co_3O_4 and pure Co_3O_4. In addition, rGO/Co_3O_4 delivered a highly reversible specific capacity of about 1,000 mAh g^{-1} after 130th cycle at 74 mA g^{-1}, revealing excellent cycling stability (Yang et al., 2010b).

The issue of large volume changes was also effectively addressed when compounding transition metal oxides with graphene. Ajayan and others investigated the fabrication of 3D graphene backboned hybrid architectures using a hydrothermal method, which not only facilitates the rapid diffusion of electrons, but also accommodates large volume

changes of the FeO_x. As a result, the as-prepared FeO_x/graphene architecture achieves a specific capacity of over 1,100 mAh g^{-1} at 0.5 C and around 270 mAh g^{-1} at 80 C. After 1,500 cycles, capacity retention can be almost 100%, (Gong et al., 2013).

SnO_2 nanomaterials have attracted widespread attention due to their high theoretical capacity (790 mAh g^{-1}), high specific surface area and low synthesis cost (Chen et al., 2021). In 2009, Honma et al. first assembled a 3D layered SnO_2/graphene electrode with a reversible capacity of 810 mAh g^{-1}. Compared with the bare SnO_2 electrode, the cycle performance is improved and the charging capacity can still be maintained at 570 mAh g^{-1} after 30 cycles (Paek et al., 2009). In 2019, Yang et al. synthesized a SnO_2 nanospheres/graphene composite by in situ hydrothermal method. The structure of the composite is a special "sandwich" structure composed of SnO_2 nanospheres and a graphene matrix. The graphene layer can facilitate the formation of an electron transport network, while the SnO_2 nanospheres act as spacers to separate adjacent graphenes. When charged and discharged at a current density of 400 mA g^{-1}, the capacity of 658 mAh g^{-1} can still be maintained after 50 cycles, and the average Coulombic efficiency reaches 96.3% (Yang et al., 2019).

Graphene/silicon based composite as anode

Silicon is considered to be a candidate for lithium-ion battery anode materials due to its high theoretical capacity (3,579 mAh g^{-1}), abundance, wide distribution and low cost. However, the expansion and contraction of the silicon itself during lithiation and delithiation generates significant mechanical stress, which causes the silicon particles to fracture and pulverize after several cycles, severely reducing the specific capacities and cycling stability (Zhang et al., 2015). The introduction of graphene into the silicon material forms a graphene/silicon composition that not only provides a high specific capacity for the anode, but also significantly improves the conductivity of the electrode and acts as a buffer against the dramatic volume changes in the silicon material during charging and discharging, making the silicon material less susceptible to structural damage and maintaining the structural stability of the electrode.

Dou' group used a simple mixture of silicon and graphene as the anode for lithium-ion batteries (Chou et al., 2010). At a current density of 100 mA g^{-1}, the specific capacity of graphene/Si composite can reach 1,168 mAh g^{-1} and the Coulombic efficiency can reach 93% after 30 cycles. At the same time, compared with nanosize Si and graphene, the cycle stability of graphene/Si composite is better. Cho's group successfully improved the kinetics and cycling stability of silicon anodes through the sophisticated fabrication of amorphous (a) silicon nanoparticles backboned-graphene nanocomposite (a-SBG) (Ko et al., 2014). The a-SBG provides ideal electrode structures with amorphous silicon nanoparticle islands (<10 nm) uniform dispersing on both sides of graphene sheets. Benefiting from

the structure and composite merits, a-SBG shows a high specific capacity of 2,858 mAh g^{-1} with high initial Coulombic efficiency of 92.5%, excellent energy density of 468 Wh kg^{-1} at a specific power of 7 kW kg^{-1} and good cycling stability. Ye and co-workers studied the effect of graphene weight ratio on electrochemical performance (Ye et al., 2014). Comparative experiments were set up with silicon to graphene weight ratios of 1:2, 1:1, 2:1, and 3:1. The graphene/Si with a ratio of 3:1 performed best in terms of initial capacity and cycling performance.

In order to apply the graphene/Si composite material to the anode electrode of lithium-ion batteries effectively, Jangid et al. proposed a concept of a lower limit on the Si size scale. Interestingly, they found that Graphene-based interlayer will be useless for improving the cycling stability of Si-based electrodes when Si dimension is lower than 50 nm (Jangid et al., 2020). Otherwise, graphene still plays an important role in enhancing the performance of silicon cathode materials. Also, the loading density of the electrode is important as it affects the energy density of the whole battery. A loading density of 2.5–3.5 mAh cm^{-2} is equivalent to the contribution of 1 mg cm^{-2} of silicon anode, the minimum requirement for conventional full cells. Ji and co-workers prepared graphene and silicon composite with Si encapsulated in thin graphite foam anode (Ji et al., 2013). The initial specific capacity of the silicon/graphene/thin graphite foam electrode was 983 mAh g^{-1} for a Si loading density of 1.5 mg cm^{-2} and the specific capacity was maintained at 370 mAh g^{-1} after the 100th cycle, which is much higher than that of the commercial graphite-based electrode.

