

Influence of Graphene-modified Graphite Anode on the Fast Charging Performance of Lithium Batteries

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Abstract. With the exploding demands of high power output and fast charging capability on electric vehicles, in consumer electronics, power tools, aerospace, grid scale, etc., high-rate capability LIBs are highly desired for their wide range of applications. The graphite—anode with the highest commercial success so far—has fundamental limitations for the high-rate chargeability of LIBs because it has a small layer-to-layer distance and prolonged lithiation/delithiation diffusion paths, and an elevated likelihood of lithium plating under fast charging. Graphene – a nano-material with ultra-high electric conductivity, superior mechanical strength, and a unique two-dimensional structure – offers a versatile platform to modify the graphite anode. This review describes in detail how the modification of graphite with graphene improves the rate capability for LIBs: especially those focusing on progress made to enhance Li⁺ transport kinetics and structural stability by means such as fabrication of three-dimensional hierarchically porous structures, interlayer expansion, and SEI film formation and stability. A review of the state-of-the-art literature shows a clear enhancement in electronic conductivities upon incorporating graphene, lithium-ion diffusivity, and mechanical stability of composites anodes which can offer great promise to improve the rate capacity, cycle life, and safety.

Keywords: Graphene; Graphite anode; Fast charging performance.

1. Introduction

Energy is the core driving force for the progress of human civilization and social development. While traditional fossil fuels such as oil, coal and natural gas have driven the development of modern industry, they have also caused serious problems such as resource depletion and environmental pollution [1]. Therefore, developing efficient, clean and sustainable new energy sources has become an inevitable choice to break through the energy and environmental predicament. However, the supply of renewable energy has the problem of mismatch in time and space, which limits its large-scale application. Thus, it is particularly crucial to develop high-performance energy storage and conversion systems to balance the imbalance of energy supply and demand [2].

Graphite has long dominated the market of anode materials for lithium-ion batteries due to its advantages such as low cost, moderate theoretical specific capacity, low and stable working potential [3]. Under the condition of high current fast charging, lithium ions accumulate on the surface of the anode, which can easily make the lithium intercalation potential of graphite approach the deposition potential of lithium metal, causing serious lithium plating and lithium dendrite growth problems. This not only leads to capacity attenuation but also brings safety hazards such as short circuits and thermal runaway [4]. In addition, the graphite layers are connected by relatively weak van der Waals forces. During the repeated insertion and extraction of lithium ions, the co-insertion of solvent molecules may cause the graphite structure to peel off, affecting the cycle stability [5]. To break through these bottlenecks, the modification of graphite has become a research focus. Among them, the composite modification using two-dimensional material graphene is regarded as a highly promising technical route.

This paper is intended to systematically review the latest research progress and mechanism of action of graphene-modified graphite anodes for improving the fast charging performance of LIBs, and it will discuss the advantages and inherent defects of pure graphite anodes in detail, and further

introduce the major approaches of graphene modification and their mechanism in boosting fast charging performance. This will be followed up with a discussion on the limitations of existing graphene functionalization techniques as applied to real-world situations and finally, it shall offer a view of the future in terms of research directions and technology trends.

2. Research on Pure Graphite Anodes

2.1. Advantages and Disadvantages of Pure Graphite Anodes

Graphite, as the mainstream anode material for commercial lithium-ion batteries at present, is favored for its numerous advantages that meet the development needs of fast-charging lithium batteries[6]: high energy density, low charge and discharge platform, providing a stable electrochemical performance basis for lithium batteries; good cycle stability, maintaining excellent cycle life under conventional charge and discharge conditions; abundant resource reserves, low cost, and mature processing technology, enabling low-cost and large-scale commercial application in the lithium battery industry.

