Research Progress on Graphene and Its Derivatives in Enhancing the Energy Density of Lithium-Ion Batteries

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Abstract: The improvement of the energy density of lithium-ion batteries is constrained by key bottlenecks such as insufficient electronic conductivity of electrode materials, sluggish ion transport kinetics, and poor cyclic structural stability. Graphene and its derivatives, with their ultra-high electrical conductivity, excellent mechanical flexibility, and enormous specific surface area, provide multi-dimensional solutions to breaking through the aforementioned bottlenecks. This paper systematically reviews the latest research progress of graphene-based materials in enhancing the energy density of lithium-ion batteries, and focuses on analyzing their modification strategies and action mechanisms in silicon-based anodes, high-nickel cathodes, and current collectors/conductive agents. For the modification of silicon-based anodes, graphene can effectively inhibit the volume expansion of silicon and maintain the structural integrity of electrodes by constructing three-dimensional confined coating structures and carrying out synergistic nanoscale design, and typical composite systems are significantly superior to pure silicon anodes. For cathode optimization, thermally reduced graphene oxide (rGO), as a conductive framework, can construct a three-dimensional continuous conductive network that runs through the entire electrode, which increases the lithium-ion diffusion coefficient of high-nickel ternary materials by approximately three times, and significantly improves the rate performance and cycling stability. For the innovation of battery structure, graphene-based flexible current collectors and composite conductive agents increase the volumetric energy density and power density at the system level by reducing interface impedance and decreasing the proportion of inactive materials. This paper further discusses the main challenges faced by graphene-based materials, including high preparation cost, complex dispersion process, and low initial coulombic efficiency, and prospects future development directions such as heteroatom doping, defect engineering, and macro-scale preparation. Graphene and its derivatives are expected to transform from "miracle materials" in laboratories into "cornerstone materials" that drive the breakthrough of lithium-ion battery energy density, and provide core support for new energy vehicles and intelligent energy storage systems.

Keywords: Lithium-Ion Battery; Graphene; Carbon-Based Materials; Energy Density

1. Introduction

The global lithium-ion battery market is projected to grow from USD 64 billion in 2025 to USD 206.4 billion by 2032, exhibiting a compound annual growth rate (CAGR) of 18.2% (Lithium-ion Battery Market Size, Share, and Growth Forecast, 2025–2032). This rapid expansion is driven by the urgent demand for high-energy-density batteries in electric vehicles (EVs) and energy storage systems. Current mainstream lithium-ion batteries, with an energy density of 250–300 Wh/kg, fail to meet the requirements of long-range EVs (>500 km range) and lightweight aircraft. The key to overcoming this energy density bottleneck lies in electrode material innovation, and graphene and its derivatives, owing to their unique two-dimensional structure, ultra-high electrical conductivity (>15,000 $cm^2/(V·s)$), and theoretical specific surface area (2630 m^2/g), offer novel technical pathways for electrode system reconstruction.

Graphene-based materials are being explored across multiple dimensions in lithium-ion batteries. On the anode side, monolayer graphene achieves a theoretical specific capacity of 744 mAh/g via bidirectional lithium storage, approximately double that of conventional graphite [1]. More critically, graphene-silicon composites (with silicon's theoretical capacity of 4200 mAh/g) effectively mitigate silicon's volume expansion (>300%), addressing its fatal flaw of poor cycle stability. On the cathode side, graphene acts as a conductive framework to construct a three-dimensional continuous conductive network, significantly enhancing the electron transport kinetics of cathode materials such as lithium iron phosphate and high-nickel ternary compounds, thereby enabling their high theoretical capacities to be fully utilized [2]. At the battery structural level, graphene-based flexible current collectors and composite conductive additives reduce the proportion of inactive substances and optimize interfacial contact, thereby improving volumetric energy density and power density at the system level.

However, graphene-based battery materials still face challenges including high production costs, complex dispersion processes, and low initial Coulombic efficiency, which hinder their large-scale commercialization. In recent years, researchers have made significant progress in enhancing graphene conductivity, improving interfacial compatibility, and reducing costs through strategies such as heteroatom doping, defect engineering, and structural optimization. This review systematically summarizes the research advancements in graphene and its derivatives for boosting lithium-ion battery energy density. It elaborates on the key physicochemical properties of graphene and its energy storage mechanisms, respectively discusses application strategies and mechanisms in silicon anode modification, cathode conductive framework construction, flexible current collectors, and conductive additives, summarizes existing challenges, and prospects future development directions. This study aims to provide theoretical references for the material design and engineering application of graphene-based high-energy-density lithium-ion batteries.

2. Suppression of Silicon Anode Expansion in High-Energy-Density Lithium-Ion Batteries by Using Graphene and Its Derivatives as Anode Materials or Anode Reinforcements

Graphene, with its unique mechanical and electrical properties, has been widely utilized in enhancing the energy density of lithium-ion batteries. Graphene is the thinnest two-dimensional material known to date (single atomic layer), with extremely high stiffness (Young's modulus of approximately 1 TPa) and strength (intrinsic strength of approximately 130 GPa), as well as a high fracture strain (approximately 30%). These characteristics make it an ideal high-strength and high-toughness material [3], which can be used as a silicon anode material for lithium-ion batteries to suppress the volume expansion of silicon anodes. A significant application is its use as a modifying material for electrode active materials, such as encapsulating and constraining silicon anodes or buffering their volume expansion to mitigate the severe consequences thereof.

2.1 Opportunities, Challenges of Silicon Anodes and Inhibition Mechanism by Graphene

Silicon-based materials are ideal anode materials for improving the energy density of lithium-ion batteries due to their ultra-high theoretical specific capacity of up to 4200 mAh/g[4]. However, they will undergo volume expansion of more than 300% during charge-discharge cycles, leading to particle cracking, pulverization, loss of electrical contact with the current collector, and acceleration of side reactions that trigger the continuous growth and evolution of the solid electrolyte interphase (SEI) film, ultimately resulting in rapid capacity fading of the battery(Figure 1)[5]. Graphene and its derivatives have become ideal matrix materials for suppressing silicon expansion owing to their unique two-dimensional structure and excellent mechanical properties. Graphene is the thinnest two-dimensional material known to date (single atomic layer). Studies have shown that graphene exhibits high fracture strain (≥1.0), ultimate tensile strength on the order of hundreds of GPa in all three directions [6] and extremely high stiffness (Young's modulus of approximately 1 TPa)(Figure 2) [3]. These characteristics render it an ideal material with both high strength and high toughness. The combination of such high strength and flexibility enables it to effectively constrain and buffer the expansion stress of silicon anodes, laying a foundation for constructing stable composite electrode structures.

