

Review on Graphene Composites as Anode Materials for Lithium - Ion Batteries

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Abstract:

This review explores the research progress of graphene composites with cobalt tetroxide (Co_3O_4), titanium dioxide (TiO_2), and silicon (Si) as anode materials for lithium-ion batteries. Graphene, with its excellent electrical conductivity, mechanical flexibility, and high specific surface area, plays a key role in the composites: it effectively enhances the conductive network of the electrode, buffers the active materials, accommodates the huge volume changes during lithium-ion insertion and extraction, and inhibits particle agglomeration. Co_3O_4 -graphene composites significantly improve the accessibility of high theoretical capacity and cycling stability; TiO_2 -graphene systems mainly overcome the bottleneck of poor intrinsic conductivity, exhibiting excellent rate performance and ultra-long cycle life; for Si with ultra-high capacity, graphene matrices or coating layers are core strategies to alleviate its severe volume expansion and maintain structural integrity. Cyclic voltammetry measurements are performed on different composites to compare the performance differences between composites and pure substances as anode materials for lithium-ion batteries, providing important directions for the development of high-performance lithium battery anodes.

Keywords: graphene; cobalt tetroxide (Co_3O_4), titanium dioxide (TiO_2), silicon (Si), composites, lithium-ion batteries, cyclic voltammetry

1 Introduction

In today's world, people's attention to energy has shifted from non-renewable fossil energy to abundant renewable resources. Among various renewable energy sources, electric energy is the most crucial one and is needed everywhere in life. In recent years, with the development of electronic facilities such as

portable electronic products, new energy vehicles, and industrial devices, people's requirements for new-type batteries have become more diverse: longer cycle life, higher energy density, and lower cost of use. There are a large number of secondary batteries in the market. Compared with other batteries, lithium-ion batteries have the advantages of no memory effect, low self-discharge rate, good energy storage

performance, and a wide range of operating temperature and voltage platforms, making them the most promising secondary batteries to meet people's higher demands [1,2]. For lithium-ion batteries, the selection of anode materials directly determines the strength of their working performance. Therefore, finding more suitable anode materials has always been an arduous task for lithium-ion batteries. Graphite has long been a common and widely used anode material for lithium-ion batteries. Although it has good charge-discharge performance, its theoretical lithium storage capacity is low, which limits its energy density and makes it not outstanding compared with other batteries. To improve anode materials, the new-type material graphene is introduced. Due to its excellent electrical conductivity, thermal conductivity, and good toughness, these unique properties enable it to well improve the specific energy density and charge-discharge performance of lithium-ion batteries. In addition, graphene also has a two-dimensional structure that other materials do not have, which can wrap and load a variety of materials and form corresponding three-dimensional network structures. It can well reduce the expansibility and overload of the wrapped or loaded materials, avoiding aggregation and fusion caused by excessive materials. This performance makes graphene an extremely favorable carrier to composite with other materials that have obvious advantages in improving the performance of lithium-ion batteries. Graphene can be more widely applied to other anode materials to prepare graphene composites with more excellent electrochemical performance.

Starting from the composites formed by different anode materials and graphene, this paper comprehensively discusses the research and influence of different graphene composite materials as anode materials for lithium-ion batteries on the performance of lithium-ion batteries.

2 Metals, their oxides and graphene composites

Metals and their oxides have the potential to be excellent anode materials due to their high theoretical specific capacity, good conductivity, structural diversity, favorable lithium storage performance, and abundant resources. However, they also have inherent drawbacks such as poor electrical conductivity, significant volume expansion, pulverization, unstable SEI (Solid Electrolyte Interface), and limited cycle stability and rate performance.

Graphene, on the other hand, boasts advantages as an ideal carrier, buffer, and conductive matrix, including high electrical conductivity, large specific surface area, excellent mechanical strength, and flexibility. In lithium batter-

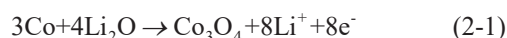
ies, it promotes the formation of Li^+_2C_6 around the anode material, enabling the theoretical capacity of lithium-ion batteries to reach a high value of 744 mAh/g [3,4]. Meanwhile, studies have found that the defects in graphene, a 2D material, allow Li^+ to pass through via additional pathways. Direct use of graphene as an anode material may pose significant issues. Therefore, leveraging graphene's excellent spatial properties, new composites are prepared by combining it with metals and their oxides through methods such as sol-gel, chemical reduction, and electrochemical deposition.