However, for a graphite anode, there are many problems to meet the rapid charging demand of Li-ion batteries. The biggest problem is that its electrochemical properties will be seriously degraded in the process of large current charge and discharge, which is a major technical hurdle for the realization of fast charging technology [6]. Graphite anodes experience severe capacity loss during rapid (high current) charge cycles, which limits its effective utilization for a longer period of time; the high current density encourages the lithium plating at the surface of the graphite, a harmful reaction which not only consumes active lithium irreversibly but also has disastrous safety implications, including internal short circuit due to the dendritic lithium growth. Furthermore, increased polarization and side reactions at the electrode–electrolyte interface speed up the degradation of the solid electrolyte interphase (SEI), undermining the structure, which leads to progressive loss of rate capability and long-term cyclability. Together, all greatly limit the use of graphite as a negative electrode for high rate Li-ions batteries. Therefore, enhancing the fast charge capability of graphite is one of the key issues for developing high-rate batteries.

2.2. Modification Strategies for Pure Graphite Anodes

As for pure graphite anodes, the modification strategies are mostly focusing on solving the problems of capacity fading, Li plating risks, and interfacial stabilities under high current fast charge. The key points of such strategies are to improve ion/electron transportation ability, inhibit Li plating, and enhance structural stability [7]: controlling the morphology and structure of graphite through etching method or template method for preparing porous graphite or building core-shell structured graphite, which increases the lithium-ion diffusion channel and decreases the concentration polarization, therefore alleviating capacity fading during fast charging; introducing heteroatom doping such as introducing N, B, P etc. heteroatoms in graphite lattices for creating defects site with higher electronic conductivities and faster adsorption and diffusion rates of lithium ions; doping with metals/metals oxides via introducing nanoparticles like Sn or Si or Fe₃O₄ which have synergetic effect on graphite for storing Li together with accelerating ions transport due to the catalytic effect from the particles in order to enhance the kinetics under fast charging; optimizing the electrolyte/electrode interface through addition of film forming additives (e.g., fluoroethylene carbonate) to the electrolyte, or coating the surface of the graphite electrode with conductive polymer or ceramic coatings for building a stable SEI film that can reduce the side reaction and Li plating risk in fastcharging process.

3. Graphene Modified Graphite Anode Strategy

3.1. The Advantages of Graphene

Due to the special two-dimensional layered structure and excellent physical properties (such as electric conductivity, due to their unique physical (e.g., mechanical properties, flexibility) properties, have widely used as modifiers on graphite anode materials in LIBs [8]. Defined by its large specific surface area, flexibility, high mechanical strength, excellent electric and heat conductivity, with outstanding mechanical strength, electrical conductivity and good chemical stability, it can be used as a suitable assistant material for enhancing the lithium storage capacity and fast charging behavior of graphite-based electrode. Ma et al [9]. used the supercritical CO₂ exfoliating method to prepare MLG from natural graphite, which was subsequently used for modifying graphite anodes. The charge-discharge profiles showed that the charge-discharge plateau was wider for MLG modified graphite anodes than for the pure graphite anode at different current densities, indicating a larger effective capacity; furthermore, MLG modification promoted Li⁺ ion transport kinetics, leading to enhanced rate capacity and cycle stability for the obtained cells.

Among numerous fundamental studies, based on the excellent electrical conductivity of graphene, researchers have applied graphene to enhance the overall electrical conductivity of graphite anode materials. Moreover, the layers of few-layer graphene can reversibly slide against each other, which is regarded as a good "buffer" material suitable for graphite materials that undergo slight dimensional changes during the lithiation/delithiation process, alleviating the stress generated in this process. Graphite anode materials experience slight volume expansion and deformation during the insertion of lithium ions. Due to its elasticity and mechanical properties, the introduction of graphene can effectively buffer the volume expansion of graphene/graphite composite materials [5-6]. Additionally, the introduction of graphene not only improves the electrical conductivity of these composite materials but also contributes to their capacity, mainly through: insertion of lithium ions into interlayer defects in graphene; adsorption of lithium ions on both sides of the graphene layers; and binding of lithium ions to "covalent" sites within graphene materials (elemental doping modification).

In addition, doping various heteroatoms (such as N, B, etc.) is expected to further enhance the lithium-ion storage capacity of graphene. Therefore, using graphene to modify the graphite anode can not only alleviate the volume expansion effect of graphite during lithiation/delithiation and improve cycling stability but also facilitate charge transfer, thereby increasing the fast charging rate. Moreover, as an excellent thermal conductor, graphene can reduce the risk of overheating during fast charging of the battery.

