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Recent Progress of Graphene as Cathode materials in Lithium Ion Batteries

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Abstract. Graphene, composed by one-atom-thick planar sheet with sp^2 bonded carbon atoms, which is regarded as the basis for all fullerene allotropic forms. Its combination with electrode materials ($LiFePO_4$, $LiMn_2O_4$, etc.) could dramatically increase the electrochemical performance of the rechargeable battery system. With relative poor rate capability, charge capacity, and cyclability of lithium ion batteries, this review analyses the prospects of graphene materials serve as lithium ion battery electrodes to meet such demands. Some important advances have been summarized, ranging from the synthesis of graphene-based lithium ion battery electrodes to their properties and underlying principles for electrochemical improvement of such materials.

1. Introduction

Currently, the research community is participating in abundant efforts to achieve high-effective and environmentally-friendly energy storage devices which are pivotal for the exploitation of alternative energy and thus for the replacement of fossil fuels and traditional energy sources. [1,2] In this regard, rechargeable lithium ion batteries (LIBs) outcompete other potential batteries and play a vital role in energy storage due to its high energy/power density, long life cycle, low self-discharge property, no memory effect and low toxicity [3,4]. The superiority of LIBs results from several factors: Firstly, Lithium possess the lowest reduction potential of any discovered element, contributing to the highest probable cell potential. On top of that, lithium ranks the third in the periodic table, which means it has nearly the smallest radius compared with other single-charged ion, allowing Li-based batteries to possess high gravimetric capacity and power density. [5] Lastly, multivalent cations not only always possess higher charge capacity, but also show poor mobility. However, one of the primary rate-limiting factors for battery power performance is ionic diffusion, which requires high mobility, contributing to the denial for the development of many alternative elements and the further approval of Lithium. [6] Therefore, LIBs are currently the most popular energy storages for powering portable electronics and are growing for automotive, defense and aerospace applications. Notwithstanding their pervasiveness and dominance in the market place, intensive efforts and great researches have been made to enhance the properties of LIBs [7]. In addition, various of new applications, such as electric vehicles (EVs), power tools, uninterrupted power sources (UPS), microchips and wireless communication devices, are the major driving forces to improve the battery performance [8].

Recently, many investigations have gone into revolutionary novel nanoarchitectures to enlarge the capacity and lifespan of the LIBs. Among kinds of candidates, graphene has emerged as one of the most foremost contenders. [9] In 2004, Andre Geim and his colleagues from Manchester University, UK,



firstly employed micromechanical cleavage of pyrolytic graphite to produce a single-layer graphene. [10] It currently becomes the internationally-heated issue due to its special structural and physical properties, which has significant potential to be applied in LIBs electrode materials. [11] Graphene is the one-atom-thick sheet of sp^2 -bonded carbon atoms in a honeycomb crystal lattice and it has high theoretical specific area ($2600 \text{ m}^2/\text{g}$), demonstrating its comparatively impressive Lithium storage capacity. In addition, the outstanding electronic mobility of graphene itself ($15000 \text{ cm}^2/(\text{V}\cdot\text{s})$), salient thermal conductivity ($3000 \text{ W}/(\text{m}\cdot\text{K})$), and favorable chemical stability and mechanical property (tensile modulus 1.01 TPa), working together to enable graphene to be an advantageous matrix of composite electrode material. Moreover, managing the monolayer graphene sheet in solution could lead to the tuning of the thickness of the graphene sheets, inter layer spacing, and morphology. These structural control of the graphene materials may affect the properties of lithium storage. Current batteries associated with conventional graphite show relatively low theoretical capacity (372 mA h g^{-1}) and long diffusion distance of Li ions. Graphene has already shown potential as the beneficial substitute, for example latest reports have shown graphene-based electrodes display higher specific capacities than many other electrode materials. [12, 13] Also, one paper states that 2D edge plane sites could enhance the adsorption and diffusion of Li ions, reducing charging time and increasing power output. Other studies suggest that graphene could be used as suitable building blocks for functional graphene-based materials because of unique structural and physical features of high flexibility, large surface area, superior stability, excellent electric and thermal conductivity. [14] Obviously, the use of graphene in energy storage devices is being particularly promising.

