

Review Article

Graphene-Based Composites as Cathode Materials for Lithium Ion Batteries

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Owing to the superior mechanical, thermal, and electrical properties, graphene was a perfect candidate to improve the performance of lithium ion batteries. Herein, we review the recent advances in graphene-based composites and their application as cathode materials for lithium ion batteries. We focus on the synthesis methods of graphene-based composites and the superior electrochemical performance of graphene-based composites as cathode materials for lithium ion batteries.

1. Introduction

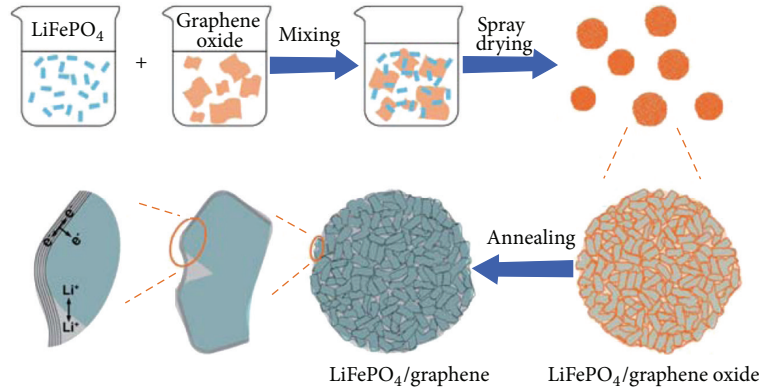
Graphene is a free-standing 2D crystal with one-atom thickness of carbon atom. Those carbon atoms are sp^2 -hybridized atoms arranged in six-membered rings in a honeycombed network which is also considered as the fundamental foundation for fullerenes, carbon nanotubes, and graphite [1]. Graphene was discovered by Novoselov and coworkers in 2004 [2]. Owing to their great contribution for the study of graphene, Geim and Novoselov were awarded the Nobel Prize which was the third Nobel Prize in the field of carbon materials. As a kind of carbon materials, graphene has attracted increasing attention in a variety of fields because of its large specific surface area, good flexibility, superior chemical/thermal stability, and extraordinary electrical, and thermal, mechanical properties. With so many advantages, it is desirable to utilize the unique properties of graphene in composites through the incorporation with all kinds of functional materials [3–11]. One of the most important applications of graphene-based composites is electrode material for lithium ion batteries [12–15]. In this review, we focus on the synthesis methods and electrochemical performance of graphene-based composites as cathode materials for lithium ion batteries.

2. $LiMPO_4$ ($M = Fe, Co, Mn, V$)-Graphene Composites as Cathode Materials for LIBs

$LiFePO_4$ has been extensively investigated as cathode materials for LIBs because of low-cost, low toxicity, and relatively high theoretical specific capacity of 170 mA h/g. A significant restriction for $LiFePO_4$ is its poor electronic conductivity (as low as $10^{-9} \text{ S cm}^{-1}$) which exerts negative effects on the performance of LIBs. A concept of establishing a conducting network formed by carbonaceous materials has been proposed to improve the rate performance of electrode materials [16]. Graphene possessing high conductivity, chemical stability, and mechanical performance has been demonstrated to be excellent additive to improve the electrochemical performance of $LiFePO_4$ as cathodes for LIBs. With the help of graphene, the electrons could be transferred easily between current collectors and the $LiFePO_4$ particles, reducing the internal resistance of the batteries and enhancing the output power. On the other hand, the excellent mechanical properties of graphene sheets are of benefit for the structure stability of electrode materials, resulting in an improved cyclic stability. Therefore, graphene sheets are beneficial to improve the properties of $LiFePO_4$. The first publication about $LiFePO_4$ -graphene composites was finished by Ding and coworkers

TABLE 1: Electrochemical performance of 3D LiFePO₄-graphene composites in publications.

