# Graphene-based anode materials in Li-Ion batteries

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**Abstract.** Doubtlessly, one of the most used electric power storage technologies at the moment is the lithium-ion battery (LIB). Meanwhile, in order to meet increasing needs for the present LIB performance, the improvement on the anode materials of LIB is one of the major study approaches. Among a wide range of options like silicon, metal oxides, and other compounds and mixtures, this review will mainly focus on the graphene-related LIB anode materials. By discussing the preparation processes and the electrochemical performance of various types of graphene-based and graphene-coated materials that are used for the anode of LIBs, the improvements of the addition of graphene in other materials have been reviewed, and the patterns of that have been analysed. This review helps summarize the current typical research results of the electrochemical properties of LIB anode materials based on graphene and gives suggestions about the future research focus on this specific category of materials by referring to the comparison of the data reviewed.

**Keywords:** graphene, anode material, electrochemical performance, lithium-ion battery.

## 1. Introduction

Among different sorts of batteries, the lithium-ion batteries (LIBs) have considerable popularity because of their outstanding capacities, the compact and lightweight nature, the feasibility and compatibility for various uses. Nowadays, LIBs can be found in almost every electronic device. In order to face the increasing demands of battery performance such as the need for higher energy densities, higher rates of charge/discharge, and longer battery life (or cycling stability), huge efforts have been made to a typical approach, which is the improvement of materials' characteristics of LIB components, such as the discoveries of sorts of the base materials of the battery and the structures or existing forms of these materials. One of the critical components of LIB that determines the overall electrochemical performance is the anode of the battery. Many different study approaches have been conducted to research and discuss about the alternatives of LIB anodes, including carbon, silicon, and metal oxides (including their different existing forms, compounds and mixtures). Meanwhile, methods for material modification such as doping, coating, and composition are also the focuses of studies and research. The modification methods can radically change the physical structures and physical properties of a certain material, which is also a consequential factor of the change in electrochemical performance of LIB. Sometimes these methods are used in combinations for further enhancement of the overall electrochemical performance or for specialized aspects of improvement or adjustment.

Among these materials, graphene, a kind of carbon, is a distinctive nanomaterial that has gained popularity in recent years due to its exclusive properties, such as the thickness of one atom, one of the

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best stiffness and thermal conductivity, the impermeability to gases, the possession of both brittleness and ductility, etc. [1]. Therefore, in order to meet increasing needs of the performance of a certain material, graphene is usually applied to be mixed with that certain substance by different modification methods. When it comes to the LIB anode, graphene can be both used as a basal material in the doping method and the composites and a coating material for other basal materials which usually are possessing excellent electrochemical performance. For example, as mentioned before, the stunning thickness of graphene and its ductility together provides a large surface area when it is configured into special structures like layers and pores, and the stiffness of graphene maintains the shape of the entire structure of a combined material.

Typical studies of each representative material in certain categories will be discussed in the analysis sections of this review, which mainly focuses on the preparation process and methods, and the electrochemical performance measured in the experiments, such as specific reversible capacities at different current rates, the battery cycling pattern or stability, and the Columbic efficiency. The materials will be introduced and analyzed in a sequence of doped graphene kinds, graphene coatings, and graphene composites. Meanwhile, in some cases, bare materials will be compared with the improved ones, which aims to demonstrate the effect made by the addition of graphene through modifications.

## 2. Doped graphenes

Doping is a method of performance enhancement which eliminates some defects of the application of graphene in the LIB anode. The doped structures of graphene with other chemical substances are advantageous for the use of the LIB anode, since they possess characteristics like higher specific surface area and porosity, which results in better electrochemical performance. There are various kinds of doped graphene. In this review, some of the common ones are discussed, including Nitrogen-doped graphene and Boron-doped graphene. Additionally, different preparation processes can be used in the doped graphene with the same substance.