In this paper, we mainly review the latest advances on the application of graphene-based materials for LIBs electrodes. As there are numerous studies regarding to the use of graphene in cathode materials for LIBs, this review article attempts to summarize some of those studies, draw conclusions on the underlying physicochemical mechanisms and explore further research possibilities. In the followed sections, the exact mechanism of LIBs and several graphene composite cathode materials will be discussed.

2. Mechanism of Li ion battery

Commonly, LIBs comprise of anode and cathode, they are immersed in electrolyte and separated by the polymer membrane. This appliance configuration maintains unaltered from the initial edition. [15] The first LIB was constructed by Yoshino with a LiCoO_2 cathode and discharged carbon anode: [16]

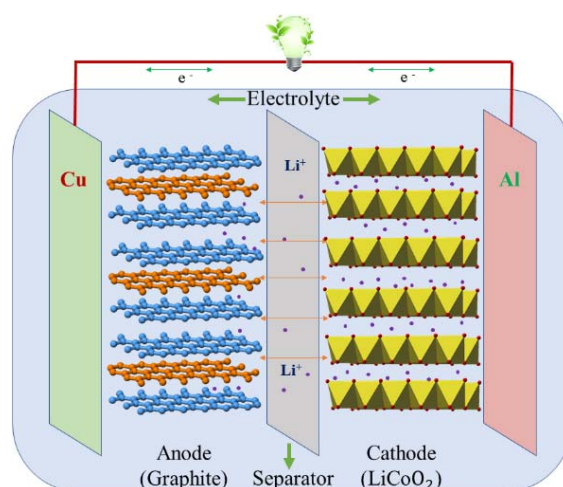
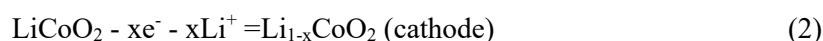
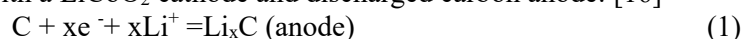


Figure 1. Basic structure of a LIB (LiCoO_2)

As demonstrated in the Fig. 1, Li ions insert into the anode after extracting from the cathode during the charging process, the reverse reaction processes during the discharge. The similarities between LIBs and traditional batteries are the redox reactions at the electrolyte/electrodes interfaces. Nevertheless, the differences are notable as well. For typical galvanic battery system, the redox reactions appeared simultaneously with the advancing or receding of the electrode surfaces, but not accompanied by either a change in the local atomic environment and chemical composition or the solid-state mass diffusion in the electrodes. In comparison, the heterogeneous redox reactions in LIBs are always accompanied by volume expansion as well as solid-state mass diffusion. [17]. the voluminal variation is one of the issues that new materials tend to solve.

The anode, cathode and electrolyte are the most significant materials that determine the electrochemical properties of a LIB. Graphite material is currently the most pervasively employed anode material, with its merits of low cost, sufficient resource and the capability to provide low and stable operation voltage. Nonetheless, since every six carbon atoms only combine 1 Li ion to form a LiC_6 , a Li ion storage structure, contributing to the relatively low specific capacity of graphite (theoretical specific capacity is 372 mAh g^{-1}). [18] However, cathodes provide an even lower Li storage capacity than anode materials do, making the cathode material a crucial factor limiting the properties of LIBs. The energy density of LIBs is often determined by the discharge potential and Li storage capacity of the cell. The discharge potential of the cathode is proportional to the reduction of Gibbs free energy during the insertion of Li ions into the electrode. The elements influencing the Li storage capacity are listed as follows: (1) the available space for accommodating the Li ions; (2) the ability of the electrode material to change the valence states; and (3) the reversibility of the redox reactions. [19] In order to satisfy the increasingly considerable demand of energy storage, those key factors mentioned above are the motivation and the direction of further investigation of new and modified composite materials.