In this review, among the materials formed by the combination of metals, their oxides and graphene, the focus is on cobalt tetroxide (Co_3O_4) and titanium dioxide (TiO_2).

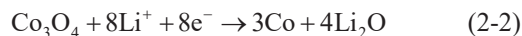
2.1 Cobalt tetroxide (Co_3O_4)/graphene composites

Cobalt tetroxide (Co_3O_4) nanocomposites, characterized by high capacity, stable cycling performance, and excellent overall properties, have recently emerged as a highly promising anode material for lithium-ion batteries. Their charge-discharge behavior relies on the reversible reaction between the oxidation of cobalt and the formation of lithium oxide, which is distinct from the extensive lithium ion intercalation and deintercalation processes exhibited by conventional lithium-ion anode materials. This unique charge-discharge mechanism enables efficient utilization of lithium ions, thereby enhancing the theoretical specific capacity.

The mechanism for the charging process (delithiation) is as follows:



The mechanism for the discharging process (lithiation, lithium intercalation) is as follows:



In the above single charge-discharge reaction of cobalt tetroxide, one molecule of cobalt tetroxide can react with 8 lithium ions, resulting in a high theoretical specific capacity of 1100 mAh/g [5,6]. Currently, existing research achievements have enabled the preparation of cobalt tetroxide nanotubes, whose theoretical specific capacity is nearly twice that of graphite anode materials. However, during cyclic charge-discharge processes, the electrolysis and polymerization of cobalt tetroxide can still lead to instability in the electrode structure, which in turn reduces the conductivity of the electrode material and it is more likely to cause irreversible capacity loss, thereby reducing the service life and effective performance of lithium-ion batteries. Nevertheless, by compounding cobalt tetroxide nanomaterials with a graphene nanolayer structure as the

base, the problem of significant capacity degradation of lithium-ion batteries during charge-discharge processes can be greatly alleviated.

A commonly employed method is to control the morphology of cobalt tetroxide to enhance its interaction with graphene, and insert cobalt tetroxide nanomaterials into the interlayer structure of parallel multi-layer graphene. However, this structure cannot effectively prevent the aggregation of cobalt tetroxide nanomaterials. Studies have shown that completely wrapping cobalt tetroxide nanoparticles with graphene can prevent their agglomeration. Consequently, the composite material formed by cobalt tetroxide and graphene significantly improves the electrical conductivity of the material and exerts a good buffering effect on the volume expansion during charge-discharge processes. The greatest advantage of the graphene composite material prepared by this method is that it can achieve a high modification effect while reducing the usage of graphene, and the resistance of the wrapped cobalt tetroxide nanoparticles is more than three times lower than that of pure cobalt tetroxide nanoparticles. Electrochemical performance tests using galvanostatic discharge/charge experiments and cyclic voltammetry tests at a scanning rate of 0.1 mV/s were conducted on cobalt tetroxide nanomaterials, graphene materials, and cobalt tetroxide-graphene nanocomposites, yielding the cyclic voltammetry curves of potential versus current as shown in Figure 1.

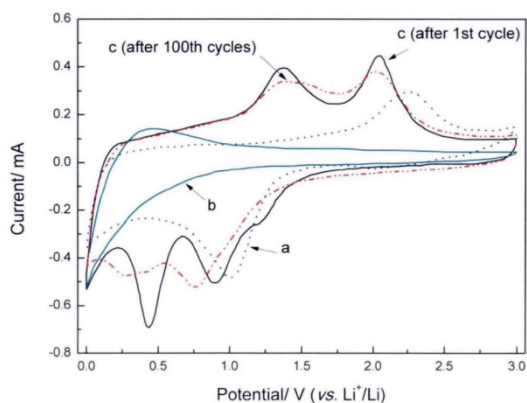


Figure 1 (a) Cyclic voltammetry curve of cobalt tetroxide nanomaterial electrode; (b) Cyclic voltammetry curve of graphene nanomaterial; (c) Cyclic voltammetry curve of cobalt tetroxide-graphene nanocomposite [7]

