

Advances of graphene application in electrode materials for lithium ion batteries

LU XiaoYu, JIN XiHai & SUN Jing*

State Key Lab of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China

Received July 12, 2015; accepted August 20, 2015; published online September 9, 2015

The demands for better energy storage devices due to fast development of electric vehicles (EVs) have raised increasing attention on lithium ion batteries (LIBs) with high power and energy densities. In this paper, we provide an overview of recent progress in graphene-based electrode materials. Graphene with its great electrical conductivity and mechanical properties have apparently improved the performance of traditional electrode materials. The methods and electrochemical properties of advanced graphene composite as cathode and anode for LIBs are reviewed. Two novel kinds of graphene hybrid materials are specially highlighted: three-dimensional porous and flexible binder-free graphene-based materials. Challenges for LIBs and future research trend in the development of high-performance electrode materials are further discussed.

lithium ion batteries (LIBs), graphene, cyclability, rate capability, nanomaterials, three dimensional structure, flexible and binder-free electrode

Citation: Lu X Y, Jin X H, Sun J. Advances of graphene application in electrode materials for lithium ion batteries. *Sci China Tech Sci*, 2015, 58: 1829–1840, doi: 10.1007/s11431-015-5927-8

1 Introduction

As an impending problem, energy crisis has gained increasing attention worldwide and requires solutions in mainly two issues: exploring renewable energy resources and searching for effective secondary energy sources [1]. After harvesting sustainable energy from wind, water, sunlight, etc., suitable technologies for energy storage are needed for available usage. Moreover, an upcoming revolution of electric vehicles (EVs) and hybrid electric vehicles (HEVs) has claimed great challenges for lithium ion batteries, which is the most commonly used energy storage device currently [2]. Although we have witnessed very impressive progress in recent years not only in laboratory but also in real utilization, there are still many issues that restrict the promotion of

EVs and HEVs, e.g. driving distances, speed and equipment such as air conditioning. Thus, an urgent demand for LIBs with high energy and power density is put forward. Since the energy density and power density of LIBs are highly dependent on the properties of electrode material, there are already reviews focusing on the development of electrode materials in recent years to advance lithium ion batteries [3,4].

Graphene, typically defined as a monolayer of sp^2 carbon atoms arranged into a honey comb crystal structure, has gained great research interest since the direct observation and characterization of mechanically exfoliated graphene by Novoselov et al. in 2004. Because of its high theoretical specific surface area, superior electrical and thermal conductivities, outstanding chemical/thermal stability and good mechanical properties [5], graphene has been applied in numerous fields, e.g. lithium ion batteries, supercapacitors, fuel cells, photovoltaic devices, photocatalysis and Raman

*Corresponding author (email: jingsun@mail.sic.ac.cn)

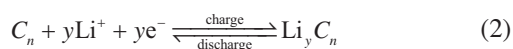
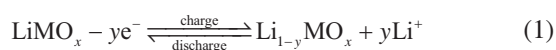
enhancement [6]. In the field of LIBs, it is necessary to point out that the graphene in most of the researches involved in this review is not technically graphene. Although CVD and some mechanical methods can produce graphene with perfect crystallinity, the poor yield makes them impossible for practical usage in LIBs [7]. Instead, reduced graphene oxide (rGO) is often used for its feasible mass production and few layered graphene property. The synthesis of rGO usually starts with oxidation of graphite, which expands the distances between the layers of graphite sheets. rGO is obtained eventually after ultrasonication, thermal expansion or other treatment and further reduction. Even though the electrical conductivity has been greatly improved during reduction, there are inevitable residual oxygen atoms and defects on the surface and edge of rGO.

When rGO is directly used as anode material, it exhibits much better performance than graphite due to its high specific surface area. Whereas major researches aim at composite materials because of the significant synergistic effects that greatly enhance the overall electrochemical performance, which has been demonstrated in both cathode and anode materials for LIBs. Researches concerning this field have become as important as morphological design of electrode materials and development of novel electrolyte [8–11].

Since graphene is a perfect 2D building block with its superior mechanical and surface properties, recently researchers find it interesting to fabricate hybrid electrode materials with unique 3D structures, showing extraordinary rate capability and cyclic performance. As the fast development of flexible and wearable electronic devices, graphene-based hybrid paper has been proved to be promising in the fabrication of flexible energy support. For these concerns, we further comment on the progress in the 3D macroscopic and flexible binder-free graphene-based electrodes applied in LIBs.

2 Graphene-based cathode materials

A lithium ion battery is typically composed of a positive electrode (cathode), a negative electrode (anode), a membrane that allows only lithium ions travel through and electrolyte that support the transport of lithium ions between the cathode and anode [12]. The main battery reactions are reversible lithium ion insertion/extraction cycles between the two electrodes, which can be described as follows:



So far, LiCoO₂-graphite is the leading LIB system that powers most of the portable devices. However, LiCoO₂ suffers from limited storage of cobalt, environmental pollu-

tion and overcharge during cycles causing potential safety problems [13,14]. Thus, supplementary cathode materials such as lithium metal oxide LiMO₂ (M= Ni, Mn) and poly-anion-based LiMPO₄ (M= Fe, Co, Mn, V) have been explored and extensively studied [15].

LiFePO₄ (LFP) is another popular cathode material and has already been implemented in commercial cells. Owing to a higher theoretical capacity (170 mA h g⁻¹) than LiCoO₂ (140 mA h g⁻¹), low toxicity, good cyclability and low cost, LFP is regarded as a promising candidate to replace LiCoO₂. However, with an olivine-type structure, the lithium ions in LFP crystalline form a one-dimensional chain along the (010) direction. The one-dimensional channel for lithium intercalation and de-intercalation brings about low Li⁺ transport ability (about 10⁻¹⁴ cm² s⁻¹) [16] along with even poorer electronic conductivities (10⁻⁹ S cm⁻¹) [17] than LiCoO₂ (10⁻⁴ S cm⁻¹) [18] and LiMn₂O₄ (10⁻⁶ S cm⁻¹) [19]. In the researches of LiFePO₄/graphene composite as LIB cathode materials, graphene usually plays a role of conducting additive [20–23]. Ding et al. [24] conducted a pioneer work of preparing LiFePO₄/GS composites through a coprecipitation method. About 100 nm LFP nanoparticles (NPs) are uniformly dispersed on the surface of graphene sheets. The composite shows an initial capacity of 160 mA h g⁻¹ at 0.2 C, while bare LFP has a capacity of only 113 mA h g⁻¹. Ha and Lee [25] proposed a size constrained *in-situ* polymerization method to fabricate nanoscale LiFePO₄-rGO composite. The capacity of LFP-rGO at 0.1 C rate is 162 mA h g⁻¹ and 44% retention of capacity was obtained at a rate as high as 60 C. The fast transport was enabled by structural features owing to the enhanced dispersion of conducting 2D graphene network. Recently, Wang et al. [26] reported a synthesis method of composite consisting of (010) face-oriented LiFePO₄ nanoplatelets wrapped in a nitrogen-doped graphene aerogel (Figure 1). The 3D porous structure of graphene framework endowed large BET surface area, which enhanced electronic transport and ion diffusion. Along with (010) facet exposed LFP nanoplatelets that shortened the Li⁺ diffusion in bulk material, the hybrid exhibited great synergistic effect. Hence the composite showed 78 mA h g⁻¹ at 100 C and a long-term cyclic stability (89% capacity retention over 1000 cycles at 10 C). Similar to LiFePO₄, other LiMPO₄/graphene (M= Mn, V) composites also behaved better than their control samples [27–29].