### *2.1. Nitrogen-doped graphene (N-doped graphene) LIB anode*

The N-doped graphene mainly can be produced in ways of thermal reduction, sacrificial template, and ammonia treatment and freeze drying [2-4]. Hu et al. studied the N-doped graphene synthesis through the process of thermal reduction, including mixing with ammonium hydroxide, vacuuming and heating [2]. The N-doped graphene demonstrates a vastly improved electrochemical performance in general when it is compared with the bare graphene. This material demonstrated a high reversible capacity (up to 900 $mAhg^{-1}$) and hugely reinforced cycling performance in the experiment process. After 550 times of exhaustive charge and discharge at a 2 $Ag^{-1}$ current rate, the resultant specific capacity was 453 $mAhg^{-1}$, and, as the cycle count reached 2000 at a 10 $Ag^{-1}$ current rate, the resultant specific capacity was 180 $mAhg^{-1}$. In the 2000-cycle endurance test, the final capacity of the LIB maintained 85%, 87%, 94% of its reversible capacity in the first cycle under 30 $Ag^{-1}$, 20 $Ag^{-1}$, and 10 $Ag^{-1}$ respectively, together with nearly a 100% Coulombic efficiency. Ma et al. suggests that N-doped graphene is the best anode choice for Li storage among all other alternatives like graphite by researching the adsorption of Li atoms (the Li atom's average absorption energy is 1.26 eV for N-doped graphene) and the reversible capacity (a 1262 $mAhg^{-1}$ reversible specific capacity is achieved by the N-doped graphene) of different doped graphenes [5].

### *2.2. Boron-doped graphene (B-doped graphene) LIB anode*

The B-doped graphene is typically treated by one method: chemical mixing and heating. Sahoo et al. conducted a synthesis process which results in 5.93% of Boron doped in the structure of the graphene, and a nearly 66.2% increase in discharge capacity at 1 A $g^{-1}$ was discovered from the B-doped graphene anode compared to the bare graphene, which resulted in a higher rate of Li diffusion and thus vastly increased the overall capacity of the LIB [6]. In another study focusing on the Li diffusion occurring on doped graphene, the three kinds of B-doped graphenes have achieved low energy barrier

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value (0.44 eV, 0.31 eV, 0.43 eV, respectively) compared to that of three corresponding N-doped graphenes (0.95 eV, 1.75 eV, 2.62 eV, respectively) and increased Li uptake, which demonstrates their effectiveness of being the anode materials of LIB compared to N-doped graphene [7].

## 3. Graphene coatings

The addition of a coating of graphene is also an effective approach to improve a certain LIB anode's electrochemical performance. Graphene is rarely researched as a coating material in terms of the LIB anode. Nevertheless, graphene coatings can be applied on Si nanoparticles, Si composites, and other composites. Generally, the application of the graphene coating is effective to make progress on the energy densities of different LIB anodes, especially the Si-based ones.

### *3.1. Graphene-coated Si-based LIB anode*

Si-based LIB anode materials that have graphene coatings are mainly categorized into Si oxides, Si nanoparticles, and other Si composites. As the only practically verified Si-based material, the graphene-coated Si nanoparticles will be discussed in this review. Through the synthesis of graphene and Si nanoparticles using ionic liquid, a graphene-Si nanoparticle hybrid material can be produced. Zhou et al. measured that the graphene-Si nanoparticle hybrid anode could originally achieve specific charge capacity of 2319 $mAhg^{-1}$, and the capacity of discharge at the $100^{th}$ cycle remained 902 $mAhg^{-1}$, which hugely exceeds that of the graphite electrode (372 $mAhg^{-1}$) [8]. Though a huge loss in the capacity that cannot be recovered was observed initially, the anode showed a good stability in the following cycles. Another approach of this type of material is the crumpled graphene-coated Si nanoparticles, which is prepared by a synthesis process consisting mixing and annealing. The experimental battery using this material as the anode performed 250 charge and discharge cycles at 1 A $g^{-1}$ current rate continuously, and it maintains a specific reversible capacity of 940 $mAhg^{-1}$, which is significantly better than the crumpled graphene itself (338 $mAhg^{-1}$). Particularly, during the experiment, 50% of the battery capacity loss was measured during the first 15 cycles, and then only about 0.05% of capacity loss was discovered for each cycle [9]. Therefore, it is possible to resolve that Si-based materials with graphene coatings applied in LIB anode can vastly improve the specific reversible capacity and charge and discharge stability of LIBs, which are the main aspects of the electrochemical performance.