3.2. Construct a Three-Dimensional Multi-Level Pore Structure

Graphene is a two-dimensional material with a thickness of only one carbon atom, composed of carbon atoms in sp² hybridized orbitals forming a hexagonal honeycomb lattice. Its unique structure endows it with excellent properties such as high strength, high electron mobility, high thermal conductivity, high specific surface area, and relatively high chemical and electrochemical stability. It can be applied in fields such as composite materials, semiconductor materials, energy storage materials, catalysts, and catalyst carriers. Constructing three-dimensional porous graphene materials can significantly improve the dispersion of graphene. Meanwhile, the multi-level pore structure of three-dimensional graphene helps to reduce the sieve effect by providing continuous electron channels and shortening the ion diffusion path; thereby enhancing the effective utilization of the pore volume and specific surface area of carbon materials while improving their electrochemical performance. Therefore, it is widely used in supercapacitors and electrocatalysis among other fields.

Constructing a three-dimensional multi-level pore structure is one of the core strategies for modifying graphite anodes with graphene. Peng et al [10]. constructed a three-dimensional conductive structure using carbon nanotubes (CNTs) and graphene, and prepared a high-conductivity and low-defect CNT/graphene macroscopic film by regulating the reduction degree. This movie was presented as a

interlayer in the lithium metal anode, which increased the ion diffusion rate and electron transfer rate, achieving uniform Li plating/stripping so that the Li metal anode can exhibit high CE and high capacity in application. This structure can improve the fast-charging performance of graphite anodes from both mass transfer and structural buffering dimensions. Graphene has a large specific surface area and excellent mechanical properties. When combined with graphite to construct a three-dimensional multi-level pore structure, on one hand, it can provide rich transmission channels for lithium ion diffusion, reduce concentration polarization under high current fast charging, and accelerate the rate of lithium ion intercalation and deintercalation. On the other hand, the pore space of these multi-level pores can act as a buffer zone for volume deformation of graphite during fast charging, alleviate structural stress on graphite particles caused by high current charging and discharging, preventing electrode pulverization and shedding. Xi et al[11]. simultaneously modified graphene through heteroatom doping while constructing a three-dimensional structure. They created this multi-level three-dimensional structure using soft template methods along with composites involving transition metal sulfides or carbon nanotubes; they also regulated both the doping amount and configuration of heteroatoms to study electrochemical performance in lithium- or sodium-storage applications for doped three-dimensional graphene. Using the same template approach for fabrication of a three-dimensional porous composite anode based on a combination of graphene and graphite, the porous structure provided by the graphene can increase the contact area between electrode and electrolyte, while providing a certain degree of structural stability in fast charge-discharge processes; the specific capacity retention rate at 10C is higher than that of graphite anodes with pure graphite anodes by over 30%. This is due to the fact that its porous structure can not only shorten the lithium ions' diffusion length, but also inhibit the agglomeration and the structural collapse of the graphite material. Moreover, this 3D conductive framework made of graphene can increase the total electrical conductivity in an electrode and lower the charge transfer resistance under a high-rate condition, thus further improving its rate capability.

3.3. Increase the Layer Spacing

The introduction of graphene can effectively expand the interlayer spacing of graphite through intercalation, composites, and other methods, solving the problem of large interlayer diffusion resistance for lithium ions in pure graphite anodes. The interlayer spacing of pure graphite is relatively small, and the kinetics of lithium ion intercalation/extraction are hindered during high current fast charging, which is prone to cause lithium plating and capacity decay. However, graphene, with its two-dimensional layered structure, can be inserted between the graphite layers to form a "graphite-graphene" interlayer structure that utilizes the interlayer characteristics of graphene to expand the graphite lattice and increase the interlayer spacing.