Methods	Cycling stability	Rate capacity at 10C (mA h/g)		References
		Composites	Without graphene	
Sol-gel	140% after 100 cycles	60	45	[21]
Mechanical mixing	—	109	75	[22]
Spray drying	70% after 1000 cycles at 10C	130	110	[23]

FIGURE 1: Illustration of the synthesis procedures and the microstructure of LiFePO₄-graphene composites [23].

in 2010 [17]. The composites were prepared by a coprecipitation method, which delivered a specific capacity of 160 mA h/g while there was only 113 mA h/g for bare LiFePO₄. A research carried out by Su and coworkers demonstrated that graphene sheets were powerful planar conductive additive to enhance the electrochemical performance of LiFePO₄ [18]. The results showed that with a much lower fraction of graphene additive than those of commercial carbon-based agents, LiFePO₄ displayed better charge/discharge performance than commercial cases. In a later study, LiFePO₄-graphene composites were prepared through a facile hydrothermal route followed by heat treatment [19]. Except the liquid reaction, a solid-state route also was used to prepare LiFePO₄-graphene composites [20]. The composites with a structure of scattering graphene sheets among LiFePO₄ delivered a specific capacity of 161 and 70 mA h/g at 0.1C and 50C.

To improve the electronic conductivity and transformation rate of Li⁺, 3D porous LiFePO₄-graphene composites were fabricated [21–23]. A case in point is that 3D hierarchical self-assembled LiFePO₄-graphene composites were prepared by a facile template-free sol-gel method [21]. Another way to 3D LiFePO₄-graphene composites included the synthesis of 3D graphene networks by CVD and following mechanical mixing of graphene networks and LiFePO₄ nanoparticles [22]. The electrochemical performance of the above two composites is shown in Table 1.

A more effective method to prepare LiFePO₄-graphene composites with excellent performance was a spray-drying route [23]. This method is illustrated in Figure 1. LiFePO₄ nanoparticles were wrapped by homogeneously and loosely graphene 3D networks to form LiFePO₄-graphene composites with a microsized spherical secondary structure. The spherical secondary structure was of benefit for Li⁺ diffusion,

resulting in a high-specific capacity of 70 mA h/g at 60C discharge rate.

The electrochemical performance of LiFePO₄ could be further improved by modifying it with both graphene sheets and carbon layers [36–40]. For example, LiFePO₄@graphene composites were prepared by a solvothermal route firstly. Then, the mixture of the above LiFePO₄-graphene and citric acid was annealed at 873 K in Ar/H₂ to form LiFePO₄@C-graphene composites [36]. Another similar route was employed to synthesis LiFePO₄@C-graphene composites by using sucrose instead of citric acid [37]. Both of the above composites showed the specific capacity of 110 mA h/g at a rate of 5C. LiFePO₄-graphene-C nanofibers also were fabricated by using a combination of electrospun and sol-gel techniques [38]. As cathode materials for LIBs, the composites possess high capacity, good cycling performances, and high rate capacity. A microwave-assisted hydrothermal method also was developed to synthesize LiFePO₄/C-graphene composites with high efficiency and low cost [39].

FePO₄ as a cathode material for LIBs also has drawn much attention recently. It can be prepared at low temperature and by a facile route. Besides, amorphous FePO₄ exhibited continuous charge/discharge voltage profile. However, its conductance is unexpectedly lower than that of LiFePO₄, resulting in its poor properties. To enhance the electrochemical performance of FePO₄, FePO₄-graphene composites were synthesized from an easy and simple chemical method [41]. The composites delivered a specific capacity of 156 mA h/g after 100 cycles with a coulombic efficiency of nearly 100%. At a large current density of 2.5 A/g, the capacity could retain at 100 mA h/g. In a later study, FePO₄-graphene composites with hollow nanospheres were prepared by a hydrothermal method [42]. Those composites exhibited high rate capability and good cycle stability arising from the thin wall of

the hollow nanospheres and fast electron transport through the graphene networks.

Compared to LiFePO_4 , $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ is an attractive cathode material for LIBs, because its average extraction/reinsertion voltage is about 4.0 V, and its theoretical capacity is 197 mA h/g. Its intrinsic low electronic conductivity (240 nS/cm at room temperature) limits its rate capacity. Although some approaches, such as doping by metal ions and carbon coating, have been employed to enhance its performance [43], graphene sheets seemed to be a more effective additive to improve its electrochemical performance. Liu and coworkers prepared $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ -graphene composites and investigated their electrochemical performances [44, 45]. The composites prepared by a sol-gel route showed excellent rate capacity and cycling stability. The research also discovered that graphene was a more efficient carbon coating compared with the conventional carbon, which showed the advantages of graphene to improve the properties of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$. Therefore, the rate capacities of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ -graphene composites were much higher than those of bare $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ and the hybrids of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ and conventional carbon. $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ /graphene composites with 3D structure were synthesized by a spray-drying process [46]. The properties of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ could be improved further by coating the $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ with a carbon layer. The composites could deliver a capacity of 131 mA h/g at 10C after 100 cycles [47].