3. Application of graphene as cathode materials in Li ion batteries

As mentioned above, graphene is regarded as the elementary foundation for all fullerene allotropic forms. Its molecular structure is shown in Fig. 2. [20] Thanks to its planar state, graphene can be rolled into 1D carbon nanotubes (CNTs) further categorized into single- or multi- walled by taking the graphene layers into consideration, wrapped into 0D spherical Bucky balls, or can be piled into 3D graphite generally madding up of more than ten graphene layers. In this regard, graphene can be considered the basic building block for all carbon materials.

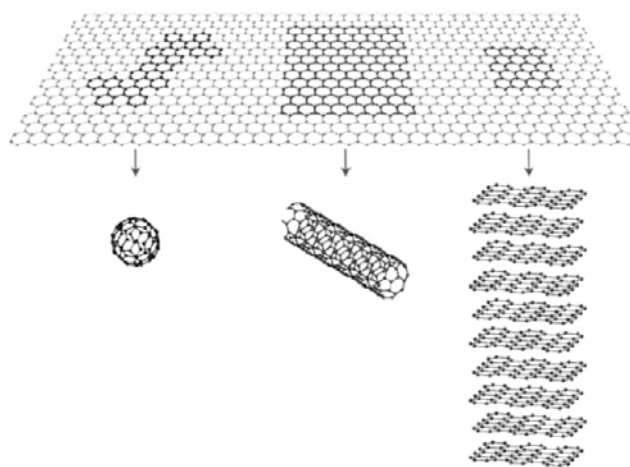


Figure 2. Structural information of graphene and other carbon forms

Graphene displays brilliant properties: large surface area and short ion channel, which offers great ability of Li ion storage and transfer, high conductivity and exceptional electric qualities, which is the firm foundation for its electrochemical performance, impressive stability and expansion buffer, which prolongs the life span of batteries. These advantages all indicate that graphene is very suitable of being basic material of electrodes and conductive additives in LIBs.

3.1. LiFePO_4 /graphene composites

Informed by the pioneer work of Goodenough [21], the LiFePO_4 (LFP) with olivine structure is a promising electrode material for LIBs cathode, which displays various advantages, such as low cost, high theoretical capacity (170 mA h g^{-1}), high electrochemical voltage, safety performance, environmental friendliness and outstanding thermal stability. [22] However, the wide application of LFP in LIBs is drastically restricted due to the low Li^+ diffusion rate ($\sim 10^{-14} \text{ cm}^2 \text{ s}^{-1}$) and limited electronic conductivity (10^{-9} - $10^{-10} \text{ S cm}^{-1}$). Strategies have been created to solve the problems since then. Among these methods, the combination with graphene is considerably attractive. Many tests have demonstrated the enhanced performance of the LFP/graphene hybrid material, for instance, the improved conductivity and reversibility, higher specific capacity with wonderful purity and crystallinity. (Fig.3) This section will introduce some novel LFP/graphene composite structural designs and synthetic strategies.