Figure 2 MG snapshots on (a) xy plane and (b) yz plane respectively, and (c) perspective views of the graphene layer at the initial state and when stretched along the x-axis to critical points I' (ε=0.5) and II' (ε=0.62). The structure after compression and before stretching is marked as "initial state". Points I' and I" are marked by solid red lines in Figure 2. The opening angle is indicated by red arrows, and the stretching direction is indicated by black arrows.[6]

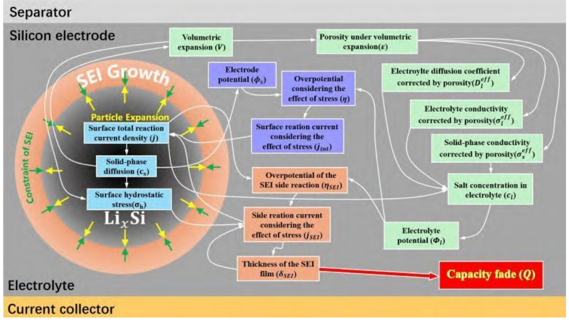


Figure 1. Schematic Diagram of Capacity Fading caused by the Growth of the SEI Film on the Silicon Anode of Lithium - ion Batteries Considering the Mechanical-chemical Coupling Effect [5]

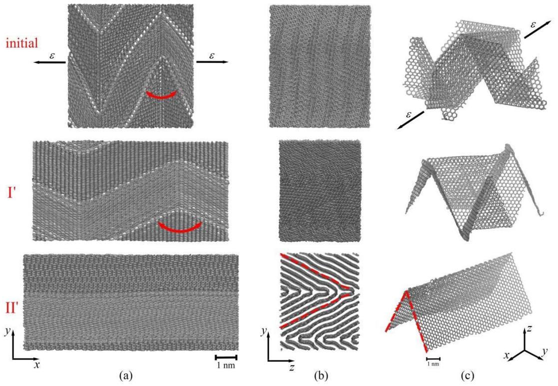


Figure 2. The Ultimate Tensile Strength in Three Different Directions

The above physical properties indicate that graphene and its derivatives are electrode modification materials that can effectively constrain and buffer the volume expansion of silicon anodes, and have unique advantages as ideal reinforcing agents for silicon anodes in lithium-ion batteries.

2.2 Core Inhibition Strategies for Graphene and Its Derivatives

Based on the above advantages, researchers have developed various graphene/silicon composite structures, with the core concept being to use graphene for constructing confined and buffering spaces.

2.2.1 Sandwich interlayer structure

Apart from graphene-wrapped silicon anode materials, the sandwich interlayer structure can also inhibit the volume expansion of silicon anodes and improve the electrochemical performance of lithium-ion batteries. Another strategy for enhancing the energy density of lithium-ion batteries using this structure is as follows[7]: First, silicon nanoparticles are surface-modified with cetyltrimethylammonium bromide (CTAB) to render them positively charged. Then, silicon particles are anchored between graphene oxide (GO) layers via electrostatic attraction between negatively charged GO sheets and the positively charged silicon particles. Next, citric acid (CA) is added as a cross-linking agent and an additional carbon source to further connect the silicon particles and GO sheets. Finally, through freeze-drying and heat treatment at 800 °C in a nitrogen atmosphere, GO is thermally reduced to rGO, and CA is carbonized into amorphous carbon. Ultimately, a composite material with silicon nanoparticles (~50 nm) as the core, coated with reduced graphene oxide (rGO) and amorphous carbon derived from pyrolyzed citric acid (Si@rGO@CA) is obtained. In this structure, the rGO network provides high-conductivity pathways, accelerates electron transport, and effectively buffers the volume change of silicon; the CA-derived carbon acts as a binder to strengthen the connection between silicon particles and rGO and improve the structural integrity, while also serving as a secondary buffer layer to further stabilize the structure.

Tests have shown that this composite material exhibits excellent cycling stability and rate performance: At a current density of 0.5 A g^{-1}, Si@rGO@CA-2 exhibits the best comprehensive performance after 200 cycles, with a specific capacity remaining at 946.6 mAh g^{-1} and a capacity retention rate as high as 95.3%. At current densities of 0.1, 0.2, 0.5, 1, and 2 A g^{-1}, Si@rGO@CA-2 delivers reversible capacities of 1514.4, 1421.7, 1278.6, 1149.9, and 1005.1 mAh g^{-1}, respectively. When the current density is restored to 0.2 A g^{-1}, the capacity recovers to 1385.0 mAh g^{-1}, indicating excellent structural stability. Even after 300 cycles at a high current density of 1 A g^{-1}, it still maintains a capacity of 644.4 mAh g^{-1}(Figure 3).

Figure 3 (a) Coulombic voltammetry curves of Si and (b) Si@rGO@CA-2 for the first 5 cycles; (c) Galvanostatic charge-discharge curves of Si@rGO@CA-2 at different current densities; (d) Rate performance and cycling performance of Si@rGO@CA-1, Si@rGO@CA-2 and Si@rGO@CA-3 at a current density of 0.5 A g^{-1}; (e) Lithiation/delithiation voltage curves of

Si@rGO@CA-2 at different current densities; (f) Lithiation/delithiation voltage curves of Si@rGO@CA-2 at a current density of 0.5 A g^{-1}; (g) Lithiation/delithiation voltage curves of Si@rGO@CA-2 when the current densities are 0.1 A g^{-1} and 1 A g^{-1}, respectively; (h) Long-term cycling performance of rGO, Si@rGO@CA-1, Si@rGO@CA-2 and Si@rGO@CA-3 for the first two cycles at a current density of 0.1 A g^{-1}, and a current density of 1 A g^{-1} is adopted for subsequent cycles. [7]

In this strategy, silicon nanoparticles are uniformly encapsulated and separated between rGO sheets, forming an effective conductive network and providing space for buffering volume expansion. rGO in this composite material acts as a mechanical buffer layer, effectively suppressing the volume expansion of silicon, while constructing a continuous conductive network to improve electron transport efficiency.