Huang et al [12]. designed a molybdenum disulfide nanosheet (rGO/IE-MoS₂) material with widened interlayer spacing, which was grown in-situ on the surface of reduced graphene oxide (rGO). This material was used as an interlayer coating for lithium-sulfur battery in order to overcome the shuttle effect of LiPSs. The 3D network structure of rGO, combined with the two-dimensional layered structure of MoS₂ nanosheets, synergistically improves the electronic conductivity and the Li⁺ migration kinetics of the composite. Additionally, it can provide plenty of catalytically active sites, giving this material good adsorptive ability and effective catalytic conversion performance towards LiPSs. With the incorporation of carbon intercalation, the interlayer distance between the MoS₂ nanosheet increases from 0.65nm to 1.03nm, thereby reducing the energy barrier for Li⁺ migration. The resulting battery with rGO/IE-MoS₂/CFP used as an interlayer shows remarkable rate performance and good cycle life: its reversible capacity is up to 1202 mAh·g⁻¹ at 0.1 C, a capacity decay rate of only 0.078% per cycle for 500 cycles at 1C, and an outstanding high-rate performance of up to 789 mAh·g⁻¹ at 4C. In the case of graphite anodes modified by graphene, Li⁺ can intercalate in the defect between graphene layers or adsorb at both sides of graphene layers. The larger distance between layers offers a more spacious channel to diffusional Li⁺, lowering the migration energy barrier, thereby enhancing ion transport for fast charging. In addition to this, doping graphene by heteroatoms like N or B would not only increase the interlayer spacing of the graphite but also

introduce extra lithium storage sites, further improve the lithium storage capacity and the fast charging performance of the graphite anode.

3.4. Stabilization Regulation of SEI Film

A stable solid electrolyte interphase (SEI) film plays a vital role to enable fast charge in graphite anode. The graphene modification could suppress the rupture and regeneration of the SEI film through interface regulation, thus promoting interfacial stability. For a pristine graphite anode during fast charge, high current density promotes more parasitic reaction at the interface with the electrolyte, leading to repeated SEI rupture and reformations. This would not only consume electrolyte/lithium source but also increase the probability for Li plating. When coating with graphene on graphite surface, it works like “barrier” to separate the direct contact of graphite with the electrolyte and favours the preferential SEI formation at the graphene surface.

Yin et al have studied the potential dependent configuration of adsorbed ion and grapheme capacitance curve with respect to layer no [13], With an increase in layer number, the electronic properties change from metallic to graphite-like and the charging mechanism changes from co-ion desorption for SLG to ion exchange domination for FLG. The excellent chemical stability and mechanical properties of graphene lead to the development of a thinner, denser, and more rupture-resistant SEI film to mitigate SEI damage caused by graphite volume deformation; Furthermore, Nitrogen-doped graphene is able to control SEI composition through heteroatoms, enriched by introducing stable elements (LiN_xO_y) for improving the ionic conductance and stability. At the same time, the large thermal conductivity of graphene suppresses the local increase in temperatures during rapid charging which limits the thermally driven SEI degradation and contributes to the interface stability.

4. Challenges and Development

When using graphene as a material for preparing graphene/graphite composite anode materials, the high electrical conductivity and mechanical strength of graphene will optimize the electronic transmission efficiency and structural stability of graphite anodes, thus improving the fast charging performance of lithium batteries. But there are still a lot of difficulties in the follow-up study. First, the interface structure of graphene–graphite has to be controlled accurately. If the interfacial bonding force is insufficient, interface separation is likely to occur during fast charging, which will impede charge transfer. Second, during fast charging, the rate of lithium ion intercalation and deintercalation increases; as a result, the graphite layers are prone to volume expansion and stress concentration due to the rapid accumulation of lithium ions. Although introducing graphene can alleviate this problem, the uniform dispersion of graphene in the graphite matrix needs to be addressed. Otherwise, local agglomeration of graphene may form blind spots for lithium-ion transfer. Thirdly, fast charging requires extremely high stability of the SEI film on the anode surface. The introduction of graphene will change the electrochemical environment on that surface. It is now clear how to control both the composition and the thickness of the SEI film, such that they remain stable but do not hinder the lithium ion transfer at fast charge cycles. Apart from this, current investigations in modified graphite with graphene are mainly at the lab scale (pilot) level and not ready for industrial applications yet. To achieve commercialization, two major difficulties need overcoming: first is achieving low-cost large-scale dispersion and composite processes for graphene; current techniques, including the use of liquid-phase exfoliation or vapor-phase deposition, are expensive and hard to scale up to industrial-scale production of graphite anodes; is that the condition of preparing composite anode should be compatible with current lithium battery manufacturing process and also obtain high-performance composites, which have uniform rate capability;—nts a core obstacle for industrialization.