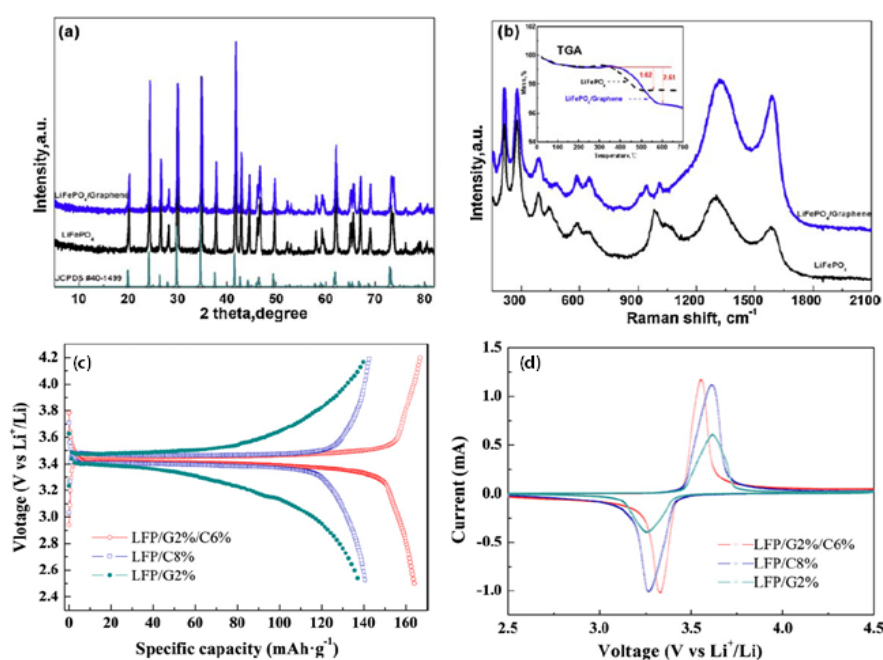


Figure 3. (a) XRD and (b) Raman patterns of porous LiFePO_4 and LiFePO_4 /graphene composite; (c) Charge and discharge profiles and (d) Cyclic voltammetry curves of various LiFePO_4 /graphene composites.

By uniting the merits of porous LiFePO_4 and distinctive properties of graphene, Yang et al. developed 3D porous LiFePO_4 -graphene (LFP/G) composite cathode through a simple template-free sol-gel process. [23] This hybrid creation discards the disability of graphene to be poorly-dispersed in mixture and embraces graphene's capability to supply a modified interfacial contact thanks to its high surface area, flexible structure, and superior conductivity. Besides, the 3D porous structure can promote electrolyte ions percolation into electrode materials and enable electrode materials to function efficiently. In another study, Tian et al. [24] built LiFePO_4 nanoparticles supporting on 3D graphene aerogel (LFP/GA), which was prepared by a hydrothermal method. The interconnected GA-based composite displays fast mass, high mechanical strength, electron transport kinetics, making it an ideal conductive

and porous network for designing and fabricating high performance cathode materials with 3D ion diffusion channels. As the studies show, LFP/GA can provide plenty of merits for the Li ions insertion and extraction reactions. Firstly, the abundant pores and channels inside the 3D framework could store the electrolyte and fast Li supply. Secondly, the interlaced graphene can increase the total conductivity of the composites and thus facilitating the quickly electron transfer. Finally, the LFP nanoparticles uniformly distributed on graphene could decrease the ionic diffusion resistance, increase the specific surface area, and shorten the Li ion transport pathways. Therefore, the LFP/GA possesses a high specific capacity of 167 mA g^{-1} at 0.1C , and a remarkable cyclic stability.

The synthetic strategies are also multiform. Zhou et al. [25] reported a facile method to prepare $\text{LiFePO}_4/\text{graphene}$ composites with high performance using the spray-drying route. LiFePO_4 nanoparticles were dispersed loosely and homogeneously on graphene 3D networks with a micro sized spherical nanostructure. Such secondary spherical nanostructures were beneficial for Li^+ diffusion, leading to a high capacity of 70 mAh g^{-1} at a rate of 60C . In another work, Ding et al. [26] constructed $\text{LiFePO}_4/\text{graphene}$ composite by a coprecipitation method, which is markedly efficient. However, this preparation process mentioned above are so complicated that it takes time and energy to manipulate. A novel paper, written by Wang et al., employed conventional solid-state synthesis to prepare LFP/graphene composites. The graphene sheets shown no effect on the olivine structure of LiFePO_4 particle with the sizes were about 200 nm . Furthermore, the graphene sheets can scattered by LiFePO_4 particles and formed 3D porous network. The composite displayed an initial specific capacity of 161 mA h g^{-1} at a discharge rate of 0.1C and remained 70 mA h g^{-1} at 50 C . These results suggest the favorable and positive effects of graphene nanosheets.