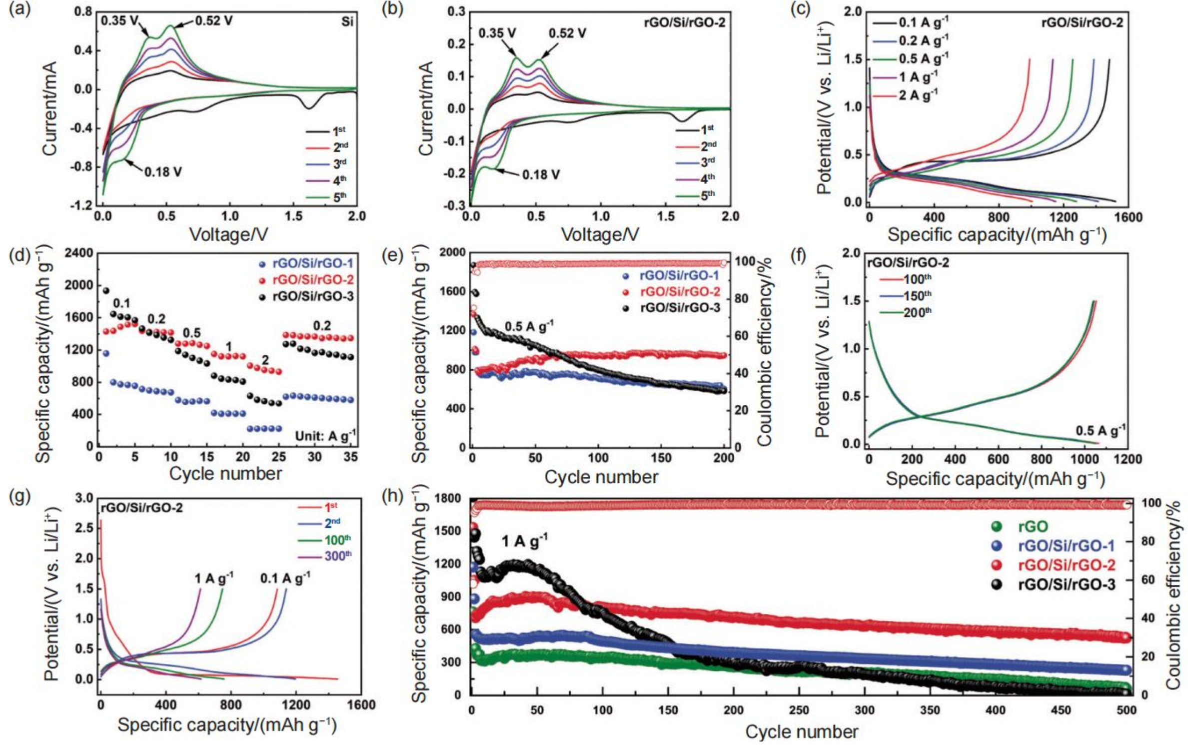


Figure 3. Sandwich Interlayer Structure

2.2.2 Overview of other cases

Coating and confinement structure: The core strategy is to wrap silicon particles (such as porous silicon) with reduced graphene oxide (rGO) to form an "elastic armor". For example, by constructing a hierarchical structure of "porous silicon core + carbon intermediate layer + rGO shell", the rGO shell can effectively confine the volume expansion of silicon particles and prevent structural pulverization. The optimized composite delivers an initial specific discharge capacity of 2589.9 mAh g^{-1} at 0.1 A g^{-1}, and retains a capacity of 626.3 mAh g^{-1} after 400 cycles at 1 A g^{-1}, which significantly improves the cycling stability[8].

Synergistic design of nanocrystallization and porosification: The core strategy is to in-situ encapsulate silicon nanoparticles between nitrogen-doped graphene nanosheets to form a three-dimensional buffer framework. For example, the silicon/nitrogen-doped graphene composite prepared in one step by arc discharge method, in which graphene layers provide buffer space and conductive network. The material maintains a capacity of 1030 mAh g^{-1} after 100 cycles at 200 mA g^{-1}, and still retains a high capacity at a high rate of 2 A g^{-1}, demonstrating excellent structural stability and ion transport capability[9].

2.3 Summary

In conclusion, this chapter systematically elaborates the single-point optimization of graphene and its derivatives as functional additives addressing the core bottleneck of severe volume expansion of silicon anode materials during charge and discharge. The core strategy lies in utilizing graphene's excellent mechanical properties (high strength and high flexibility) and two-dimensional structural characteristics, and constructing physical confinement and buffer space for silicon particles through elaborate material composite and structural design. The common essence of these strategies is: at the material scale, the introduction of graphene directly "repairs" and "enhances" the inherent defect (volume expansion) of silicon active materials. The optimized composite material maintains high specific capacity, while its cycle stability and rate performance are significantly improved, which proves the effectiveness and diversity of graphene in solving the single-point bottleneck of silicon anodes.

3. Graphene and Its Derivative Conductive Networks for Performance Enhancement of Cathode Materials

3.1 Bottlenecks in the Improvement of Energy Density of Cathode Materials

Common commercial cathode materials for lithium-ion batteries, such as lithium iron phosphate (LFP), ternary materials (NCM), and spinel-type $LiMn_2O_4$, suffer from inherent drawbacks including low electronic conductivity, slow lithium-ion diffusion rate, and structural instability during cycling (e.g., voltage decay). These issues prevent the full utilization of their high theoretical specific capacity in practical applications, becoming the critical bottleneck restricting the energy density and power density of the batteries. Traditional conductive agents like carbon black only provide limited point-to-point contact, resulting in limited performance improvement.