Spinel LiMn₂O₄ and its derivatives are another type of attractive cathode for their three-dimensional Li⁺ diffusion paths, along with higher electronic conductivity than LFP. However, the low theoretical specific capacity (148 mA h g⁻¹), phase changes during battery cycling and Mn²⁺ dissolution into the electrolyte [30] restrict its reversible capacity to only about 100 mA h g⁻¹. Therefore, LiMn₂O₄ doped with guest molecular (LiM_xMn_{2-x}O₄, M= Ni, Fe, Co, et al.) [4,31] has been proposed and proved effective in preventing Mn

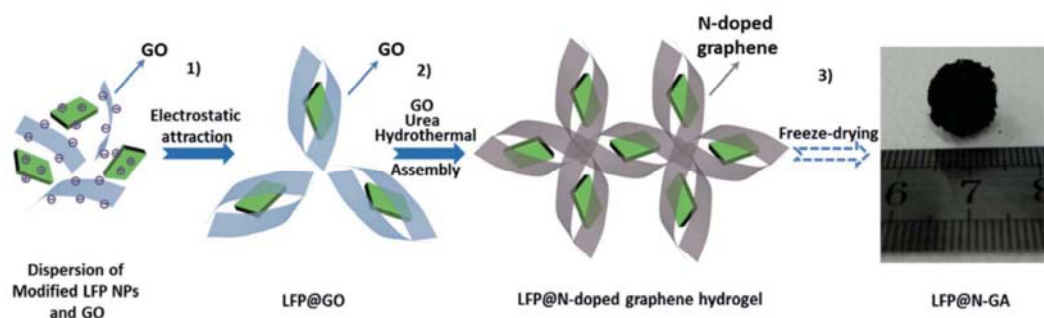


Figure 1 (Color online) Preparation process of LFP@N-GA: 1) Interactions between positively charged LFP NPs and negatively charged GO sheets via electrostatic attraction; 2) self-assembly and N-doping; 3) freeze-drying to obtain LFP@N-GA. Reproduced from ref. [26] with permission of the Royal Society of Chemistry.

in $\text{LiM}_x\text{Mn}_{2-x}\text{O}_4$ from dissolution. On the base of the existing results, graphene was introduced to fabricate a sandwiched $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ -graphene composite as the cathode material [32]. The conductive graphene network not only ensured fast electron transport, but also greatly increased the coulombic efficiency due to the suppression of electrolyte decomposition on the surface of electrode material, which resulted in an improved rate capability and cyclic retention than graphene free sample. Even the undoped LiMn_2O_4 -graphene hybrid also showed high capacity and superior rate capability (107 mA h g^{-1} at 50 C) [33].

Besides, some other promising cathode materials (e.g. V_2O_5 , LiMO_2 , $\text{M} = \text{Ni, Mn, Co, et al.}$) hybridized with graphene were investigated [34,35]. Rao et al. [35] developed a synthesis route of microemulsion followed by ball-milling to prepare $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$. After proper hybridization with graphene, the resulting composite revealed a reversible capacity of as high as 153 mA h g^{-1} at 5 C rate.

In the application of cathode material, graphene forms an effective electron conducting network which apparently enhance the rate capability and cyclability. To achieve this goal, graphene must be mixed with the cathode material in proper ratio and strategy [27]. Due to the poor dispersion of reduced graphene oxide in aqueous solution and bad effect of solid phase blending, more efficient method of producing mixture with ideal morphology is required. Moreover, even with a low weight ratio (less than 10% in the references) in the composite, the production cost is still an important issue that could limit its usage in commercial applications.

3 Graphene-based anode materials

The anode material plays a role in LIBs as important as the cathode material. In current, with the large specific surface area and stable structure during Li^+ intercalation/de-intercalation, graphite is widely used as the commercial anode material for LIBs. However, because the intercalation potential (0.1 V versus Li/Li^+) is close to Li metal, latent hazard of dendrite-like lithium precipitation exists and may

cause internal short-circuit. The relatively low theoretical specific capacity (372 mA h g^{-1}) also inhibits its underlying utilization in EVs and HEVs, which require higher capacity and better rate capability. A lot of alternative materials in substitution of graphite have thus been explored and evaluated: such as graphene, group IV element or elemental oxides, transition metal oxides/sulfides and so on.

As far as we know, the role of graphene hybrid material applied in LIB anode is much more important than that in cathode electrode. In the cathode composite material, graphene usually functions as conducting additives and dispersing agents for nanomaterial. In addition to these functions, graphene in the anode composite material not only contributes to the total specific capacity but also accommodates the huge volume changes during cycles.

3.1 Graphene as anode materials for LIBs

Owing to the large specific surface area and excellent electrical conductivity, graphene itself is a suitable candidate as anode material for LIBs. Unlike graphite, graphene can store lithium ions not only on both sides but also on its edges and defects, resulting in enhanced lithium storage capability [36].

Based on these considerations, both theoretical and experimental investigations have been conducted for graphene [37–39]. Graphene prepared by oxidation-reduction method with low defective density and few layers was usually incipiently considered ideal for lithium storage. However, Pan et al. [39] found out that highly disordered graphene nanosheets were more promising in applications in LIBs for their high reversible capacities and good cyclability. Since the reduction methods including chemical reduction with hydrazine, electron beam irradiation and low-temperature pyrolysis profoundly influenced the condition of rGO, the researchers found out rGO prepared by the latter two physical methods exhibited exceptionally high reversible capacities ($1013\text{--}1054 \text{ mA h g}^{-1}$), which was much higher than hydrazine reduced GO (330 mA h g^{-1}). After comparing different parameters (surface functional

groups, specific surface area, interlayer spacing and Raman intensity ratio I_D/I_G of the three samples, they drew a conclusion that disordered graphene nanosheets were responsible for the great capacitive enhancement for the additional reversible storage sites like edges and other defects on graphene as shown in Figure 2.