3.2. $\text{LiMn}_2\text{O}_4/\text{graphene}$ composites

LiMn_2O_4 was proposed for use in LIBs cathode in 1983 with a spinel type structure, which is currently being applied in many commercial electrical vehicle batteries in terms of low cost, adequate materials, and nontoxicity. Nonetheless, there is a primary issue that confines LMO's further practice in applications like electric vehicles (EV). The LMO has poor stability with the electrolyte after just a few cycles resulted from several reasons. For instance, the dissolution of Mn^{2+} into the electrolyte; the Jahn–Teller effect of Mn^{3+} during the phase changing; the loss of crystallinity during cycling; and cation mixing between Li and Mn. [27] To overcome all those issues, many methods have been tried, such as coating the surface by metal oxides, doping cations into crystal structure, and making an inactive surface layer by carbonaceous materials. Among these strategies, graphene's characteristics make itself stand out. It can provide a high contact area and offer a highly conductive matrix, which can facilitate the transportation of Li ions and electrons into the electrode. Graphene itself, however, could also evolve into different forms for various properties.

P. Robert et al. synthesized graphene nanoribbon (GNR) using a mild chemical unzipping approach on the basic of the longitudinal cutting mechanism of MWCNT. The as-prepared GNR is employed as a modified material on LiMn_2O_4 by a wet-coating strategy. The GNR-LMO composites exhibited a compact layer and better surface coverage than the CNT-LMO. (Fig.4) The direct contact between the electrode and the non-aqueous electrolyte can be avoided under better surface protection. On top of the advanced structural foundation, the electrochemical performance is also satisfactory. Plenty of tests have shown, such as CV(Fig.4), Raman spectra, EIS, that the GNR-LMO cathode possesses impressive electrochemical performance with high current density, suppressed charge transfer resistance, longer calendar life, negative shift in polarization, and high rate capabilities. Moreover, the GNR-LMO cathode delivered the high retention capacity of 90% after 50 cycles at 1C .

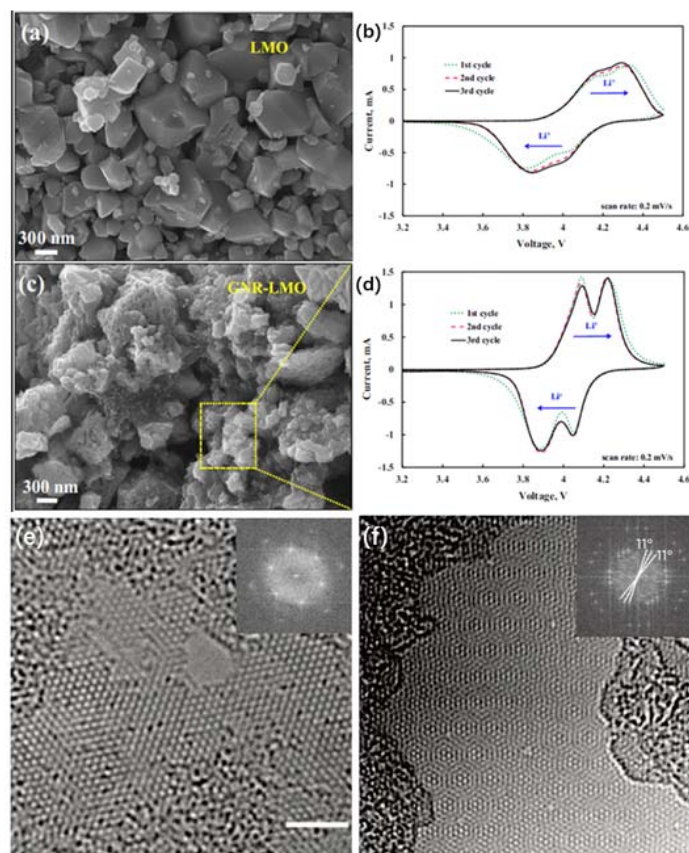


Figure 4. FE-SEM images of LMO (a) and GNR-LMO (c). CV curves of LMO (b) and LMO-GNR (d); (e) HRTEM image of a single-layer region. The inset is the FFT pattern; (f) Moiré pattern of an atomic-scale; the inset is the FFT pattern with the rotational angle of 11°