3.2 Core Mechanism and Improvement Pathways of Graphene and Its Derivatives

The core action mechanisms of graphene and its derivatives for improving the performance of cathode materials include constructing a three-dimensional continuous conductive network throughout the electrode and shortening the diffusion path of lithium ions, etc. Benefiting from its perfect two-dimensional honeycomb lattice structure, graphene has extremely high electron mobility and outstanding conductivity. At room temperature, the electron mobility of graphene can exceed 15,000 $cm^2/(V\cdot s)$ (even exceeding 200,000 $cm^2/(V\cdot s)$ in a suspended state), which is far higher than that of traditional semiconductor materials such as silicon. Moreover, graphene has an ultra-high electrical conductivity, with its sheet resistance as low as ~30 Ω/sq (independent of thickness) [10]. When the doping content of graphene in the material reaches its percolation threshold (φc), graphene sheets overlap and lap with each other to form a three-dimensional interconnected conductive network. At this time, the resistivity drops sharply by orders of magnitude, electrons can migrate freely in the network through direct "contact conduction", and the electrical conductivity increases significantly and tends to be stable.In addition, under the condition of high external electric field or local electric field concentration (such as at the edges or defects of graphene sheets), electrons can also be emitted from the graphene surface through Fowler-Nordheim tunneling. This effect provides additional current paths, and can further enhance the overall conductivity, especially under high pressure or dynamic load.[11] These characteristics greatly improve the electrical conductivity and structural stability of materials doped with graphene and its derivatives.

3.3 Typical Application Schemes and Cases

The aforementioned excellent properties have led to the widespread application of graphene and its derivatives in improving the electrical conductivity and structural stability of cathode materials for lithium-ion batteries. Several typical application cases are listed below.

3.3.1 Thermally Reduced Graphene Oxide (rGO) Doped Modified High-Nickel Ternary Material (NCM811)

High-nickel layered oxide cathode materials (e.g., $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$, abbreviated as NCM811) are regarded as promising next-generation cathode materials due to their high specific capacity and relatively low cost. However, NCM811 faces a series of challenges in practical applications: cation mixing (Li^+/Ni^{2+}) easily occurs during charge-discharge cycles, harmful phase transitions (from H2 phase to H3 phase) and anisotropic lattice volume changes lead to gradual structural collapse and poor cycling stability; residual lithium compounds (e.g., LiOH, Li_2CO_3) on the material surface readily react with HF in the electrolyte to form an insulating layer (e.g., LiF), hindering lithium-ion transport and accelerating the dissolution of transition metals; the inherent limited electronic conductivity restricts charge transfer at high rates, leading to poor rate performance; during long cycles or at high voltages, intergranular cracks between primary particles and intragranular cracks inside particles destroy the electrode's conductive network and expose more fresh surfaces to trigger side reactions with the electrolyte(Figure 4). The simple rGO blending doping method used in this case can effectively construct a 3D conductive network, significantly improving the conductivity, rate performance, and cycling stability of NCM811.

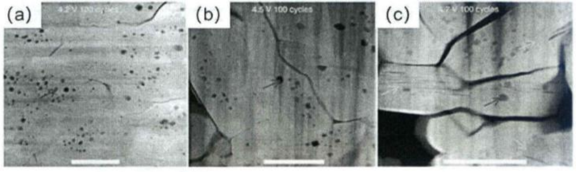


Figure 4. The Surface Undergoes Side Reactions with the Electrolyte.

Figure 4 Low-magnification HAADF images of $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ after 100 cycles under different high cut-off voltages. Red arrows indicate voids, and the yellow arrow in (c) indicates intragranular cracks. The scale bar is 500 nm [13]

In this study, reduced graphene oxide (rGO) with superior electrical conductivity obtained via high-temperature thermal reduction was directly blended with NCM811 by the physical blending method. Scanning electron microscopy (SEM) reveals that rGO sheets adhere to the surface of NCM811 particles or intersperse among the particles, forming a three-dimensional conductive network. Electrochemical tests demonstrate that rGO doping significantly improves the electrochemical performance of the material. Compared with the pristine NCM811, the rGO-doped composite exhibits enhanced initial Coulombic efficiency, rate performance and cycling stability. Among all the prepared samples, 2rGO1-NCM811 delivers the optimal comprehensive performance: in terms of initial Coulombic efficiency, the composite delivers an initial discharge specific capacity of 179.9 mAh g^{-1} at 0.1 C with an initial Coulombic efficiency of 77.6%; for cycling stability, it retains 73.1% of its initial capacity after 50 cycles at 0.5 C; it also shows excellent rate performance, maintaining a high specific capacity even at a high current density of 5 C, and exhibits outstanding capacity recovery (96.1%) after rate capability testing. Electrochemical impedance spectroscopy (EIS) confirms that rGO doping effectively reduces the charge transfer resistance (Rct) and lithium-ion diffusion resistance. The lithium-ion diffusion coefficient (DLi^+)increases from $0.7\times10^{-14}cm^2\ s^{-1}$ for the pristine material to$2.3\times10^{-14}cm^2\ s^{-1}$ for the doped composite. Moreover, the higher the reduction degree of rGO (i.e., the better its electrical conductivity), the more significant the modification effect. As the reduction degree of rGO increases, DLi^+ of the composite further increases (3rGO2-NCM811 reaches $3.6\times10^{-14}cm^2\ s^{-1}$), indicating that the highly conductive rGO network greatly accelerates the charge transfer kinetics within the electrode.[12]

In this case, graphene significantly optimizes the electrochemical performance of NCM811 through a dual effect: constructing a three-dimensional conductive network to improve electronic/ionic conductivity and enhancing mechanical/chemical stability. Its two-dimensional structure not only provides an efficient conductive pathway, but also acts as a physical barrier to protect the active material, thereby prolonging the cycling life of the battery and improving the performance at high rates.