Compared to LiFePO_4 , LiMnPO_4 is another attractive cathode for LIBs due to its higher Li^+ intercalation potential of 4.1 V, resulting in about 20% higher energy density than that of LiFePO_4 . However, the electrical conductivity of LiMnPO_4 is ultra low (lower than LiFePO_4 by five orders of magnitude). Fe-doping of LiMnPO_4 has been demonstrated to be an effective method to improve its performance [48]. But its performance still lies behind the demand of consumers. Therefore, $\text{LiMn}_{1-x}\text{Fe}_x\text{PO}_4$ -graphene composites were prepared to improve the electrochemical performances [49, 50]. $\text{LiMn}_{0.75}\text{Fe}_{0.25}\text{PO}_4$ -graphene composites with high electrical conductivity and low ionic resistance led to excellent rate properties for the otherwise extremely insulating $\text{LiMn}_{0.75}\text{Fe}_{0.25}\text{PO}_4$ cathodes. A further investigation showed that the interaction between $\text{LiMn}_{0.75}\text{Fe}_{0.25}\text{PO}_4$ nanorods and graphene via charge redistribution not only anchored the nanorods onto the graphene sheets but also modified their surface chemistry, resulting in an ultra-high rate capacity as cathodes for LIBs [50].

The fundamental of using graphene to improve the properties of phosphate could be indexed to follow aspects. Firstly, graphene with high conductivity could enhance the conductance of electrode materials compared to unmodified phosphate. Secondly, the good mechanical property of graphene could maintain the microstructure of phosphate and improve the cyclic stability.

3. Lithium Metal (Mn, Co, Ni) Oxide-Graphene Composites as Cathode Materials for LIBs

LiMn_2O_4 with advantages of low cost, environmental friendliness, and high abundance has drawn much attention in

recent years [51]. Its low electrical conductivity resulted in a low-rate capacity. Published papers have demonstrated that graphene sheets were effective agents to improve their conductivity and rate capacity. LiMn_2O_4 -graphene composites with high rate capacity were synthesized by a microwave-assisted hydrothermal method [52]. The composites exhibited reversible capacities of 117 and 101 mA h/g at 50C and 100C. In another study, LiMn_2O_4 -graphene composites were synthesized by self-assembly approach combined with a solid-state lithiation method [53]. The enhancement in electrochemical properties could be attributed to the superior Li^+ diffusion kinetics and improved stability across a wide voltage window in crystalline LiMn_2O_4 -graphene composites. Especially, their capacities approached the theoretical value, and the cycling stability was enhanced.

$\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ as a promising candidate for LiCoO_2 has attracted a lot of interest [54]. It shows a high energy density, good stability, enhanced safety, and low cost. However, the cation disorder occurred during calcination results in the deterioration in the kinetic property. To enhance its electrochemical performance, $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ -graphene composites were prepared as cathodes for LIBs. It was reported by Jiang and coworkers that $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ -graphene composites prepared by mechanical mixing could deliver a capacity of 115 mA h/g at 6C [55]. $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ -graphene composites prepared by microemulsion and ball-milling route could deliver a reversible capacity of 150 mA h/g at a rate of 5C, much higher than that of bare $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ [56]. The improved performance was attributed to the grain connectivity and high electronic conductivity. $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ -graphene also was prepared by a high mechanical ball-milling method. They exhibited the high capacity of 180 mA h/g with good cycle stability [57].

4. Sulfur-Graphene Composites as Cathode Materials for LIBs

The lower specific capacities of cathode materials (about 150 mA h/g for layered oxides and 170 mA h/g for LiFePO_4) compared to those of anodes (370 mA h/g for graphene and 993 mA h/g for tin) have been a limiting factor to improve the energy density of LIBs. As a cathode for LIBs, sulfur possesses a theoretical specific capacity of 1675 mA h/g which is about five times higher than those of traditional cathode materials [58]. Its disadvantages of the low electrical conductivity and dissolution of polysulfides in electrolyte also are obvious. Sulfur-graphene composite has been demonstrated to be one way to improve the electrochemical performance of sulfur in LIBs.