### *3.2. Other graphene-coated composite LIB anode*

So far, few reports have appeared on the other types of graphene-coated composites that can be applied to LIB anode. The only practical approach that will be discussed in this review is the electrochemically reduced graphene coated ultrathin Ni-Co double hydroxide nanosheets ($Ni_xCo_{2x}(OH)_{6x}$@eRG). This material is obtained through two steps of syntheses: Ni-Co double hydroxide synthesis through chemical reaction and Ni-Co/graphene synthesis through chemical mixing. In an experiment, by applying on the LIB anode, the $Ni_xCo_{2x}(OH)_{6x}$/graphene nanosheets can achieve a 1308 $mAhg^{-1}$ capacity during the discharge process and a 996 $mAhg^{-1}$ capacity during the charge process, which are higher than the $Ni_xCo_{2x}(OH)_{6x}$ can do (a 1180 $mAhg^{-1}$ capacity during discharge and a 847 $mAhg^{-1}$ capacity during charge respectively). As LIB had experienced 50 charge and discharge cycles, the coated anode could offer a 787 $mAhg^{-1}$ capacity in discharge, while the $Ni_xCo_{2x}(OH)_{6x}$ anode was only able to deliver that of 100 mAh $g^{-1}$ [10]. Hence, the graphene coating on the anode material has shown its significance in the LIB electrochemical performance development. Especially, in the previous case, by applying the graphene coating, the battery life of the LIB sample was vastly improved.

## 4. Graphene composites

The graphene composite is the most widely used form of graphene in LIB anode, which is particularly attributed to its distinct chemical and physical features. There are a large number of studies focusing on LIB anodes using various sorts of graphene composites. This discussion in this review contains two typical graphene composites, which are the metal oxide/graphene composite and the Si-based material/graphene-based composite.

### *4.1. Metal oxide/graphene composite LIB anode*

There are many metal oxide alternatives that can be used to mix with graphene in order to produce composites for application as an anode in LIBs, such as CuO, $Mn_3O_4$, $Co_3O_4$, $V_2O_3$, $WO_x$, ZnO, $Fe_3O_4$, etc. This review will mainly discuss about CuO, $Mn_3O_4$, $Co_3O_4$/Graphene composites through their experimentally verified electrochemical properties. With a variety of advantages outweighing the defects, the metal oxide/graphene composite use in the LIB anode is a promising approach in the reinforcement of LIB electrochemical performance.

The first example is the CuO/graphene (CuO/G) composite. The CuO/G composite synthesis was conducted through the process of chemical mixing, heating, hydrothermal reaction, centrifuge, water-washing and drying. The CuO/G composite has a higher capacity than the CuO anode because of the graphene's bigger active surface area and substantial quantities of grain boundary regions of the CuO nanoparticles in the composite: in the discharge test at a rate of 67 $mAg^{-1}$, the CuO/G, and the CuO anode showed their initial discharge capacities of 817, and 752.4 $mAhg^{-1}$ respectively. The graphene added to the composite enhanced the reversible capacity and improved the battery life in the process of cycling (a 52.7% improve in the reversible capacity retention after 50 cycling processes) [11]. Though the electrochemical properties of the CuO/G composite anode are not superior to that of graphene itself, it can be concluded that graphene has shown its effectiveness in the enhancement of electrochemical performance when it is combined with other certain materials [11].

Another typical material in this category is the $Mn_3O_4$/graphene nanosheet composite. Nam et al. synthesized the $Mn_3O_4$/graphene nanosheet composite ($Mn_3O_4$/GNS) through the following process: chemical mixing, deionized water-washing, centrifuge, and drying [12]. Through the electrochemical performance examination, at a 60 $mAg^{-1}$ current density, the stable specific capacity during the discharge was over 500 $mAhg^{-1}$ and did not demonstrate significant capacity reduction after 40 cycles, which was superior than pure $Mn_3O_4$ nanoparticles (at the $10^{th}$ cycle, the capacity declined to less than 150 $mAg^{-1}$). The $Mn_3O_4$/GNS composite's specific reversible capacity was well-maintained in different current densities with a Coulombic efficiency reached more than 99%. In changing current density cases, the reversible capacity even slightly became higher than its original capacity. This has shown that graphene has an important effect in reinforcing the reversibility and specific capacity in the $Mn_3O_4$/GNS composite, which results in better overall electrochemical performance of LIB.