Although there have been related studies on theoretical calculations for graphene/graphite composite anodes, such research still needs to be further deepened. The scope of the study should cover key dimensions such as the loading thickness of graphene, the defect density of the graphene sheets, the

type of heteroatom doping, and the mass ratio of graphene to graphite. Firstly, the loading thickness of graphene not only influences the transport rate of Li^+ ions on the anode, but it can also change the interfacial mechanical property of the anode. For this reason, it is crucial to study the loading thickness of graphene. Second, not only the defect density of a graphene sheet but also the modification via heteroatoms doping drastically changes diffusion barrier and transportation path for Li^+ ion inside anode phase, thus influencing the battery's fast charging rate capability. Regarding the ratio of graphene to graphite: when this proportion is higher, electronic conductivity improves more significantly; however, it is necessary to consider whether this will reduce volumetric energy density in turn; conversely, when this proportion is lower it cannot effectively improve charge transfer efficiency or structural stability during fast charging. Therefore, there should be an optimal range for this ratio. A theoretical in-depth explanation regarding how these experimental conditions regulate fast charging performance in lithium-ion batteries with graphite anodes will provide important guidance for subsequent preparation processes involving graphene-modified graphite anode materials.

At present, most graphenes used to modify the graphite anode are obtained by reducing GO precursors. Such methods have drawbacks like costly manufacturing process, the possibility of contamination with unwanted substances in the reducing step, and daunting problems of mass production. In order to reach a commercializable use case of graphene-based modified graphite anodes regarding the fast charge capability in Li-ion batteries. There are three important areas that need to be addressed: The first area is the development of low-cost, high-quality graphene production processes. Second, optimizing the graphene-graphite composites preparation methods and designing industrially friendly technology for uniform dispersion of graphene in graphite with maintaining the structural integrity of the composite anode is necessary. Third, a systematic investigation on the methods of regulating their performances in industrial production scale should be conducted so that the fluctuation of their performances caused by the fast charging can be reduced at large-scale production, thus enabling downscaling from laboratory-based science to real-world application.

5. Conclusion

In this paper, we will discuss in detail how the modified graphite with graphene can improve or optimize the rate capability of LIBs: clarifying the key role of graphene to address the fast charging bottlenecks for graphite anode. Through building up a 3D multi-level pores structure to make graphene shorten the lithium ion diffusion distance and reduce the interface transmittance; expanding the interlayer spacing of graphite to relieve the volume stress during Li^+ ions intercalating/deintercalating and structural collapsing; stabilizing the SEI film to inhibit the growth of lithium dendrites and occurrence of side reactions, finally realizing a concerted enhancement on both the rate performance, cycle life, and safety of the composite anode. This set of modification concepts overcomes intrinsic drawbacks of pristine graphite anode (i.e., low interlayer diffusional kinetics and susceptibility to LIP at high charge rates), providing them with an effective technological route to upgrade their performances. Meanwhile, it provides both the theory and experimental basis for using two-dimensional materials in the field of modifying battery electrodes and is of great significance to promote the application of high-power lithium-ion batteries.

Further studies of the graphene-modified graphite anodes will develop toward a refined design, coordinated modification, and engineering application. On the one hand, it is necessary to combine molecular simulation and in-situ characterizing methods to deeply explore the interaction mechanism between graphene and graphite to realize atom-level precise control of the modified structure. Meanwhile, on the other side, cheap massive processes of modification of graphene composites must be created as well as joint optimisation together with conductors and adhesives in order to form combined electrode interface management systems. Moreover, the combination of graphene modification and other new types of carbon material or metal oxide composites will be able to extend the fast charging limit of graphite anode in the future and meet the real demand at last (such as electric vehicles / portable electronic device) which require power lithium ion battery.

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