3.3.2 Graphene oxide (GO)-coated modified polyanion cathode material ($LiFeSO_4F$)

Tavorite-type $LiFeSO_4F$ is a promising polyanionic cathode material. Although it exhibits a high lithium ion conductivity (approximately three orders of magnitude higher than $LiFePO_4$) and a working voltage of ~3.6 V, its extremely low electronic conductivity ($\sim10^{-11}$ S cm^{-1}) severely restricts its electrochemical performance. To address this issue, a mild solvothermal method combined with electrostatic self-assembly was employed to prepare graphene oxide (GO)-coated $LiFeSO_4F$ composites. The GO forms a continuous coating layer on the material surface and constructs a three-dimensional conductive network, which significantly enhances the electronic conductivity from 8.16×10^{-11} S cm^{-1} to 1.65×10^{-4} S cm^{-1}, an improvement of approximately seven orders of magnitude. Electrochemical tests demonstrate that the GO-coated material achieves an initial discharge capacity of 113.2 mAh g^{-1} at a 0.1 C rate, with a capacity retention rate of as high as 99% after 100 cycles(Figure 5). It can still deliver a discharge capacity of 30.3 mAh g^{-1} at a high rate of 10 C. Furthermore, the GO layer effectively suppresses side reactions at the electrode/electrolyte interface as a physical barrier, promotes the formation of a stable solid electrolyte interface (SEI) film, and its flexible structure also buffers volume changes during charge-discharge processes.[14]

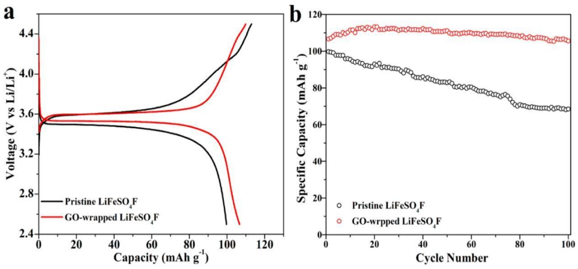


Figure 5. (a) First Charge-discharge Curves and (b) Cycling Performance of the Pristine $LiFeSO_4F$ Material and the GO-coated $LiFeSO_4F$ Material at a Charge-discharge Rate of 0.1C [13]

This case indicates that the GO coating strategy can simultaneously improve the electronic conductivity, interfacial stability, and structural integrity of cathode materials, providing an effective low-temperature modification approach to resolve the performance bottleneck of cathode materials with high ionic conductivity but low electronic conductivity.

3.4 Summary

In conclusion, this chapter systematically elaborates the single-point optimization of graphene and its derivatives as high-efficiency conductive network constructors targeting the core bottlenecks of cathode materials, such as low electronic conductivity and poor structural stability. The core mechanism relies on the utilization of graphene's excellent two-dimensional electrical conductivity (high electron mobility) and structural properties. Through strategies including physical doping and surface coating, three-dimensional continuous electron conduction pathways are constructed between or on the surface of cathode active particles. The essence of this optimization path is as follows: at the material scale, the inherent defects of cathode active materials (low conductivity, excessive side reactions, and prone to structural damage) are directly "connected" and "protected" by introducing the graphene conductive network. Whether it is improving the electron/ion transport kinetics of high-nickel ternary materials (NCM811), or significantly enhancing the rate capability and cycling performance of polyanionic materials with low electronic conductivity (e.g., $LiFeSO_4F$), the introduction of graphene effectively compensates for the shortcomings of cathode materials, allows their theoretically high specific capacity to be fully exploited, and thus contributes to the improvement of the overall energy density of batteries from the cathode side. However, although separate "single-point optimization" for cathode and anode active materials can significantly improve their intrinsic performance, as a complex electrochemical system, the ultimate energy density output of a battery is also restricted by system-level factors such as electrode structure, interface, and even current collector. Therefore, to achieve maximum energy density, the research perspective needs to leap from "material optimization" to "system design". The next chapter will focus on this topic, discussing how to expand the application of graphene and its derivatives from the interior of active materials to the overall structure level of electrodes and even batteries. For example, as novel flexible current collectors or multifunctional composite conductive agents, graphene can innovate the "skeleton" and "blood vessels" (current collectors and conductive networks) of batteries, synergistically improve the energy density, power density and mechanical reliability of batteries from the perspective of system integration, so as to construct a more complete and efficient path for improving energy density.

4. Graphene-based Flexible Current Collectors for Enhanced Energy Density

Graphene and its derivatives, besides being used as active materials to improve the performance of individual components in lithium-ion batteries, can also serve as core design elements for innovating battery assemblies and optimizing electrode structures. This transcends the mere modification of individual materials and enters a higher level of battery system design and integration, aiming to achieve global optimization of comprehensive performance metrics such as energy density, power density, and cycle life through the optimization of synergistic interactions among components.

4.1 System-Level Limitations of Conventional Current Collectors

With the rapid development of emerging fields such as wearable electronics and flexible displays, there is an increasing demand for flexible, high-energy-density lithium-ion batteries to match these applications. Current collectors are core components responsible for supporting electrode active materials and collecting current in battery systems. In traditional designs, aluminum foil is typically used for the positive electrode, and copper foil for the negative electrode, due to their respective advantages of high oxidation potential/corrosion resistance and excellent electrical conductivity. However, conventional current collectors suffer from drawbacks including poor mechanical flexibility, high density, and weak adhesion to electrode materials. For instance, the areal density of traditional copper foil (Tra-CuCC) is 56.6 g/m², with a fracture strain of only 1.9% [14]. Additionally, the contact between traditional metal foils and active materials is limited: active material slurries are merely coated on the surface of metal foils, where only the active material near the foil substrate directly contacts the current collector. The upper active material layer relies on conductive networks formed by conductive additives and binders for electron transport, resulting in a relatively high interfacial resistance. Moreover, metal foils are dense and do not provide pores; ions must fully traverse the pores within the active material layer itself. If the active material has low porosity or poor pore structure (e.g., certain battery materials), ion transport is restricted, negatively impacting rate performance [15]. These issues severely hinder the battery's performance retention under bending conditions and the overall improvement of energy density.

4.2 Design Rationale for Graphene-Based Flexible Current Collectors

Graphene exhibits physical properties of extreme thinness and flexibility, structural properties of an exceptionally large specific surface area(theoretical value is as high as 2630 m²/g[16]), and electrical properties of ultra-high conductivity. These characteristics enable it to function as a carbon-based conductive agent or novel flexible current collector for lithium-ion batteries, contributing indirectly or directly to enhanced energy density and improved battery performance. By leveraging these properties, thinner, lighter, and bendable novel current collectors can be designed, fundamentally altering component attributes-a re-design and replacement of traditional battery components (current collectors) that constitutes a system-level innovation .