Encouraged by these findings, heteroatomic chemical doping, such as nitrogen and boron, exerted an effective way to tailor the properties of graphene and endow graphene with higher capacity for lithium storage relative to pristine graphene [40–42]. Our group [43] developed a one-step hydrazine-assisted solvothermal synthesis of nitrogen-doped reduced graphene oxide. The pristine GO was dispersed in DMF, which acted as the solvent, reducing agent and nitrogen source. After 180°C solvothermal treatment with well-adjusted hydrazine weight ratio (1.4:1), the as-prepared n-rGO showed very high conductivity (2716.2 S m^{-1}) and good dispersibility (0.5 mg mL^{-1}) in DMF. We have further conducted numerous researches based on this work [44–46] and the n-rGO prepared through this method turned out very promising candidates as anode materials. Usually, nitrogen doping of graphene was accomplished through post treatment, which made the process complicated. Therefore we introduced a new route [47] to prepare n-rGO directly from n-GO. Melamine as the nitrogen source was added into the suspension during chemical oxidation of graphite. The as-prepared n-rGO could deliver a reversible capacity of 600 mA h g^{-1} at 0.1 C, while rGO as a comparison showed only 350 mA h g^{-1} .

Despite these great properties of graphene and its derivatives, great challenges still remain. Besides expense concerns, graphene suffers from fast capacity loss in the first few cycles probably caused by morphological changes and formation of the SEI layer.

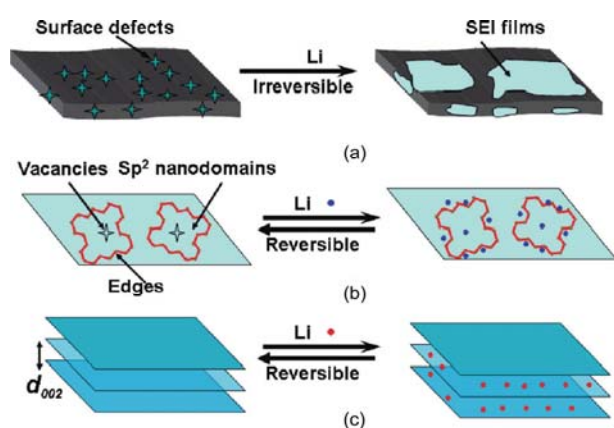


Figure 2 (Color online) (a) Irreversible Li storage at the interface between the graphene nanosheets and electrolyte; (b) Reversible Li storage at edge sites and internal defects (vacancies etc.) of nanodomains embedded in graphene nanosheets; (c) Reversible Li storage between (002) planes. Reprinted with permission from ref. [39]. Copyright 2009, American Chemical Society.

3.2 Si/SnO₂-graphene composites as anode materials for LIBs

Si and SnO₂ are both regarded as promising anode materials for LIBs for their high theoretical capacities (4200 mA h g^{-1} for Si and 782 mA h g^{-1} for SnO₂). They both react with lithium in an alloying-dealloying processes (e.g., Sn (or Si) + $4.4\text{Li} \leftrightarrow \text{Li}_{4.4}\text{Sn}$ (or Si)) [3] and both suffer from poor cycling stability resulting from the huge volume change (>300%) and low rate capability due to the poor electrical conductivity. In the Si/SnO₂-graphene composites, graphene can not only create voids that efficiently buffer the volume change but also enhance electronic conductivity and contribute to the total capacity.

The first way to fabricate Si/graphene hybrids is directly mixing graphene sheets with prepared Si [48,49]. Zhou et al. [48] developed an electrostatic attraction directed self-assembly approach, followed by heat reduction. Positively charged Si NPs were obtained by pretreating Si NPs with poly (diallyldimethylammonium chloride) (PDDA). The strong electrostatic interaction between PDDA functionalized Si and negatively charged GO lead to the formation of Si-NP@G, with uniformly dispersed Si NPs encapsulated in graphene sheets. The Si-NP@G showed excellent cyclic stability of 1205 mA h g^{-1} at 100 mA g^{-1} over 150 cycles. When the current densities increased from 400 to 800 and 1600 mA g^{-1} , the composite still displayed reversible capacities of 1452, 1320 and 990 mA h g^{-1} . Due to the enormous volume changes during cycles, 0 dimensional Si NPs would lose contact with graphene backbone for pulverization and fracture. To deal with this problem, Lee et al. [50] introduced silicon nanowires (SiNWs) to hybridize with graphene. SiNWs were firstly fabricated by metal-assisted chemical etching (MaCE), followed by mixing with GO under vacuum filtration using anode aluminum oxide (AAO) filter. The obtained graphene/SiNW composite film was transferred onto the current collector using hot-pressing and directly utilized as the anode for LIBs. The unique structure that multilayered graphene enveloped SiNWs exhibited great structural stability during alloying-dealloying processes due to the restriction of graphene. The resulting graphene/SiNW without any polymeric binders showed better capacity retention than the conventional type of electrode prepared using binders and SiNWs as the anode. This work demonstrated the importance of robust adhesion between graphene and active anode materials.

Considering the shortcomings such as dispersion and loose contact between graphene and silicon, researchers have come up with another method of directly Si growth on graphene surface [51,52]. Recently, Ko et al. [51] reported an unprecedented self-compacting behavior of their amorphous silicon nanoparticles backbone-graphene nanocomposite (a-SBG). After porous graphene was prepared by freeze-drying and reduction, amorphous silicon NPs (particle size <10 nm) were deposited on both sides of graphene

sheets through chemical vapor deposition (CVD) (Figure 3). During long-term battery test at current density as high as 14 A g^{-1} , the a-SBG displayed an excellent capacity of 1103 mA h g^{-1} over 1000 cycles. The negligible capacity loss was attributed to the porous structure that accommodates volume changes, high electrical conductivity endowed by graphene matrix and a high surface reaction area due to nanometric-size effects.

SnO_2 is also regarded as a promising replacement as anode material for its more than doubled theoretical capacity (782 mA h g^{-1}) of graphite (372 mA h g^{-1}). Essential volume changes have been verified by *in-situ* TEM observations, which explained a main reason for capacity fading [53]. In this case, our group proposed a synthesis method of SnO_2 nanorods directly growing on graphene/n-doped graphene [54,55]. After 50 cycles, the GS/ SnO_2 hybrid maintained a capacity of 710 mA h g^{-1} at 100 mA g^{-1} , which is much better than the bare Sn nanorods (237 mA h g^{-1}) [54]. Enhanced lithium storage properties have been achieved in GS/ SnO_2 hybrid electrode for mainly two reasons: 1) The SnO_2 nanorods *in-situ* grown on graphene sheets are well dispersed in graphene matrix, which inhibits particle aggregation and fracture during cycles, 2) graphene creates enough void space to buffer volume changes and meanwhile