Doped graphene as anode

The introduction of a small amount of impurity atoms into graphene can change its local electronic structure, which in turn exhibits very different physicochemical properties. It was found that the bonding pattern of carbon atoms in the doped graphene is changed, which can provide more active sites for lithium ions and thus enhance their lithium storage performance. Among all types of element doping, nitrogen (N) doped graphene structures have received much attention, which not only shows excellent rate performance and very high capacity, but also allows for fast charging and discharging in times ranging from tens of seconds to 1 hour (Wu et al., 2011a). This N-doped graphene offers excellent rate and cycling performance due to its heteroatomic defects, increased interlayer distance, improved electrode/electrolyte wettability, and enhanced electrical conductivity.

By studying nitrogen-doped graphene nanosheets, Li and others found that the defects increase further with the number of cycles and the battery capacity showed an upward trend (Li et al., 2011). And there is an increase in capacity from an initial 450 mAh g^{-1} to 684 mAh g^{-1} after 500 cycles. In 2019, Qian et al. proposed the preparation of graphene nanoribbons doped with high nitrogen content (11.8 wt%) (Qian et al.,

2019). Until now, most of the reported N-doped graphene-based materials have low nitrogen content (<10 wt%), which is attributed to the introduction of nitrogen atoms mostly concentrated at the edges and defects of the graphene lattice (Wu et al., 2011b; Liu et al., 2014; Chen et al., 2018; Li et al., 2020). The researchers produced graphene nanoribbons with high nitrogen content by hydrothermal reduction of graphene oxide nanoribbons in urea solution. The high nitrogen content makes the anode of lithium-ion battery show more excellent performance. Zhan and co-workers prepared iodine-doped graphene by heat treatment, and the specific capacity could still be maintained at 1,565 mAh g^{-1} after 200 cycles at 100 mA g^{-1}, which was much higher than that of undoped graphene (Zhan et al., 2015). Similar to nitrogen-doped graphene, iodine-atom-doped graphene shows an increase tendency in capacity at long cycles, which is related to the change in the degree of defects during the cycling process. Yun et al. studied sulfur-doped graphene nanosheets at charge and discharge rates of 1 and 30C, which resulted in a twofold and threefold increase in reversible specific capacity compared to undoped graphene (Yun et al., 2014).

Discussions

Lithium-ion batteries are the mainstay of the automotive battery and large-scale power storing industry. In the last decades, extensive efforts have been devoted to the theoretical research and commercial application of graphene and its derivatives in these fields of energy conversion and storage. It is mentioning that the two-dimensional structured graphene materials have greatly boosted the development of new electrode materials for lithium-ion batteries due to superior electrical conductivity, flexibility and lightweight characteristics. Both the functionalized graphene and graphene-based composites have manifested considerable progresses towards energy density and cycling life. Specially, when combining graphene with other high capacity anode materials, the elaborately-designed hybrid electrodes demonstrate outstanding synergistic effect, contributing to the sufficient electrolyte penetration, low-impedance charge transport channel and superior structure stability by efficiently restraining particle aggregation, volume expansion and pulverization of active components during cycling.

In spite of great improvements in specific capacity, rate and cycle performance, it is still challenging to precisely and comprehensively illustrate the complex lithium storage and failure mechanism of this graphene-based composite materials. And then, there still has a large space for its electrochemical performance improvement towards energy density and power density. At the same time, the quality of

graphene itself is cost-consuming to achieve defect-free and 100% single-layer rate at this stage, resulting in the failure of graphene-based lithium-ion batteries to achieve the expected performance. Briefly, people should continue to explore the underlying lithium storage mechanisms of graphene composites by virtue of advanced *in situ* characterization methods at atomic scale. Secondly, electrode configuration optimization and new-system graphene composites exploitation are highly desirable to achieve the balance among the safety, performance, cost and environmental friendliness characteristics when functioned as lithium-ion battery anodes. Afterwards, with the continuous development of graphene preparation technology, it is expected that the quality of graphene will be intrinsically improved. The application of graphene composite materials in lithium-ion batteries is highly anticipated to make fundamental breakthroughs in issues such as charging and battery life, and make significant contributions to the field of power batteries.

Author contributions

YT, PW, GZ, and ZL co-wrote the manuscript, GZ and ZL conceived the project and obtained the funding sources. All authors have approved the final version of the manuscript.

Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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