4.3 Typical Cases

4.3.1 Composite Graphene-Modified Aluminum Foil for Positive Electrode Current Collectors

A scheme for modifying aluminum foil (MG-AGD-Al-CCs) using composite graphene from a two-dimensional planar optimization perspective is presented below. The design goal is to reduce weight, enhance interfacial properties, and improve corrosion resistance-effectively an "upgraded version" of traditional aluminum foil current collectors. First, high-quality, thin-layer aqueous graphene dispersions (AGD) are prepared via electrochemical exfoliation. To address the poor vertical conductivity of wet-coated graphene coatings, two conductive additives-micron-sized flake graphene (MG) and Ketjen Black (KB)-are respectively introduced into the graphene slurry to form composite conductive slurries (MG-AGD and KB-AGD). These slurries are then coated onto aluminum foil to fabricate the modified current collectors MG-AGD-Al-CCs and KB-AGD-Al-CCs.

In half-cell tests using lithium iron phosphate (LFP) as the positive electrode, batteries assembled with MG-AGD-Al-CCs demonstrate superior comprehensive performance, including a specific capacity of 154.4 mAh/g at 0.1 C, rate capabilities with capacity retention rates of 83.7% and 81.2% at 5 C and 10 C, respectively, a capacity retention rate of 93.4% after 300 cycles at 1 C, and excellent cycle stability with maintained capacity retention after 1800 cycles at 5 C/10 C, alongside the smallest charge transfer resistance (Rct) and minimal voltage gap during charge-discharge, significantly alleviating polarization (Figure 6). The performance enhancement is attributed to the graphene coating, which increases contact area, enhances adhesion, constructs a co-continuous conductive network, and provides corrosion protection. [17]

In this scheme, the substrate is a fully conventional two-dimensional aluminum foil. The modification process is a simple wet coating (coating, drying), highly compatible with existing battery electrode manufacturing processes (coating, rolling, slitting), with low transformation costs and easy industrialization promotion. The optimization core lies in constructing a micron-scale (1.6 μm) composite graphene functional thin layer on the aluminum foil surface. This layer modifies the surface electrical, mechanical, and chemical properties through the unique characteristics of nanomaterials (graphene, microsheet graphene). Leveraging graphene's high conductivity, large specific surface area, high strength, and chemical inertness, and strategically adding microsheet graphene to construct a three-dimensional conductive network to compensate for insufficient interlayer conductivity, this method successfully "upgrades" traditional aluminum foil into a high-performance positive electrode current collector with lower interfacial resistance, stronger interfacial bonding, superior anti-corrosion ability, higher mechanical strength, while minimizing weight increase. All performance enhancements are achieved without altering the existing battery manufacturing system, demonstrating extremely high potential for industrial application.

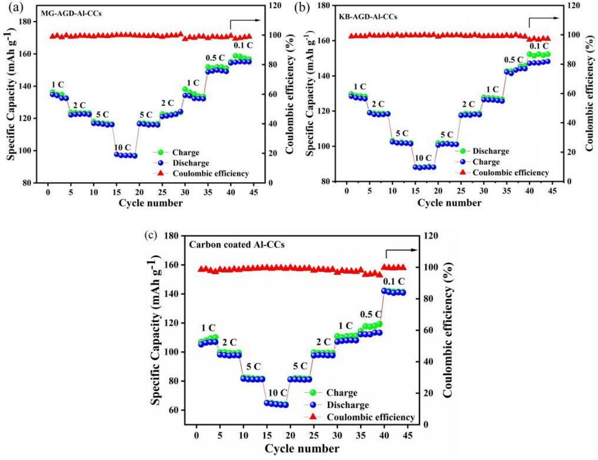


Figure 6. Polarization Phenomenon

Figure 6 Rate performance of (a) LiFePO4/MG-AGD-Al-CCs batteries, (b) LiFePO4/KB-AGD-Al-CCs batteries, (c) LiFePO4/Carboncoated Al-CCs batteries [17]

4.3.2 Three-dimensional nickel-plated carbon fiber current collector

There is another scheme for composite graphene-modified nickel-plated carbon fiber three-dimensional current collectors (MG-Ni-CF-CCs). Its design concept is more cutting-edge: constructing a three-dimensional conductive framework to provide more loading space for active materials and more optimal ion transport paths, which is a disruptive component design. First, nickel is plated on carbon paper (CF) by electrochemical deposition to prepare three-dimensional current collectors Ni-CF-CCs. Then, the aforementioned optimized MG-AGD composite slurry (with 2% MG addition and 50 µm wet film) is coated on the optimal Ni-CF-CCs to obtain MG-Ni-CF-CCs(Figure 7).

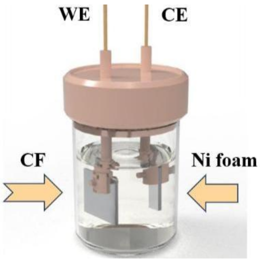


Figure 7. Schematic Diagram of Nickel Electroplating Via Electrochemical Deposition [17]

Through testing, the unmodified Ni-CF-CCs can only be charged up to a cutoff voltage of 3.8 V due to the corrosion of nickel at high potentials (>3.8 V). In contrast, the MG-Ni-CF-CCs can be charged up to a cutoff voltage of 4.2 V thanks to the protection provided by the graphene coating. Moreover, the battery assembled with MG-Ni-CF-CCs outperforms the Ni-CF-CCs in all aspects, including specific capacity (160 mAh/g at 0.1C, compared to 148.4 mAh/g for Ni-CF-CCs) as well as rate capability and cycling stability (after 700 cycles at 5C and 10C, the capacity retentions reach 85.9% and 85.3%, respectively, both higher than those of the unmodified samples). Additionally, the graphene coating not only provides corrosion protection but also further improves interfacial contact and charge transport. [17]

In this design, the MG-Ni-CF-CCs achieve comprehensive breakthroughs in the structure, electrical conductivity, mechanical strength and electrochemical performance of the current collector through the synergistic optimization of the three-dimensional conductive skeleton design, graphene modification and the selection of lightweight, high-strength materials. This design not only solves the problems of traditional current collectors, such as limited contact area, long ion transport path and easy corrosion, but also provides a new component solution for the development of lithium-ion batteries with high energy density and high power density, showing remarkable forward-looking and disruptive potential.