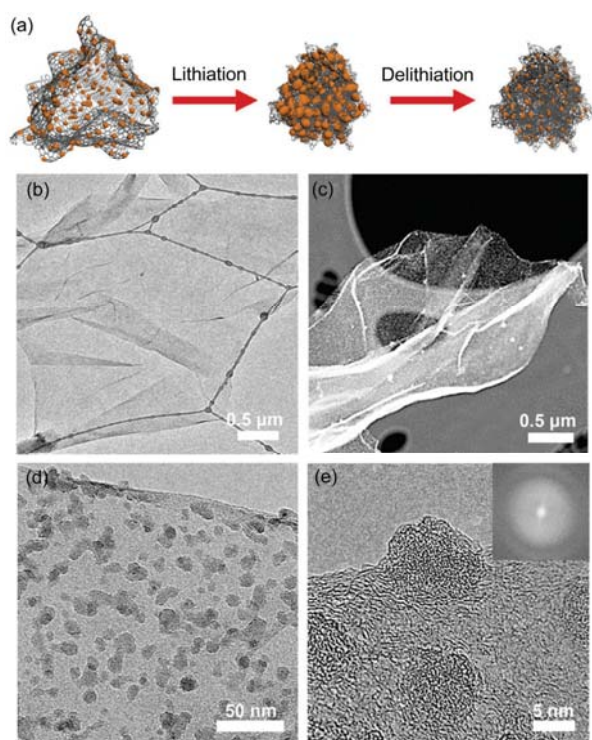


Figure 3 (Color online) (a) Schematic view of a-SBG nanocomposites before and after electrochemical cycling. Low magnification TEM image of (b) reduced graphene oxide and (c) a-SBG. Higher magnification TEM images of (d) a small area of the a-SBG surface and (e) an individual hemispherical amorphous silicon particle, with the corresponding indexed FFT inset image. Reprinted with permission from ref. [51]. Copyright 2014, American Chemical Society.

guarantees benign electrical conductivity. Liu et al. [56] synthesized boron-doped, carbon coated SnO_2 /graphene hybrids (BCTGs). With phenylboronic acid as boron source, the hybrid showed superior electrochemical performance as the anode for LIBs with a stable capacity of 1165 mA h g^{-1} at 0.1 A g^{-1} after 360 cycles and great rate capability of 600 mA h g^{-1} at 3.2 A g^{-1} . Owing to the 2D core-shell architecture and B-doped carbon, BCTGs possessed enhanced electrical conductivity and more active sites for lithium storage. Recently, Zhou et al. [57] developed a facile one-step microwave-assisted solvothermal method to synthesize SnO_2 -N-doped graphene (SnO_2 -NG) composite. Thanks to the microwave-assisted solvothermal method, the whole process took only a few minutes and needed no further treatment. The discharge capacities of SnO_2 -NG reached 1123, 969, 818, 580 and 369 mA h g^{-1} at current rates of 0.3, 1, 2, 5 and 10 C, respectively. Even after 270 cycles, the SnO_2 -NG showed 853 mA h g^{-1} at 1 C, while the capacity of bare SnO_2 decreased to only 65 mA h g^{-1} .

3.3 Transition metal oxide-graphene composites as anode materials for LIBs

Transition metal oxide (MO, e.g., M = Fe, Co, Ni, Mn, or Cu) are important members of anode materials, which have been deeply investigated for their high theoretical Li-ion storage capacities ($>600 \text{ mA h g}^{-1}$) [3]. The mechanism of reaction between MO and Li is called “conversion” reaction: $\text{nano-MO} + 2\text{Li} \leftrightarrow \text{nano-M} + \text{Li}_2\text{O}$. This conversion reaction is a general rule and is also applicable to sulfides, fluorides, oxyfluorides, nitrides, phosphides, et al. During lithiation process, the volume of this kind of materials expands largely due to the resulting amorphous Li_2O . Moreover, similar to Si (or Sn) based electrodes, these materials suffer from poor electrical conductivity.

Introducing 2D plane graphene as a buffer and conducting additive has been widely investigated and it turns out feasible in solving these problems. The confinement function could compensate for volume changes and inhibit the detachment and agglomeration of metal oxide, leading to improved cycle life of the electrode. As an example, monodispersed Fe_3O_4 nanoparticles of size about 10 nm were firstly prepared by a co-precipitation method, followed by mechanically mixing with graphene oxide and thermally reduced to form a Fe_3O_4 -graphene composite [58]. The composite showed a stable capacity of 1280 mA h g^{-1} at 0.1 C and 860 mA h g^{-1} at 4 C rate. Our group [59] prepared an $\alpha\text{-Fe}_2\text{O}_3$ /GS composite using $\text{Fe}(\text{OH})_3$ sol and GO as precursors followed by hydrothermal reduction of GO. Electrostatic attraction between GO and $\text{Fe}(\text{OH})_3$ ensured good dispersion of $\alpha\text{-Fe}_2\text{O}_3$ on GS and effectively inhibited the stack of graphene sheets. The optimized $\alpha\text{-Fe}_2\text{O}_3$ /GS could deliver a reversible capacity of 950 mA h g^{-1} after 70 cycles at 0.1 mA g^{-1} current density. Detachment is a common

phenomenon during volume changes of MO, which is considered to be a main reason for capacity loss during cycles. To gain the better interfacial property, Yang et al. [60] firstly modified Co_3O_4 nanoparticles with aminopropyltrimethoxysilane (APS) to obtain positively charged surface. The GSs were wrapped around the surface of Co_3O_4 due to opposite charge states, and a continuous conductive network was established. The resulting graphene encapsulated Co_3O_4 (GE- Co_3O_4) possessed a high and stable reversible capacity of 1000 mA h g^{-1} after 130 cycles. This result was much greater than the ones of bare Co_3O_4 and mixed $\text{Co}_3\text{O}_4/\text{graphene}$ electrodes.

Compared to the above methods, *in situ* growth of metal oxide on graphene could not only improve the dispersion of nanoparticles but also enhance the interfacial contact. Lai et al. [61] used CoCl_2 salt and microwave exfoliated GO (MEGO) as precursors. Urea was sequently added in as nitrogen source and precipitator to prepare $\text{Co}(\text{OH})_2/\text{NMEG}$ (nitrogen-doped exfoliated graphene). $\text{Co}_3\text{O}_4/\text{NMEG}$ was finally produced through an annealing process. By adjusting the mass ratio, $\text{Co}_3\text{O}_4/\text{NMEG}$ with 70 wt% Co_3O_4 exhibited the best stable capacity of 910 mA h g^{-1} under 100 mA g^{-1} . Besides, a high capacity loss of about 700 mA h g^{-1} was obtained in the first cycle for thermally reduced GO (tRGO) sample, while the $\text{Co}_3\text{O}_4/\text{NMEG}$ with most of the remaining O removed or replaced by N showed low capacity loss of only 250 mA h g^{-1} . The remaining oxygen-containing groups would not only cause irreversible capacity at the first charge/discharge, but also oxidize the electrolyte, leading to irreversible capacity loss and the electrode stability.

Besides the efforts described above, there are also research works concentrating on the morphological designing of MO in MO/graphene composite [62,63]. Although enhanced cyclic stability and rate capability have been achieved already, problems such as low coulombic efficiency in the first cycle and unstable voltage plateau remain to be solved.