The first report about S-graphene composite as cathode for LIBs was available online in October of 2010, which was completed by Wang and coworkers [24]. The composites, prepared by the heat treatment of the mixture of graphene sheets and elemental sulfur, exhibited a specific capacity of 600 mA h/g after 40 cycles at a current density of 50 mA/g. An improved method of preparing S-graphene

TABLE 2: Electrochemical performance of S-graphene composites in the literatures.

Structure	Method	Capacity	References
Graphene coated by S particles	Heat mixing	400 mA h/g after 40 cycles	[24]
Sandwich-type	Solution-mixing	505 mA h/g after 100 cycles	[25]
S particles wrapped by graphene	Self-assembly	600 mA h/g after 100 cycles	[26]
S particles in graphene	Oil/water system	620 mA h/g after 60 cycles at 1C	[27]
—	Deposition from Na_2S_x	950 mA h/g after 55 cycles	[28]
Wrinkled laminar structure	Deposition from $\text{Na}_2\text{S}_2\text{O}_3$	667 mA h/g after 200 cycles	[29]
S particles in graphene sheets	Deposition from $\text{Na}_2\text{S}_2\text{O}_3$	830 mA h/g after 50 cycles	[30]
S in the pores of activated graphene	Melt-diffusion	1000 mA h/g after 60 cycles at 0.2C	[31]
S particles on graphene	Melting diffusion	957 mA h/g after 50 cycles	[32]
Ternary composites	In situ polymerization	560 mA h/g after 100 cycles	[33]
Sandwich-type	Heat mixing	800 mA h/g after 100 cycles	[34]
S in the porous graphene	Melt-diffusion	755 mA h/g at 0.1C	[35]

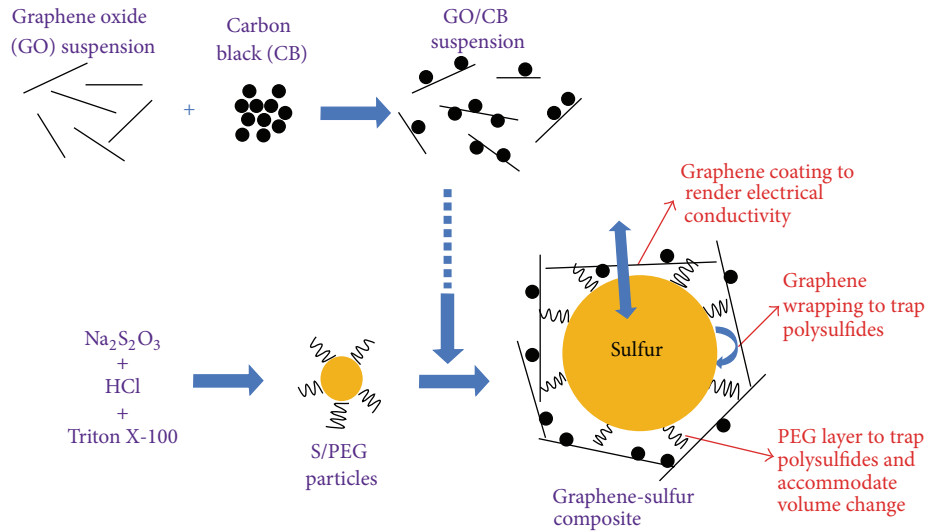


FIGURE 2: Illustration of the synthesis procedures for S-graphene composites and a proposed schematic structure of the composite [26].

by mixing graphene with the solution of sulfur was developed by Cao and coworkers [25]. The composites with a sandwich structure could deliver a specific capacity of 750 mA h/g after 50 cycles at a current density of 168 mA/g. To further improve the electrochemical performance, S-graphene composites with a wrapped structure were synthesized [26]. Improved performance was achieved by the graphene-wrapped composites which could be attributed to sulfur particles of well coated and confined by graphene sheets and meanwhile integrated polymeric cushions in composites. The synthesis method and the microstructure of composites were illustrated in Figure 2. An oil/water system also could be employed to prepare sulfur/graphene with a core/shell structure [27].