It is evident from the figure that the current curve of the cobalt tetroxide-graphene nanocomposite is higher and more stable compared to those of graphene and pure cobalt tetroxide. This is attributed to the smaller crystalline

size of the cobalt tetroxide-graphene nanocomposite compared to pure cobalt tetroxide, which reduces resistance, increases current density, shortens the conduction paths of electrons and lithium ions, reduces expansion during charge-discharge processes, and improves electrode stability. It can also be noted that, compared to a single cycle, after 100 cycles, the reduction and oxidation peaks of the cobalt tetroxide-graphene nanocomposite at approximately 1.5 V and 2.3 V tend to be gentle, which is consistent with the experimental data reported by Li et al., indicating that the resistance of the cobalt tetroxide-graphene nanomaterial is much lower than that of pure cobalt tetroxide. Its charge and discharge capacities after 100 cycles are approximately 970 and 1010 mAh/g, corresponding to an irreversible capacity loss of 3%. In contrast, the charge and discharge capacities of pure cobalt tetroxide after 100 cycles are approximately 750 and 790 mAh/g [7]. Facts have proven that the use of cobalt tetroxide-graphene nanocomposites not only improves the electronic conductivity of the anode material for lithium-ion batteries but also significantly enhances the cycling stability and performance stability of the electrode during charge-discharge processes.

Although cobalt tetroxide-graphene nanocomposites have addressed some drawbacks of pure cobalt tetroxide, they still have certain issues. During the charge-discharge cycling process, their high expansion effect may cause the separation of graphene from cobalt tetroxide, leading to the destruction and re-stacking of the graphene structure. As a result, their cycle life is lower compared to other lithium-ion batteries. In addition, they have disadvantages such as low initial Coulombic efficiency, high preparation cost and complexity, and low volumetric energy density, which remain major obstacles to their large-scale commercial application.

2.2 Titanium Dioxide (TiO₂) Graphene Composites

Titanium dioxide (TiO₂) boasts extremely high structural stability, with a minimal volume change (<4%) during the insertion and extraction of lithium ions, which is far lower than that of graphite anodes (approximately 10%). This enables it to effectively reduce the occurrence of expansion during charge-discharge processes, thereby extending the service life of lithium-ion batteries. In addition, titanium dioxide operates at a relatively high voltage, which can effectively prevent the formation of lithium dendrites and the decomposition of electrolytes, reducing the risk of battery short circuits. Although it has a large diffusion coefficient, allowing lithium ions and electrons to migrate rapidly in the anode, making it suitable for high-rate dis-

charge processes, its theoretical specific capacity is low, only 175 mAh/g, even lower than the theoretical specific capacity of graphite (372 mAh/g) [10]. This results in low storage capacity of lithium-ion batteries made with titanium dioxide as the anode material. Furthermore, titanium dioxide has low intrinsic conductivity, requiring the addition of a large amount of conductive agents, which reduces the overall energy density of the electrode. However, the two-dimensional structure of graphene and its excellent electrical properties make it an ideal choice as the conductive agent needed for titanium dioxide.

By constructing a three-dimensional conductive network based on graphene and uniformly integrating titanium dioxide nanorods into the graphene structure, titanium dioxide-graphene nanocomposites are prepared, which effectively solve the problem of low intrinsic conductivity of titanium dioxide. This increases the electron transport efficiency by 10 to 100 times, greatly reduces polarization, and supports high-rate charge-discharge. The titanium dioxide-graphene nanocomposites obtained by Y. Ma et al. [8] through a simple sol-static self-assembly technique exhibit a good rate capability of 250.1 mAh/g at 2 A/g, which is nearly 50% higher than the theoretical specific capacity of 175 mAh/g for pure titanium dioxide as the anode. Due to their abundant electrochemical active sites, large specific surface area, good conductivity, large lithium ion diffusion coefficient, and short diffusion path, titanium dioxide-graphene nanocomposites are widely favored.