3.4 Layered metal sulfide-graphene composites as anode materials for LIBs

In great demands for high performance LIBs electrode material, metal sulfides (MS_x , M= Mn, Fe, Co, Ni, Cu, Mo, W, Zr, V, etc.) based on conversion or alloying reactions have drawn increasing attention due to their higher specific capacity than traditional insertion electrode materials. Among these sulfides, layered metal sulfides (such as MoS_2 , WS_2 , ZrS_2 , VS_2 , VS_4 and SnS_2) were reported to exhibit much better cyclic performance than other ones [64]. The layered structures of these sulfides can be transferred to exfoliated pieces due to the weak Van der Waals interaction between S-S layers during the first Li insertion. Thanks to this unique property, much lower volume expansion (e.g. 103% for MoS_2) and shorter Li ion diffusion length than metal oxides are achieved.

Since both the layered metal sulfides and graphene possess 2D structures, the contact between them is much tighter than that between graphene and nanoparticle. Chang and Chen [65–67] prepared a series of $\text{MoS}_2/\text{graphene}$ composites as the anode materials for LIBs (Figure 4). Sodium molybdate, sulfocarbamide (or L-cysteine) and GO were mixed together as precursors, followed by hydrothermal treatment at 240°C for 24 h. The resulting $\text{MoS}_2/\text{graphene}$ composites showed extraordinary capacities of $1100\text{--}1290 \text{ mA h g}^{-1}$ with high capacity retention after long cycles at 0.1 A g^{-1} , and remained $900\text{--}1040 \text{ mA h g}^{-1}$ at 1 A g^{-1} . The superior electrochemical performances of $\text{MoS}_2/\text{graphene}$ composites as the anode were attributed to their robust composite structure and the synergistic effects of layered MoS_2 and graphene. Jiang et al. [68] demonstrated a facile strategy to prepare SnS_2 nanotablets anchored on graphene support ($\text{SnS}_2@\text{graphene}$), which delivered a reversible capacity of 504 mA h g^{-1} at 0.5 C rate after 200 cycles, while the pure SnS_2 only showed a capacity of 168 mA h g^{-1} with obvious capacity loss. Zhang et al. prepared hexagonal SnS_2 nanoplates lying flat on the graphene sheets. Large available surface area, high conductivity and fast transportation of electrons and Li^+ contributed to good cyclability (1005 mA h g^{-1} over 200 cycles at 0.1 A g^{-1}) and rate capability (612 mA h g^{-1} at 2 A g^{-1}).

4 Advanced constructions of graphene-based electrodes for LIBs

In recent years, researchers have realized that ideal morphologic designing is a feasible way to further improve the

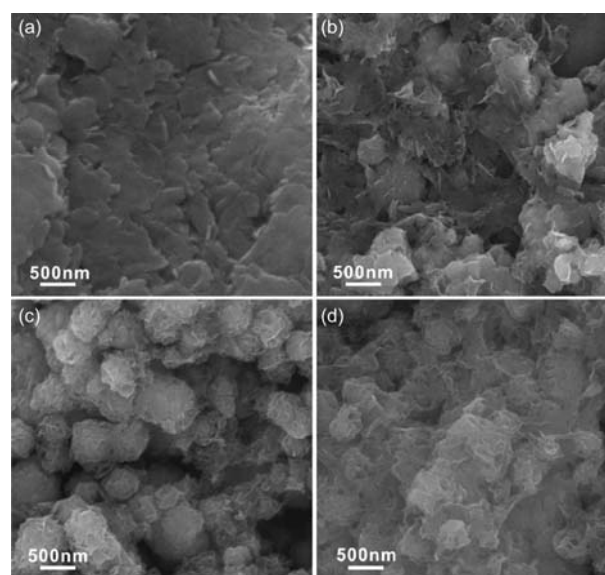


Figure 4 SEM images of (a) MoS_2 , (b) MoS_2/G (1:1), (c) MoS_2/G (1:2), and (d) MoS_2/G (1:4) prepared by hydrothermal route and annealing in H_2/N_2 at 800°C for 2 h. Reprinted with permission from ref. [65]. Copyright 2011, American Chemical Society.

performance of graphene composite materials as the electrode material. Three-dimensional architectural electrode material composed of 2D graphene building blocks and 0D/1D/2D (nanoparticles/nanorods/nanotables) active materials have been obtained through various strategies. Such porous structure with high pore volume is designed to make full utilization of the high intrinsic surface area of graphene [69]. Under the background of the quick development of flexible and wearable electronic devices, a flexible and efficient power source is urgently needed. Based on the great mechanical properties of 2D graphene, current collector and binder free electrodes with flexibility become another hot topic in the LIB technologies. Since both the two fields are greatly encouraged by the investigations of graphene hybrid LIB electrode materials, we will specifically focus on the developments of the advanced 3D macroscopic and flexible binder-free graphene-based electrode in this section.

4.1 3D macroscopic graphene-based electrodes

4.1.1 Graphene-based composite hydrogel/aerogel as anode materials for LIBs

Graphene-based hydrogel/aerogel is a 3D macroscopic architecture constructed through self-assembly of graphene sheets. Driven by a noncovalent (van der Waals force, π - π stacking, hydrogen bond) or covalent interactions, 2D graphene sheets can partially overlap and self-assemble into 3D macroscopic hydrogels [70]. The graphene hydrogel/aerogel framework possesses a high specific surface area, porous structure and continuous graphene backbone [7]. Thanks to the few stacking and interconnected nature, graphene aerogels have shown great electrical conductivity [71] and mechanical properties [72]. These features make the graphene-based hydrogel/aerogel a promising electrode material for LIBs [6].

In 2011, Chen et al. [73] pioneered the study of Fe_3O_4 nanoparticles embedded in the self-assembled graphene architecture by a mild chemical reduction of GO in water. As the anode material, a reversible capacity of 1100 mA h g^{-1} was obtained over 50 cycles at 200 mA g^{-1} . To enhance the interactions between Fe_3O_4 and graphene, Wei et al. [74] firstly dispersed APS modified Fe_3O_4 into GO solution to obtain $\text{Fe}_3\text{O}_4@\text{GO}$. Afterwards, the mixture was hydrothermally treated to form $\text{Fe}_3\text{O}_4@\text{GO}/\text{GF}$ with additional GO to connect $\text{Fe}_3\text{O}_4@\text{GO}$ with each other. The $\text{Fe}_3\text{O}_4@\text{GS}/\text{GF}$ was finally obtained by freeze drying and further thermal reduction in Ar. This method solved the problem of fracture of Fe_3O_4 and its separation from graphene foam. At a charge/discharge density of 4800 mA h g^{-1} , the resulting $\text{Fe}_3\text{O}_4@\text{GS}/\text{GF}$ still delivered a favorable capacity of 363 mA h g^{-1} , while $\text{Fe}_3\text{O}_4@\text{GS}$ only exhibited 115 mA h g^{-1} . *In-situ* growth of monodispersed FeO_x and MoS_2 in graphene-network backbone architectures were achieved by Gong et al. [75]. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{MoS}_4$

as precursors for FeO_x and MoS_2 were originally mixed with GO, followed by a normal hydrothermal treatment at 180°C for 6 h. This *in-situ* growth strategy resulted in very fine MoS_2 nanoplates and continuous amorphous FeO_x on the graphene surface. The 3D $\text{MoS}_2/\text{graphene}$ (85 wt% MoS_2) delivered a high reversible capacity of about 1200 mA h g^{-1} in the initial cycle at 0.5 C ($1 \text{ C} = 1200 \text{ mA g}^{-1}$) with no capacity loss over 30 cycles. Amazingly high reversible capacities of 620 and 270 mA h g^{-1} were achieved at 12 and 140 C . In another work of theirs [76], when commercial MoS_2 was directly used instead of *in-situ* growth, the $\text{MoS}_2/\text{graphene}$ still showed great electrochemical properties. The exceptional tight interaction between graphene and 2D MoS_2 nanoplates along with large surface area and short lithium diffusion length were expected to be the reasons for the highly reversible capacity.