To modify the interface between graphene and sulfur, sulfur was anchored on graphene sheets by using Na_2S_x as sulfur sources [28]. Graphene sheets were coated by a uniform and thin sulfur to form S-graphene composites. A similar method by employing $\text{Na}_2\text{S}_2\text{O}_3$ as sulfur source also was used to prepare S-graphene composites [29]. To improve

the electrochemical performance of S-graphene composites, graphene was treated by HF to eliminate impurities and create active sites for the nucleation of sulfur particles on graphene sheets [30]. The composites showed a specific capacity of 830 mA h/g after 50 cycles at a current density of 168 mA/g, much higher than that of S-carbon composites. Another active method for graphene is based on the thermal process with KOH [31].

S-graphene composites with a layer-by-layer structure were synthesized by melt-diffusion strategy [32]. A dwindled over-discharged phenomenon and excellent rate capability were achieved by the composites. To avoid the dissolution of polysulfides and improve the performance of composites, polyacrylonitrile-sulfur-graphene composites were prepared by an in situ polymerization approach [33]. Table 2 shows some results about S-graphene composites as cathodes for LIBs. The improved performance of S-graphene composites could be ascribed to graphene sheets, which acted as conductive agent to enhance conductivity and protective layer to block the diffusion of polysulfides.

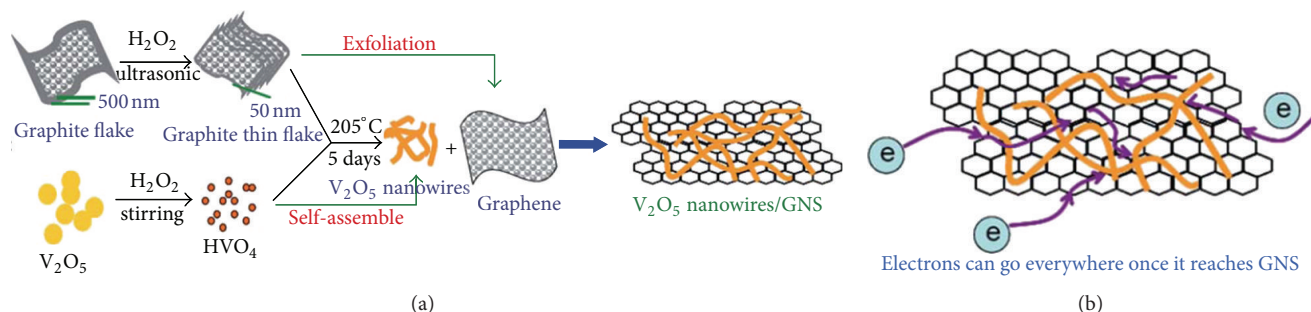


FIGURE 3: (a) Illustration of the synthesis route of V_2O_5 -graphene composites. (b) Ideal electron transfer pathway for V_2O_5 -graphene composites [60].

The enhancement of S-graphene as cathodes for LIBs could be ascribed to the following reasons. Firstly, graphene sheets as good electronic conductors could enhance the conductance of sulfur-based materials. Secondly, the layered graphene sheets with good sealability could prevent the loss of polysulfides.

5. Metal Oxide-Graphene Composites as Cathode Materials for LIBs

V_2O_5 is one of the most promising candidates for cathodes for LIBs because of its intercalation structure, low-cost, and high energy density [59]. However, the practical application of V_2O_5 is limited by sluggish kinetics of electron and Li^+ transport, resulting in low specific capacities at high rates and poor cyclability. Carbon has been introduced as a composite component to enhance electrical conductivity and prevent the vanadium dissolution. As a kind of carbon materials, graphene has attracted much attention in the field of LIBs. Especially, V_2O_5 -graphene composites were investigated as cathodes for LIBs.