Lastly, the cobalt oxide/graphene composite ($Co_3O_4$/graphene) is introduced. The $Co_3O_4$/graphene composite was synthesized through the process of chemical mixing, dispersion, filtration, and heating. in the experiment at a 74 $mAg^{-1}$ current density, it performed a 754 $mAhg^{-1}$ specific capacity, which was significantly higher than that of graphite (372 $mAhg^{-1}$) and close to a typical commercial $Co_3O_4$ (791 $mAhg^{-1}$). However, at higher current density like 1860 $mAhg^{-1}$, the reversible capacity of $Co_3O_4$/graphene anode was about 500 $mAhg^{-1}$, which was far more excellent than that of pure $Co_3O_4$ (0 $mAhg^{-1}$) [13]. Therefore, in conclusion, the overall electrochemical performance of $Co_3O_4$/graphene composite is hugely enhanced by the addition of graphene, which demonstrates a lower reversible capacity but an incredibly improved cycling stability when a higher current density is applied compared to the pure cobalt oxide. Li et al. suggests that the outcomes of applying graphene in achieving $Co_3O_4$/graphene composite's performance improvement are attributed to the layer-structure of graphene [14]. Thanks to graphene's large surface area form, the highly conductive matrix and the settlement of $Co_3O_4$ nanoparticles inside the composite were realized. Moreover, graphene can prevent detrimental interactions between active matter and various solutions throughout the cycling process and can increase $Co_3O_4$ dispersion with less aggregation [15].

### *4.2. Si-based material/graphene composite LIB anode*

Currently, another popular research approach on the graphene-based composite LIB anode focuses on the Si-based material/graphene composites. As a material with originated outstanding electrochemical performance, Si is very suitable for the applications such as a basal material of LIB anode. Even though, the addition of graphene can still create splendid positive effects on the performance of the Si-based material. In the following discussions, three main sorts of Si-based material/graphene composite will be briefly examined generally in terms of specific reversible capacity and stability during charge and discharge processes.

*4.2.1. Si nanoparticles/graphene composite.* The Si nanoparticles/graphene (SG) composite is one of the major types of Si-based material, which has been proved to have improved electrochemical performance compared to one single substance such as graphene. Luo et al. prepared the experimental sample of SG composite through the steps of synthesis of dispersion, immersion, mixing, drying, and reduction [16]. In the experiment, by using 2016-type coin cells, the SG composite anode's electrochemical performance was measured between 0.05 and 1.2 V. At a 0.4 $Ag^{-1}$ current rate, the SG composite indicated a 1350 $mAhg^{-1}$ capacity during the charge process with a 54% Columbic efficiency in the first cycle, which was a huge progress compared to the pure graphene which delivered an initial specific capacity of charge of 397 $mAhg^{-1}$. In the next following cycle, the discharge capacity declined to 1418 $mAhg^{-1}$, while the columbic efficiency is raised to 94.6%. After 1300 cycles, the discharge capacity of SG composite remained 668 $mAhg^{-1}$, which was a huge progress compared to Si nanoparticles' cycling performance (during the first 20 cycles, only 15% of the reversible specific capacity of Si nanoparticles was kept). The Si nanoparticles/graphene composite overall demonstrated an outstanding cycling performance and a high charge and discharge specific capacity in this practical experiment. Additionally, it is worth mentioning that the SG composite and the Si nanoparticles with a graphene coating possess similar electrochemical performance due to their analogical chemical structures.

*4.2.2. Si compound/graphene composite.* Another kind of composites in this big category is the Si compound/graphene composite. The study approaches on this sort of material mainly aim for specialized characteristics such as improved Columbic efficiency or cycling stability. One typical composite, the SiCN/graphene composite, will be reviewed in this section.

Feng et al. analyzed the SiCN/graphene composite thoroughly. An experiment was conducted and the composite was synthesized through the process of filtering, chemical mixing, and drying [17]. The SiCN/graphene composite's electrochemical characteristics were obtained: in a CR2032 LIB, at a 0.04 $mAg^{-1}$ discharge current rate, the specific capacity of SiCN/graphene electrode was 722.4 $mAg^{-1}$ in the first cycle, which was largely improved compared to the SiCN electrode (380.4 $mAhg^{-1}$). Though the discharge capacity of SiCN/graphene declined rapidly in the first ten cycles, it maintained stable from the $11^{th}$ cycle to the $100^{th}$ cycle and finally achieved 6.2 times of discharge capacity (475.1 $mAhg^{-1}$) after the $100^{th}$ cycle compared to that of SiCN (76.1 $mAhg^{-1}$). Meanwhile, the SiCN/graphene composite remained an improved Columbic efficiency of 97.93% in average, and the enhanced ability of high current discharge. In this part. it can be concluded that the SiCN compound achieves a specialized Columbic efficiency, and at the same time the addition of graphene vastly reinforces the discharge capacity, cycling performance, and the high-rate ability of discharge.