In addition, the anatase-phase titanium dioxide-graphene composites studied by Fu et al. [9] are also a popular type among titanium dioxide-graphene composites nowadays. Their most prominent feature is a higher theoretical specific capacity. At a scanning rate of 0.1 mV/s, they still maintain a high specific capacity of 260 mAh/g after 100 cycles, while pure titanium dioxide only achieves a reversible specific capacity of 160 mAh/g after 100 cycles. The improvement effect is even better than that of the aforementioned titanium dioxide-graphene nanocomposites.

Although various composite methods of titanium dioxide and graphene can significantly improve the theoretical specific capacity of lithium-ion batteries, their actual energy density is still lower than that of traditional graphite anodes. Moreover, when the content of graphene is too high, it will instead reduce the compaction density of the electrode, leading to the occurrence of side reactions such as lithium dendrite formation. This reduces the content of lithium ions, increases resistance, and further decreases the capacity and current density of lithium-ion batteries.

3 Silicon-based Graphene Composites

Silicon is one of the anode materials known to have the highest theoretical specific capacity for lithium ions. In lithium-ion batteries, it forms $\text{Li}_{4.4}\text{Si}$ with lithium ions, reaching a value of 4200 mAh/g, which is nearly ten times the theoretical specific capacity of traditional graphite anodes. While having a high specific capacity, silicon also undergoes a higher volume expansion during charge-discharge processes compared to the reaction of cobalt tetroxide. It forms $\text{Li}_{3.75}\text{Si}$ with a volume change as high as 270%, resulting in poor cycle stability of the material [13]. Additionally, silicon has low intrinsic conductivity. However, graphene, with its extremely high mechanical strength and flexibility, can wrap silicon nanoparticles to form a three-dimensional conductive network. When silicon nanoparticles are dispersed in a carbonaceous matrix, graphene can provide voids to effectively buffer and constrain the volume expansion of silicon, prevent the agglomeration of silicon nanoparticles, reduce the electrode resistance of silicon, and enhance conductivity.

Ma et al. [11] prepared high-performance silicon-graphene composites with a bath flower-like structure using a spray-drying method. This material not only has a high theoretical specific capacity but also exhibits excellent charge-discharge cycle performance. In constant current charge-discharge cycle tests at a current density of 200 mA/g, the reversible capacity remains 1502 mAh/g after 30 cycles, with a capacity retention rate as high as 98%. Agha et al. [12] prepared silicon-doped graphene aerogel nanomaterials, which can still maintain a very high specific capacity of 1100 mAh/g after 500 cycles at a current density of 400 mA/g.

The different types of silicon-graphene composites prepared by the above two research groups using different methods both show high reversible theoretical specific capacities when measured by cyclic voltammetry at different current densities. Moreover, in both sets of test data, a reduction peak (~ 0.2 V) and an oxidation peak (~ 0.4 V) can be observed, corresponding to the insertion of Li^+ into the silicon-graphene composite nanomaterials to form Li_xSi and the delithiation of Li_xSi to generate silicon, respectively.

For the high-performance silicon-graphene composites prepared by Ma et al., further cyclic voltammetry tests were conducted at different current densities, and the following results were obtained after 200 cycles: at a scan rate of 0.1 mV/s, the oxidation peak is located at 0.32~0.45 V, and the reduction peak is at 0.18~0.25 V, with a peak current ratio of approximately 1.0. The polarization degree is small, and the peak shape is symmetric and sharp, indicating that lithium ions can undergo a high degree of

insertion and extraction processes; at a scan rate of 1.0 mV/s, the oxidation peak is at 0.35~0.50 V, and the reduction peak is at 0.15~0.22 V, with a peak current ratio of 0.95-1.0. The polarization degree is greater than that at 0.1 mV/s, but the difference is not particularly significant, suggesting that the graphene network effectively improves the conductivity of silicon; at a scan rate of 5.0 mV/s, the oxidation peak is at 0.40~0.55 V, and the reduction peak is at 0.10~0.18 V, with a peak current ratio of 0.85~0.90. The peak position shifts significantly, which slows down the diffusion rate of lithium ions and causes a decrease in the theoretical reversible specific capacity. Although the peak current ratio is significantly lower than that at 0.1 mV/s, resulting in kinetic lag, it is still better than that of pure silicon as the anode of lithium-ion batteries (usually <0.7) [14].