There are still many other types of graphene/LMO hybrid cathodes. S.-M. Bak et al. [28] synthesized a nanocrystalline LiMn_2O_4 /graphene composite cathode for LIBs with high specific capacity and remarkable rate capability, 90% discharge capacity retention was achieved at 1 C rate over 100 cycles. Superior electrochemical properties are ascribed to the good dispersion of the graphene nanosheet and which also serves as a 3D conductive network. Furthermore, LiMn_2O_4 particles with high surface area has been maintained and the LiMn_2O_4 particles are nanosized. LMO/graphene nanosheets nanocomposite has been prepared by a facile hydrothermal method by B. Lin et al. [29] In such nanocomposite, LMO nanoparticles with the size of 10–30 nm are well crystallized and homogeneously dispersed on the graphene nanosheets. The graphene nanosheets can not only reduce the agglomeration of LiMn_2O_4 nanoparticle, but also offer a highly conductive matrix for LiMn_2O_4 . The LMO/graphene nanosheets hybrid cathode exhibited enhanced electrochemical properties than bare LiMn_2O_4 nanoparticles. These studies are all impressive and innovative, pouring more light on the future of the application of LMO/graphene hybrid cathode.

The $\text{Y}_2\text{O}_3/\text{LiMn}_2\text{O}_4$ microsphere wrapped by graphene was firstly fabricated by B. Zhu et al [30] this material presented a specific capacity of 129.3 mAh g^{-1} , and the high capacity retention of 89.3% even after 500 cycles 1C was achieved. Additionally, it shown a high capacity of 90.0 mAh g^{-1} at a rate of 30C. Analogously, a nano-architected LMO/G/ZnO Composites created by Saad Aziz et al. [31] also showed splendid electrochemistry performance. The enhancement of electrochemical performance indicated that coating some specific metal oxide and then wrapped by graphene on LiMn_2O_4 surface was an effective method to improve the rate performance and the cyclic stability of LiMn_2O_4 .

3.3. $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{graphene}$ composites

The lithium transitional metal phosphates including $\text{Li}_3\text{M}_2(\text{PO}_4)_3$ ($\text{M}=\text{V}, \text{Fe}$) and LiMPO_4 ($\text{M}=\text{Co}, \text{Fe}, \text{Mn}, \text{Ni}$) have been considered as promising materials for LIB for the reason of their appealing characteristics of high operation potential and good thermal stability. Monoclinic $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ and olivine-structured LFP are two typical representatives. However, the LVP possesses three-dimensional path for Li ions diffusion, exhibiting high-rate performance and better ionic conductivity, compared with one-dimensional channels in LFP. Basically, LVP exists in two frameworks: the NASICON (sodium superionic conductor) phase or rhombohedral, and the thermodynamically more stable monoclinic form, which are distinguished by the way “lantern” units $[\text{V}_2(\text{PO}_4)_3]$ are interconnected. Fig. 5a shows the NASICON-type LVP framework, isotypic with those of its titanium, iron, indium analogs, and chromium, consists of PO_4 tetrahedra and VO_6 octahedra connected by vertices, forming stacked “lantern” units along the $[001]$ direction. [32] The monoclinic LVP crystallizes in a structure similar to the NASICON phase. The 3D network is built by the PO_4 tetrahedra sharing oxygen vertexes and slightly distorted VO_6 octahedra. (Fig.5b) it respectively contains two vanadium sites and Li atoms occupy three distinct crystallographic positions.

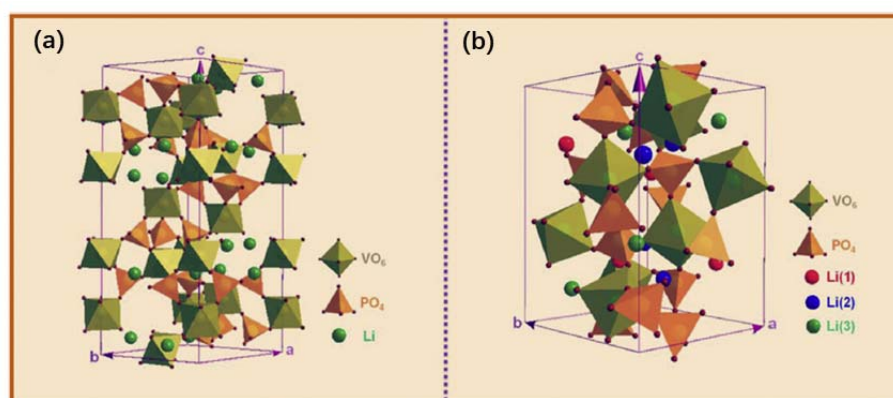


Figure 5. Polyhedral illustration of the structure of LVP (rhombohedral (a) and monoclinic (b))