*4.2.3. Si oxide/carbon-graphene composite.* The $SiO_2$/carbon-graphene composite is a representative study approach on the other Si-based composite material applied on the LIB anode. Due to its excellent electrochemical performance, anode applications based on this composite can be relatively competitive. It should be mentioned that the carbon (carbon precursor) in the composite is a coating of $SiO_2$ nanoparticles. Yin et al. experimented with $SiO_2$/carbon-graphene ($SiO_2$/C-G) as a LIB anode in a CR2032 type battery at current densities of 0.1-0.3 $mAg^{-1}$ in the voltage from 0.005 to 2.5 V [18]. The synthesis of the composite was conducted through a series of process: hydrothermal method, chemical mixing, heating, and drying. According to different pore size distributions, the big composite type can be split into several specific hybrids, and among those different kinds of hybrids, the 15-$SiO_2$/C-G demonstrated the best reversible capacity, cycling stability, and Columbic efficiency: a 906 $mAhg^{-1}$

specific capacity in the first discharge cycle, an enhanced 542 mAhg$^{-1}$ specific capacity after the 216$^{th}$ cycle compared to that of any other hybrid alternatives, and a Columbic efficiency of 99% after the first and the second charge/discharge cycles. Meanwhile, the 15-$SiO_2$/C-G possesses a very interesting pattern of the change in discharge capacity: an initial decrease and a gradual increase from the 16$^{th}$ cycle to the one last recorded cycle (the 216$^{th}$ cycle) were observed. The $SiO_2$/C-G composite's electrochemical performance at high currents is revealed as the following: at 0.5 Ag$^{-1}$, the $SiO_2$/C-G kept the specific capacity of up to 125.8 mAhg$^{-1}$, and at 1 Ag$^{-1}$, the composite's specific capacity was slightly lower, but it was still superior to that of $SiO_2$ and $SiO_2$/C. Thanks to the excellent synergistic effect of graphene, remarkable improvements in electrochemical performance have been discovered on its applications on $SiO_2$/C-G composite, including enhanced Li ion diffusion and the restrain of change in volume of the $SiO_2$ component during cycling [18, 19].

## 5. Conclusion

Through the review of studies and research, it can be concluded that graphene significantly contributes to the reinforcement of the graphene-related LIB anode materials' electrochemical performance. All the bare materials are shown to be inferior in electrochemical performance than combined materials, which means that graphene has been a key part of the LIB anode material development. The huge improvements of applying graphene mainly concentrate on the aspects of specific charge/discharge capacity, the cycling performance (especially at high current densities), and Columbic efficiency. Among all the modified materials that are discussed in this review, the SG composite has shown the best electrochemical performance compared to other alternatives in general. As the SG composite has shown outstanding electrochemical performance, it is expected to be applied on compact LIBs which are demanding for higher energy density and cycling performance, such as cell phone or laptop batteries. Moreover, for increasing applications of large size batteries such as electric vehicles (EVs) which are recently becoming more and more popular, the SG composite LIB anode material can further boost the development and popularization of EVs in terms of better battery life and the increase in lifespan of the battery module. Therefore, it is meaningful for the SG composite to be applied in various forms of batteries in order to adapt to different needs in the future advancements of LIBs.

However, there are some limitations of this review. First, only a limited number of materials are discussed as examples, while many other materials are not mentioned and explored in this review. Furthermore, only the electrochemical performance of each anode material in the review is meticulously discussed, while other important aspects of the research such as the characterization of each of these materials are not mentioned, so that the overall performance and characteristics of a certain material are not represented. Lastly, all the data in the review are collected from experimental or theoretical research, which may not reflect the performance of the materials as examples in the real-life applications.

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