3D nitrogen-doped graphene aerogel [77] was also synthesized with the addition of urea during reducing and self-assembly process. N-doped graphene not only increased the electrical conductivity and reactive sites, but also helped pin the Fe_3O_4 nanoparticles. The as-prepared N-G/ Fe_3O_4 showed high reversible capacity (1130 mA h g^{-1} over 200 cycles at a current density of 100 mA g^{-1}) and rate capability (648 mA h g^{-1} at 1600 mA g^{-1}). As displayed in Figure 5, our group constructed S- $\text{Fe}_2\text{O}_3/\text{GS}$ aerogel composites via a solvothermal synthetic process, using $\text{Fe}(\text{OH})_3$ sol and GO as precursor [45]. In this case, DMF was introduced as the solvent, which acted as both nitrogen source and reducing agents. $\text{Fe}(\text{OH})_3$ sol with ultra-small size and good dispersibility ensured uniform distribution of the final Fe_2O_3 and intimate contact between the Fe_2O_3 and GS, which facilitated fast interfacial electron and Li^+ transport. As a result, superior rate capability (930 , 660 and 520 mA h g^{-1} at 500 , 2000 and 4000 mA g^{-1} , respectively) and excellent prolonged cyclic stability at high rates (733 mA h g^{-1} over 1000 cycles at 2 A g^{-1}) were achieved. This

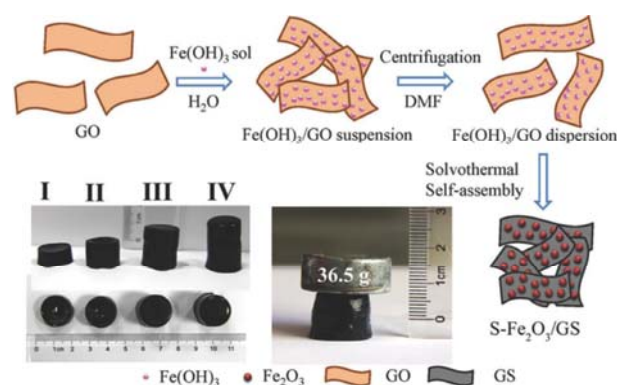


Figure 5 (Color online) Schematic illustration of preparation of S- $\text{Fe}_2\text{O}_3/\text{GS}$ aerogels. The left photograph is S- $\text{Fe}_2\text{O}_3/\text{GS}$ hydrogels with increasing size, obtained by solvothermal treatment of 10 mL (I), 20 mL (II), 30 mL (III) and 40 mL (IV) $\text{Fe}(\text{OH})_3/\text{GS}$ dispersions. The right one shows the S- $\text{Fe}_2\text{O}_3/\text{GS}$ supporting a 36.5 g iron plate. Copyright 2014, Wiley-VCH.

method was universal and could also be applied to the fabrication of SnO₂/nitrogen-doped graphene aerogels [44].

In spite of the above mentioned electrode materials for LIBs, 3D macroscopic graphene framework could also be utilized to incorporate with many other metal oxides/sulfides (CoO, TiO₂, SnS₂, CeO₂, etc.) [78–82].

4.1.2 Other 3D graphene constructed materials

The superiority of graphene-based hydrogel/aerogel lies in the high utilization of specific surface area. The transformation from monolithic hydrogel to aerogel reserves the original status of few layered graphene without severe stacking and meanwhile facilitates interconnected graphene framework. It occurs to many researchers that the post-treatments (thermal drying, freeze drying, supercritical CO₂ drying, etc.) are key issues that greatly influence the properties of graphene-based composite as the electrode material for LIBs. Nam et al. [83] prepared the porous graphene/SnO₂ composites by a typical process of thermal reduction after the self-assembly of APTES-modified SnO₂ and GO. In the thermal reduction process, they found that a fast heating rate (10°C min⁻¹) led to the formation of the 3D highly porous graphene (PG), and the 2D less porous graphene (G) was developed with a slow heating rate (1°C min⁻¹). The released gases such as H₂O, CO and CO₂ during fast heating process induced the concurrent development of such crumbled and folded architectures. The PG/SnO₂ showed a reversible capacity of 1100 mA h g⁻¹ over 100 cycles at 144 mA g⁻¹ and 690 mA h g⁻¹ at 3600 mA g⁻¹, which was much better than the performance of G/SnO₂.

Spray drying and pyrolysis have recently been used to fabricate assembled balls composed of numerous porous graphene sheets. Park et al. [84] developed a novel spray-assisted self-assembly process to create a spherically integrated graphene microstructure using a high-temperature organic solvent in a manner reminiscent of deep-frying. This method endowed the effective assembly of the GO sheets into a graphene microsphere with nanoporous channels inside. By dispersing Si nanoparticles (~100 nm) in the pristine solution, the Si/graphene microsphere prepared by this method exhibited 1500–1650 mA h g⁻¹ at a current density of 0.5 A g⁻¹. Choi and Kang [85] designed a one-step spray pyrolysis process to prepare Fe₃O₄-decorated hollow graphene balls. Using iron (III) chloride dispersed in GO solution as precursor, the Fe₃O₄ nanoparticles (~15 nm for 800°C pyrolytic temperature) uniformly distributed over the flexible hollow graphene balls. The resulting composite delivered a high reversible capacity of 690 mA h g⁻¹ over 1000 cycles at 7 A g⁻¹. The structural stability of the Fe₃O₄-decorated graphene balls during long-term cycles improved the cyclic performance at high current densities.