4.4 Summary

In summary, this chapter elevates the application of graphene to the level of "system design", and realizes a leap in thinking through the innovation of the core component of current collectors. Whether used as a functional coating to modify the surface of traditional two-dimensional aluminum foils, or to construct a three-dimensional nickel-plated carbon fiber skeleton, the graphene-based flexible current collector fundamentally optimizes the electron collection, ion transport path and mechanical support structure. This design goes beyond the performance repair of a single material, focusing on optimizing the interfacial contact, charge transport and mechanical coupling between various internal battery components (active material, conductive agent, current collector), and synergistically improves the energy density, power density and mechanical reliability of the battery from the perspective of system integration.

5. Improvement of Energy Density of Lithium-Ion Batteries by Graphene-Based Additives

5.1 Limitations of Conventional Conductive Agents

The development of new energy vehicles has imposed stricter requirements on the rate performance and cycle stability of lithium-ion batteries. Cathode materials (e.g., NCM523) exhibit low ion/electronic conductivity, which restricts high-current charge-discharge performance. The addition of conductive agents is a critical strategy to address this issue. However, conventional carbon black conductive agents (e.g., acetylene black, Super-P) are typically nanoparticulate [17]. They primarily form conductive networks through "point contacts" in electrodes [18], while linear carbon nanotubes (CNTs) are difficult to network alone. The drawbacks of conventional conductive agents, including their intrinsic low conductivity and inefficient conductive network formation (particularly under high-rate and long-cycle conditions), have become increasingly prominent in the pursuit of batteries with higher performance.

5.2 "Point-Line-Face" Three-Dimensional Network Synergy Design Concept

Graphene and its derivatives possess a large specific surface area and excellent electrical conductivity. When compounded with other carbon-based materials, their complementary advantages can yield greater performance than any single material. In the systematic engineering approach of blending graphene (2D plane), carbon nanotubes (1D line), and carbon black nanoparticles (0D point), graphene acts as a "conductive plane" providing extensive coverage and rapid electron pathways, carbon nanotubes serve as "reinforcements" connecting isolated domains, and carbon black nanoparticles act as "soldering points" to fill voids. This synergy constructs an efficient and robust macroscopic conductive network, reflecting a paradigm shift from "adding conductive agents" to "designing conductive microstructures." The optimization target is not the active material itself but the electrode environment in which the active material resides.

5.3 Typical Cases

The following describes a protocol using graphene as a conductive agent, compounded with carbon nanotubes (CNTs) and carbon black (SP) to construct an efficient 3D conductive network, thereby improving the rate performance and cycle stability of NCM523 batteries.

The process involves chemical oxidation-thermal reduction: Flake graphite is oxidized with concentrated sulfuric acid and potassium permanganate to form graphite oxide precursor, which is washed and then thermally reduced at 900°C for 3 minutes to produce reduced graphene oxide (rGO) powder. The rGO powder is then dispersed with PVP in NMP solvent via sanding for varying durations (0, 10, 30, 60 minutes), yielding four graphene slurries with distinct median particle sizes (D_{50} = 26.980, 18.698, 11.581, 9.458 μm). These slurries are further blended in a mass ratio of graphene:CNT:SP = 4:2:4 to form the final composite conductive slurry (designated "ZZ424"). Coin cells (CR2430, counter electrode: lithium foil) and 18650 cylindrical full cells (negative electrode: artificial graphite) are fabricated. The cathode formulation is consistent across all samples: NCM523: conductive agent: PVDF = 96.5:2.0:1.5(Figure 8).

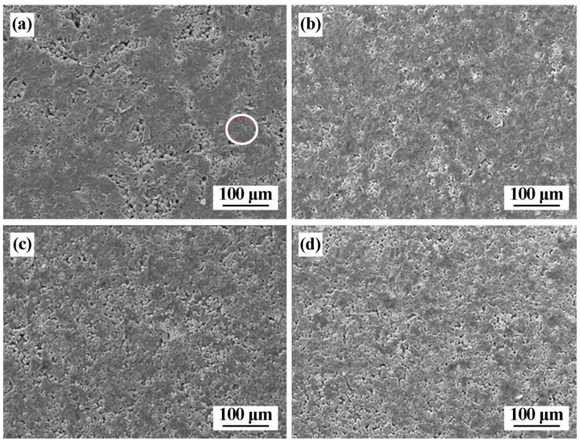
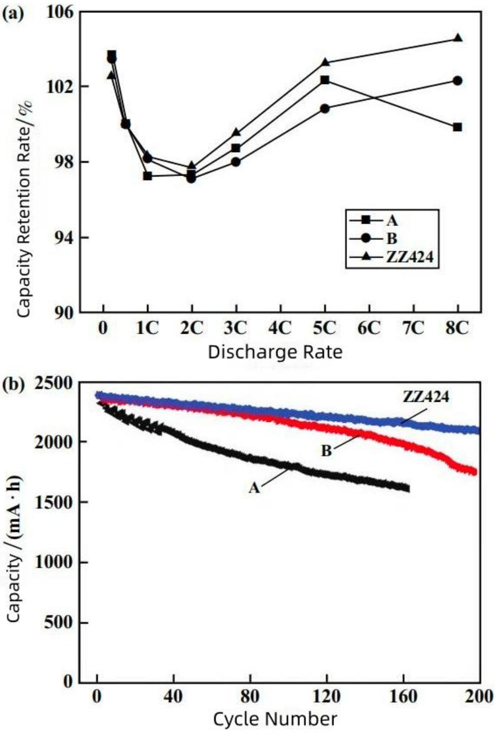


Figure 8. SEM Images of NCM523 Positive Electrode Sheets with Different Diameters of Graphene Composite Conductive Agents [19]