Monoclinic LVP, which contains three mobile Li cations could reversibly insert and extract two lithium ions with a specific capacity of 133 mA h g^{-1} . Once charged to 4.8 V, all the three Li ions removed and formed a mixed $\text{V}^{4+}/\text{V}^{5+}$ state delivering a discharge capacity of 197 mA h g^{-1} , which is the highest value for any phosphate materials reported so far. Yet it is not perfect, as same drawbacks are shared by LFP materials and LVP materials, same graphene-modified strategies have been employed to enhance its performance. Some marked works are reviewed below.

Liu et al. [33] in 2011, firstly developed the preparation of LVP/G hybrids using a facile solution-based procedure. Well-crystallized LVP nanoparticles with 50-500 nm in size are wrapped into the graphene sheets or anchored on the graphene surface. Minor amount of graphene ($<1.14 \text{ wt } \%$) in composite contribute to large improvement of the rate capability and cyclic stability. Lately, X.H. Rui et al. [34] introduced a porous carbon matrix to further enhance the electron transport. LVP nanocrystals inserted in porous carbon matrix on the surface of graphene sheets were obtained. The existence of graphene sheets can not only help to separate the LVP grains and prevent the coarsening of LVP particles, but also function as the heterogeneous nucleation site for facilitating the growth of LVP nanocrystals. There are also other methods to synthesis this composite material. For instance, B. Cheng et al. [35] reported that liquid nitrogen could be used as a coolant to synthesize nano-LVP/reduced graphene oxide. Moreover, it was firstly proposed by L. Zhang et al. [36] that the graphene can serve as a chelating agent. The researchers prepared carbon-coated $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ particles dispersed by graphene sheets. This composite presented superior rate performance, delivering high capacity of 104 mA h g^{-1} at 5 C within

the potential range of 3.0–4.3 V, respectively. Impressively, all products mentioned above displayed no obvious capacity decay at the rate of 0.1C after long cycles.

4. Concluding remarks and future prospects

To prevent the potential power shortage and to gain eco-friendly energy, there have been enormous efforts aimed to improve LIB performance, especially for electrode materials. The outstanding mass-transportation ability of nanomaterials prove themselves as promising materials. Transport in nanoparticle systems normally requires larger electrode/electrolyte contact area, shorter transport lengths for Li ions and electrons, and better accommodation of the strains due to the insertion/extraction of Li ions. However, the large volume expansion of nanoparticles during the charge and discharge cycles results in the pulverization of the electrode materials. Moreover, the high cohesive energy of some nanoparticles brings out the agglomeration of these particles and a subsequent drop in cyclability. Thus, it is necessary to disperse nanoparticles over carbon supports with strong bonding. Graphene, which has a combination of unique physical, electrical, mechanical and other functional characteristics, is a perfect candidate to improve the performance of LIBs. Indeed, various investigations have convinced a bright future of graphene. Its composites with metal oxide and its dopant with nitrogen functioned stably and stably as anode materials. Additionally, the combination of graphene and some important materials (LFP, LMO, LVP) performs even better. Graphene materials are also promising to use as conductive additives for cathode materials of LIBs. It is expected the widespread application of graphene-based materials in commercially available high-performance LIBs.

There have been ample discoveries of graphene-based cathode in Li ion battery, however, to fulfill the particle demand of long lifespan, fast charge/discharge and high specific capacity, intensive researches should be focus on several aspects: (i) Rational design and controllable preparation of cathode materials are very important for practical application. Commercially explore the relationship between the electrochemical properties of LIBs and the electrode composite's microtopography. And discover the effect of the size, structure and defects of graphene to LIBs' performance. It is believed that graphene-based materials for LIBs cathode will be largely used with continuous exploration and investigation from worldwide scientists.

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