Preparing graphene composite with macroporous structure derived from sacrificial templates is another feasible way to enhance the electrical and ion transport in the elec-

trode material. This procedure is advantageous for creating evenly arranged and internally connected continuous macropores as well as precisely controlling the pore size. Zhu et al. [86] employed polystyrene spheres (PS) as the templates. The mixed slurry composed of PS, GO and metal salt (Fe(NO₃)₂·9H₂O, Co(NO₃)₂·6H₂O) was directly painted on stainless steel and the final binder-free electrode was obtained after annealing. The resulting porous graphene/Fe₃O₄ electrode delivered 1124 mA h g⁻¹ over 100 cycles at 0.5 A g⁻¹ and 506 mA h g⁻¹ even at 10 A g⁻¹. Our group [87] prepared a 3D Fe₃O₄/macroporous graphene (FPG) composite showing superior Li storage performance. The strong electrostatic forces between GO sheets decorated with Fe(OH)₃ and carboxylic PS induced the self-assembly of three-dimensional interconnected graphene framework. With lower contact resistance and faster ion diffusion owing to the macroporous structure, the optimized FPG electrode displayed enhanced rate capability (1057, 843, 709, 569 and 500 mA h g⁻¹ at 200, 400, 800, 2000 and 4000 mA g⁻¹) and long-term cyclic stability at high current density (859 mA h g⁻¹ over 1000 cycles at 2 A g⁻¹).

Recent studies have revealed two key factors for high-performance LIBs electrode material: Fast electron/ion transport and structural stability during long-term cycles. The superiority of such 3D macroporous electrode has been demonstrated in above text and some other essays [88,89]. The upcoming challenge for this series of materials lies in the relatively complex synthetic process and difficulty in controlling the optimized 3D structure.

4.2 Flexible and binder free graphene-based electrodes

Binders and conductive agents are widely used in traditional electrodes for LIBs. They usually take up more than 20 wt% total mass of the electrode material but contribute little to the capacity. Since the fast development and introduction of graphene, graphene-based materials can be fabricated into paper-like binder-free electrodes. These graphene-based electrodes with great flexibility are very promising in future wearable electronic devices [90]. In this section, we focus on flexible and binder-free electrode materials based on graphene or graphene hybrids.

4.2.1 Graphene as anode materials for LIBs

Although there are some works on assembled graphene oxide film used as the LIB cathodes, the poor cyclic stability, low capacity and unstable discharge plateau still make it worse than the traditional cathode materials [91]. Ali Abouimrane et al. [92] conducted a pioneer study on non-annealed graphene paper by vacuum infiltration as the binder-free LIB anode material. However, the graphene paper showed a capacity of only 84 mA h g⁻¹ over 70 cycles at 50 mA g⁻¹. The possible reasons for such poor performance were insufficient reduction of pristine GO paper

(hydrazine at 90°C) and severe staking between graphene sheets which was unfavorable for Li ion infiltration. Hu et al. [93] introduced carbon nanotubes (CNTs) to fabricate CNT/GN composite free-standing hybrid papers. The hybrid paper was effectively reduced by annealing in Ar-H₂ (10% H₂) atmosphere at 800°C for 2 h. CNT in the composite not only increased the electrical conductivity but also inhibited neighbored graphene sheets from stacking. The composite paper with a CNT/GN ratio of 2:1 delivered a high capacity of 330 mA h g⁻¹ at 100 mA g⁻¹. Liu et al. [94] has developed a strategy to make graphene paper by mechanically pressing a graphene aerogel. The graphene paper exhibited a unique structure with folded graphene sheets. It showed much higher performance (568 mAh g⁻¹ at 100 mA g⁻¹ after 100 cycles) compared to graphene paper fabricated by flow-directed assembly method. Zhao et al. [95] demonstrated that holey graphene papers created via a mechanical cavitation-chemical oxidation approach showed enhanced Li storage performance. The porosity in graphene sheets greatly improved ion diffusion kinetics and could be readily tuned by adjusting the HNO₃ concentration. The optimized holey graphene sheets exhibited a reversible capacity of ~250 mA h g⁻¹ over 400 cycles at C/1.5 (1 C = 372 mA h g⁻¹) and ~70 mA h g⁻¹ over 1000 cycles at 26.6 C with no capacity loss.

4.2.2 Graphene-based composites as anode materials for LIBs

When hybridized with high-capacity metal oxides/sulfides, the free-standing graphene sheets with tunable porosity deliver even better performance. On the basis of the above work, Zhao [96] further prepared the Si-graphene with defects (Si-deG) hybrid paper with high ductility. With 65–70 wt% Si in the composite, the optimized Si-deG retained about 2500 mA h g⁻¹ (at 1 A g⁻¹) after 140 cycles. Our group [97] developed a two-step approach for the synthesis of free-standing and flexible H-Fe₃O₄/GS hybrid film.

The composite with the optimized graphene ratio (39.6 wt%) achieved reversible capacity of ~660 mA h g⁻¹ over 50 cycles at 500 mA g⁻¹. The hollow and porous spindle-like Fe₃O₄ (H-Fe₃O₄) not only acted as the active material for Li storage but also created abundant void spaces between graphene sheets for fast electrical conductivity and Li⁺ diffusion. This method could be readily applied by replacing H-Fe₃O₄ with bi-metal oxides Fe₂O₃@SnO₂ [98]. The synergistic effect of the core-shell bi-metal Fe₂O₃@SnO₂ in hybrid graphene-based free-standing paper (Fe₂O₃@SnO₂/GS) contributed to the better performance than simple Fe₂O₃ (or SnO₂)/GS. Besides, there are some other researches on hybrid graphene/MO (MO = Fe₃O₄ [99], SnO₂ [100], etc.) flexible binder-free electrode reported.

Different from the above nanomaterial (Si/SnO₂ NPs, spindle-like hollow Fe₃O₄ and so on), 2D structured nanoplate metal oxides/sulfides have been proved to own better interfacial condition with 2D graphene sheets. Graphene and sheet-like Co₃O₄ prepared with Co(OH)₂ precursor were assembled into a robust free-standing and binder-free Co₃O₄/graphene film [101]. Due to the improved interfacial electron and lithium ion transport, the Co₃O₄/graphene film showed a high capacity of ~1200 mA h g⁻¹ at 200 mA g⁻¹ with no capacity loss after 100 cycles. CoO nanosheets/graphene hybrid paper [102] prepared using β-Co(OH)₂ and GO as precursor revealed excellent cycling stability from 0°C to 55°C. Although improved interfacial status is achieved for these compact graphene composites, there are still aggregation and stacking problems along with poor ion diffusion kinetics. To overcome these difficulties, our group [103] prepared flexible and free-standing MoS₂/GS film, in which graphene forms an open porous network with few-layered MoS₂ uniformly grown on the surface of GS. During the annealing process in a Ar/H₂ (10% H₂) mixture at 800°C, rapid evolution of gaseous species (CO₂, H₂O, etc.) triggered the compact MoS₄²⁻/GO film into the MoS₂/GS porous film. Owing to the porous structure and morpholog-