FTIR results show that the graphene is rich in oxygen-containing functional groups (such as C-O-C, C=O, and O-H), which helps to improve its surface activity and wettability to the electrolyte, and promotes lithium ion diffusion. TEM/AFM results demonstrate that the as-prepared graphene has a flaky structure with good flexibility and wrinkles. The thickness is approximately 4.874 nm, which is calculated to correspond to about 14 layers, belonging to few-layer graphene. SEM results indicate that the larger the sheet size of graphene, the easier it is to agglomerate with CNTs to form bulk conductive agents, which cover the surface of active particles and may hinder the intercalation and deintercalation of lithium ions. When the sheet size is reduced, the dispersibility is improved and the agglomeration is alleviated.According to tests, the ZZ424 battery exhibits the highest capacity retention rate (104.45%) during 8C (20 A) high-rate discharge, which is superior to battery B (102.28%) and battery A (99.78%). Meanwhile, it shows excellent cycling performance: after 200 cycles of 1C/8C rate, the capacity retention rate reaches 87.90% (remaining 2121 mAh). The capacity first decreases and then increases with the increase of rate, which is attributed to the temperature rise effect under large current(Figure 9). The excellent performance of ZZ424 is attributed to the synergistic effect of the three-dimensional conductive network, which provides more efficient electron/ion pathways.[19]

This proposal demonstrates that graphene, as a core design element, is employed to innovate battery components and optimize electrode structures. This transcends the mere modification of single materials and advances to a higher level of battery system design and integration, aiming to achieve the global optimization of comprehensive performances such as energy density, power density and cycle life by optimizing the synergistic effect among various components.



(a) Rate performance; (b) Cycle performance
Figure 9. Rate Performance and Cycle Curves of Different Composite Conductive Pastes [19]

5.4 Summary

In conclusion, this chapter further expands the application perspective of graphene from "component innovation" to "electrode microstructure engineering", and achieves the thinking transition from "adding functional materials" to "constructing systematic conductive networks" through the collaborative design of multi-dimensional conductive agents. Whether it is the ZZ424 conductive slurry prepared by "point-line-plane" compounding, or the nanofiber yarn electrode based on carbon fiber framework and integrating 1D/2D conductive agents, the core is to take graphene as a key structural unit, carry out systematic compatibility with carbon materials of other dimensions (carbon black, carbon nanotubes), and actively construct an efficient, stable and permeable three-dimensional network for conductive and ion transport inside the electrode.

This design goes beyond the "single-point optimization" that simply relies on the intrinsic properties of graphene, and instead focuses on optimizing the spatial arrangement, contact interface and cooperative working mechanism among various components inside the electrode (active materials, conductive agents of different dimensions, binders, and substrates), which is a "systematic design" carried out at the electrode microstructure level. It significantly improves the electronic conductivity, ion diffusion kinetics and structural integrity of the electrode, so that the capacity potential of active materials can be more fully released under high-rate charge-discharge and long-cycle working conditions, and provides a key systematic solution for improving the energy density and power density of batteries from the perspective of electrode engineering.

To sum up, the application of graphene and its derivatives in lithium-ion batteries is deepening along the path from "material optimization" to "system design". In the future, by combining the excellent properties of graphene at the material scale with the innovative design at the electrode and even the overall battery structure level, it is expected to build a more complete and efficient energy density improvement scheme, and promote the development of next-generation high-energy-density lithium-ion batteries.

6. Summary and Prospect

6.1 Summary

This review systematically expounds on the research progress of graphene and its derivatives in enhancing the energy density of lithium - ion batteries. It covers two aspects: on one hand, utilizing the excellent intrinsic properties of graphene to conduct targeted enhancement and functional "repair" for the respective "shortcomings" of the positive and negative electrode active materials; on the other hand, taking graphene as a core design element, through innovating components and optimizing the electrode microstructure, to achieve systematic - level cooperative optimization of charge transport, mechanical coupling and interface stability within the battery. It reveals that the application path of graphene is undergoing a profound transition from "repair - type optimization" directed at single - material defects to "systematic design" that reconstructs the overall architecture of the battery.

In summary, the pathway by which graphene enhances the energy density of lithium - ion batteries is a multi - level solution system that is closely linked and progresses step by step, starting from material modification (to address the intrinsic defects of active materials), then to electrode engineering (to optimize the conductive network and interfaces), and finally to system architecture (to innovate core components such as current collectors).

6.2 Challenges and Prospects

Despite its broad prospects, the large-scale application of graphene-based battery technology still faces multiple challenges, and future research needs to achieve breakthroughs in the following directions: The mass production of high-quality graphene is costly, and its uniform dispersion process in electrode slurries is complicated, which makes it difficult to perfectly compatible with the existing large-scale, low-cost battery manufacturing systems; the high specific surface area of graphene may lead to severe side reactions with electrolytes and low initial Coulombic efficiency, impairing the actual energy density and cycle life of batteries. In addition, overly thick or stacked graphene layers may hinder ion transport; at present, most studies still focus on the performance improvement of single components or materials, and how to realize the integrated and mass-producible system integration design of graphene's advantages at the material, electrode, and component levels remains a huge challenge.

Future research should go beyond "single-point optimization" and commit to application scenario-oriented integrated system design. For example, for the fast-charging demand of electric vehicles, a collaborative scheme integrating graphene composite conductive networks, high ionic conductivity electrolytes, and thinned current collectors should be designed; for flexible electronics, all-flexible battery integration technology combining graphene-based flexible electrodes(such as high-performance NCM523 ($LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$) nanofiber yarn electrodes[20]), current collectors and packaging materials should be developed. Through multi-physics simulation and artificial intelligence-aided design, full-chain optimization from material screening to battery pack performance prediction is realized, green and efficient mass preparation technologies (such as improved redox methods, electrochemical exfoliation, and cost-reduced CVD processes) are developed, and graphene conductive slurries or prefabricated films that are highly compatible with existing battery electrode coating and rolling processes are developed to promote industrial implementation. Graphene and its derivatives have demonstrated great potential for transformation from a "wonder material" to a "cornerstone material" that drives the breakthrough of energy density of lithium-ion batteries. By deepening the understanding from material optimization to system design, and focusing on solving core challenges such as cost, process and integration, graphene technology is expected to provide core support for next-generation lithium-ion batteries with high energy density, high power density and long lifespan, and accelerate the revolutionary development of new energy vehicles, intelligent energy storage, wearable electronics and other fields.

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