$V_2O_5 \cdot nH_2O$ synthesized via a simple hydrothermal route was mechanically mixed with graphene sheets to form $V_2O_5 \cdot nH_2O$ -graphene composites [61]. The composites with a structure of $V_2O_5 \cdot nH_2O$ ribbons on graphene sheets could deliver a reversible capacity of 190 mA h/g after 50 cycles. The graphene-based composites involved a metastable monoclinic polymorph of VO_2 also were prepared by a hydrothermal method, which delivered a high capacity of 450 mA h/g [62]. Thermal decomposition also was used to prepare V_2O_5 -graphene composites by employing $(NH_4)_2V_2O_6$ -graphene as precursors [63]. The composites showed a specific capacity of 178 mA h/g after 50 cycles at a current density of 0.3 A/g. The improved performance was ascribed to the conductive network built by graphene sheets. V_2O_5 -graphene composites with a discharge capacity of 202 mA h/g after 50 cycles were synthesized by a hydrothermal route based on the hydrolysis of $VO(OiPr)_3$ [64]. A modified hydrothermal method of using graphite as precursors were developed to prepare V_2O_5 -graphene composites, as shown in Figure 3 [60]. The composites with structure of V_2O_5 ribbons on graphene sheets were obtained. Due to the improved conductance, V_2O_5 -graphene composites showed a specific capacity

of 190 mA h/g after 50 cycles. V_2O_5 with extremely stable cycling was achieved by preparing V_2O_5 /graphene composites using a facile vacuum filtration method [65]. They could deliver the capacity of 0.1 A h/g after 100,000 cycles at a current density of 10 A/g. The improvement could be ascribed to the graphene sheets which are excellent electronic conductor and could reduce the polarization of LIBs.

MnO_2 -graphene composites could be used as anodes for LIBs. They could be used as cathodes as well. MnO_2 -graphene composites were synthesized by immersing graphene sheets into a $KMnO_4$ aqueous solution [66]. A reversible capacity of 230 mA h/g after 150 cycles was obtained by employing sodium alginate as a binder. When PVDF was used as a binder, a bad performance of 115 mA h/g after 150 cycles was achieved.

6. Other Graphene-Based Composites as Cathode Materials for LIBs

Except above composites, there are a few graphene-based composites which could be used as cathodes for LIBs. A case in point is that $Ag_2V_4O_{11}$ -graphene composites were prepared for LIBs [67]. The composites were fabricated by mechanical mixing of carbon fluoride, $Ag_2V_4O_{11}$, and graphene. The ternary composites showed a specific capacity of 480 mA h/g at a rate of 5C. The impedance analysis demonstrated that the charge transfer resistance of composites is very low, accounting for excellent rate capability. FeF_3 has drawn much attention owing to its high capacity and electrical insulating. Its property could be improved by modifying it with graphene. The composites could deliver a capacity of 200 mA h/g after 80 cycles [68]. The properties of iron fluoride-graphene composites could be improved further by preparing LiF/Fe /graphene composites [69]. The composites showed a high reversible capacity of 150 mA h/g after 180 cycles.

7. Perspectives and Challenges

Herein, we have reviewed the preparation and application of graphene-based composites as cathode materials for LIBs. In those graphene-based composites, emphasis is given to the synthesis methods and the synergistic effects between

graphene and cathode materials. A variety of published papers are the evidences that graphene sheets are desirable candidates for enhancing the performance of cathode materials for LIBs to meet the demands of consumers.

Graphene-based cathode materials are of so many advantages. However, more effort should be made to overcome the following challenges for the commercial application of graphene-based cathode materials. (1) The effect of graphene precursor (GO) on the morphology of cathode materials are not very clear at this moment. There are some oxygen-containing groups on GO. Published papers have demonstrated that those groups affect the crystal growth of cathode materials. However, the detailed mechanism is not clear. (2) Rational design and controllable synthesis of cathode materials are of great significance for commercial application. (3) Developing the synthesis methods of graphene-based cathode materials, with low cost and environmentally-friendly, is very necessary for the industrial production. Although the precursor of graphene (graphite) is abundant on the earth, the common precursor of graphene is GO, needing many steps and reagents to transfer from graphite. The traditional approach for the synthesis of GO needs so many chemicals, leading to a high cost and potential damage to the environment. So many interesting results have been achieved from the investigation of graphene-based cathode materials. With continuous investigation of worldwide scientists, it is believed that graphene-based cathode materials for LIBs will be used in many fields, such as personal movable tools and hybrid electric vehicles.

Acknowledgments

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