4 Conclusions

This review study indicates that the composite of graphene with cobalt tetroxide (Co₃O₄), titanium dioxide (TiO₂), and silicon (Si) respectively can significantly enhance their performance as anode materials for lithium-ion batteries. The key role of graphene lies in providing a highly conductive network, effectively buffering the volume change of active materials during charge-discharge processes (which is particularly crucial for high-capacity Co₃O₄ and Si), and inhibiting particle agglomeration.

In the Co₃O₄ system, graphene has greatly improved the accessibility of its high theoretical capacity and cycle stability, but the low initial efficiency and high cost remain challenges. For TiO₂, graphene mainly overcomes the bottlenecks of poor intrinsic conductivity and slow ion diffusion, achieving excellent rate performance and ultra-long cycle life; however, the overall low capacity limits its energy density. As for Si with ultra-high capacity, graphene, as a flexible matrix or coating layer, is a core strategy to alleviate its huge volume expansion, prevent structural pulverization, and maintain electrical contact. Nevertheless, achieving long cycle stability under high silicon loading and solving the problem of initial efficiency are still key issues.

In general, the graphene-based composite strategy provides an effective approach for the development of high-performance, high-capacity, high-rate, and long-life anode materials for lithium-ion batteries. Future research

should focus on more precise structural design, interface optimization, large-scale preparation processes, and in-depth understanding of the synergistic mechanism in composite systems.

References

- [1] Wu F, Maier J, Yu Y. Guidelines and trends for next-generation rechargeable lithium and lithium-ion batteries [J]. *Chemical Society Reviews*, 2020, 49(5):1569-1614
- [2] Xu J, Cai S, et al. High-energy lithium-ion batteries: recent progress and a promising future in applications [J]. *Energy & Environmental Materials*, 2023, 6(5):e12450.
- [3] Xu, H., Z. Sun, and J. Chen, Graphene-based anode materials for lithium-ion batteries, in *Emerging 2D Materials and Devices for the Internet of Things*. 2020, Elsevier. p. 139-164.
- [4] K. Ullah, et al. Preparation of highly expanded graphene with large surface area and its additional conductive effect for EDLC performance. *J. Mater. Sci.: Mater. Electron.*, 26 (9) (2015), pp. 6945-6953
- [5] Larcher D, Sudant G, Leriche J-B, Chabre Y, Tarascon J-M (2002) *J Electrochem Soc* 149:A234-A241.
- [6] Xia XH, Tu JP, Xiang JY, Huang XH, Wang XL, Zhao XB (2010) *J Power Sources* 195:2014-2022.
- [7] Wang Haiteng. Research on graphene-based anode materials for lithium-ion batteries [D]. Beijing Jiaotong University, 2013.
- [8] Y. Ma, et al. Uniformly distributed TiO₂ nanorods on reduced graphene oxide composites as anode material for high rate lithium ion batteries., 771 (2019), pp. 885-891
- [9] Y.-X. Fu, et al. TiO₂ nanorods anchor on reduced graphene oxide (R-TiO₂/rGO) composite as anode for high performance lithium-ion batteries., 497 (2019), Article 143553
- [10] Al-Noaman AS, Rawlinson SF. Titanium Dioxide/ Graphene Oxide Composite Coatings for 316 Stainless Steel Dental Implants. *Eur J Prosthodont Restor Dent*. 2023 Nov 30;31(4):358-372.
- [11] He Y S, Gao P F, Chen J, Yang X W, Liao X Z, Yang J, Ma Z F, *RSC Adv.*, 2011, 1(4):495-498
- [12] F. Tang, et al. Preparation and electrochemical performance of silicon@ graphene aerogel composites for lithium-ion batteries., 854 (2021), Article 157135
- [13] Wolfenstine J. J. *Power Sources*, 1999, 79:111-113
- [14] Song S, Zhu M, Xiong Y, Wen Y, Nie M, Meng X, Zheng A, Yang Y, Dai Y, Sun L, Yin K. Mechanical Failure Mechanism of Silicon-Based Composite Anodes under Overdischarging Conditions Based on Finite Element Analysis. *ACS Appl Mater Interfaces*. 2021 Jul 28;13(29):34157-34167.