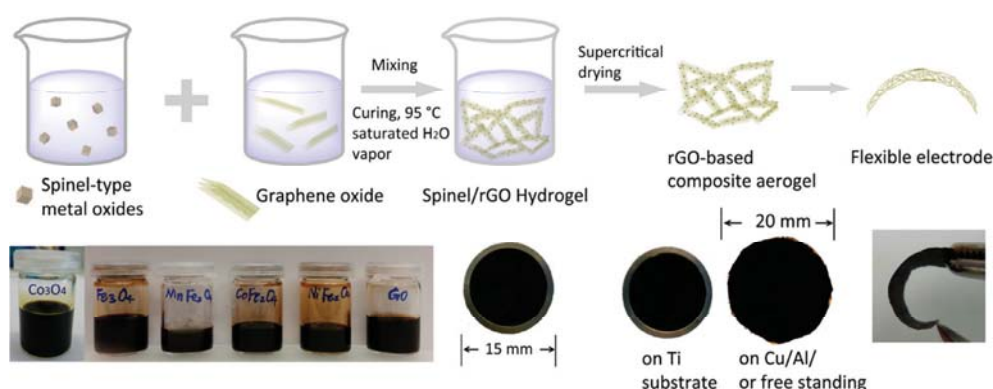


Figure 6 (Color online) Schematic illustration of the fabrication process for spinel/rGO nanocomposite aerogel films. Colloidally stable spinel-type NPs and GO dispersions are used as building blocks. The combined suspension is cured under a saturated H₂O vapor environment at 95°C for 6 h, leading to a monolithic gel film. After supercritical drying, a flexible rGO-based composite aerogel with a rationally controlled shape is obtained. The free standing aerogel films can be bent without breaking. Reprinted with permission from ref. [104]. Copyright 2015, American Chemical Society.

ical durability, the capacity of porous MoS₂/GS retained 907 mA h g⁻¹ over 1000 cycles at a high current density of 1 A g⁻¹.

Zeng et al. [104] managed to endow the flexible graphene-based hybrid film with 3D porous structure by self-assembly of GO and various oxides forming aerogel (Figure 6). Benefiting from the hierarchical porosity, conductive network, mechanical stability constructed by rGO layers and the pillar effect of NPs in between rGO sheets, the hybrid porous film (CoFe₂O₄/rGO) with controlled thickness of above 10 μm enhanced rate capability and long-term stability (330 mA h g⁻¹ for 1000 cycles at high rates of up to 4.5 A g⁻¹). Such strategy was also applicable to numerous spinel-type oxides (MnFe₂O₄, Fe₃O₄, NiFe₂O₄ and Co₃O₄).

5 Summaries and outlooks

In this review, we have summarized the recent development of graphene-based materials as the electrode materials for lithium ion batteries. Owing to the large specific surface area, high-level conductivity, mechanical rigidity and flexibility, graphene has greatly enhanced the rate capability and long-term cyclability of LIBs. This review specially highlights the advanced progresses of graphene hybrid electrode: graphene/graphene composites with unique 3D construction and the flexible binder-free electrode materials.

Wrapping and confining active nanomaterials in 2D graphene is generally accepted as an inevitable strategy for better electrical performance. Well-defined 3D porous structural graphene composites have been proved to be more favorable for the utilization of large SSA of graphene and high Li⁺ diffusivity that improve the electrochemical performance. As for the 2D flexible and binder-free graphene paper electrodes, they have raised great interests in flexible, lightweight and wearable electronics to meet demands for novel power supply for wearable displays, motion sensor, embed health monitor and so on. Although they possess high conductivity and mechanical robustness for confining nanomaterials, poor electrolyte-electrode accessibility remains to be a problem. Hence it is important and promising to create porous channels for shortening the Li⁺ diffusion length while retaining the conductive skeletons for fast transport of electrons in the bulk material. These designs and strategies for graphene-based materials can readily be applied to Na-ion, Li-O₂, Li-S batteries and even supercapacitors.

Although great efforts have been made, challenges for graphene-based electrode materials still exist. Concerning these challenges, future researches should probably focus on: 1) Mass production of high-quality graphene oxide and graphene; 2) how to create the optimized 3D porous structure with tunable pore size and connected diffusion channels; 3) endowing 2D flexible binder-free electrodes with continuous

porous channels for ion diffusion without destroying their flexibility; 4) how to improve the coulombic efficiency in the first discharge/charge process. Despite these problems, we are confident that novel graphene-based materials would achieve better performance and eventually substitute traditional ones in the future.

This work was supported by the National Hi-Tech Research and Development Program of China ("863" Project) (Grant No. 2012CB932303), and Shanghai Municipal Natural Science Foundation (Grant Nos. 13ZR1463600 & 13XD1403900).

- 1 Goodenough J B, Kim Y. Challenges for rechargeable Li batteries†. *Chem Mater*, 2010, 22: 587–603
- 2 Arico A S, Bruce P, Scrosati B, et al. Nanostructured materials for advanced energy conversion and storage devices. *Nat Mater*, 2005, 4: 366–377
- 3 Reddy M V, Subba Rao G V, Chowdari B V. Metal oxides and oxy-salts as anode materials for Li ion batteries. *Chem Rev*, 2013, 113: 5364–5457
- 4 Whittingham M S. Lithium batteries and cathode materials. *Chem Rev*, 2004, 104: 4271–4302
- 5 Huang X, Qi X, Boey F, et al. Graphene-based composites. *Chem Soc Rev*, 2012, 41: 666–686
- 6 Chen K, Song S, Xue D. Beyond graphene: materials chemistry toward high performance inorganic functional materials. *J Mater Chem A*, 2015, 3: 2441–2453
- 7 Chen K, Song S, Liu F, et al. Structural design of graphene for use in electrochemical energy storage devices. *Chem Soc Rev*, 2015, 44: 6230–6257
- 8 Chen K, Sun C, Xue D. Morphology engineering of high performance binary oxide electrodes. *Phys Chem Chem Phys*, 2015, 17: 732–750
- 9 Chen K, Xue D. Chemical reaction and crystallization control on electrode materials for electrochemical energy storage (in Chinese). *Sci Sin Tech*, 2015, 45: 36–49
- 10 Sun C, Xue D. Study on the crystallization process of function inorganic crystal materials (in Chinese). *Sci Sin Tech*, 2014, 44: 1123–1236
- 11 Chen K, Song S, Xue D. An ionic aqueous pseudocapacitor system: Electroactive ions in both a salt electrode and redox electrolyte. *RSC Adv*, 2014, 4: 23338–22343
- 12 Xu C, Xu B, Gu Y, et al. Graphene-based electrodes for electrochemical energy storage. *Energy Environ Sci*, 2013, 6: 1388
- 13 Peng Z S, Wan C R, Jiang C Y. Synthesis by sol-gel process and characterization of LiCoO₂ cathode materials. *J Power Sources*, 1998, 72: 215–220
- 14 Dahn J R, Fuller E W, Obrovac M, et al. Thermal stability of Li_xCoO₂, Li_xNiO₂ and λ-MnO₂ and consequences for the safety of Li-ion cells. *Solid State Ionics*, 1994, 69: 265–270
- 15 Tian J, Jin Y, Guan Y, et al. Application prospects of high-voltage cathode materials in all-solid-state lithium-ion batteries. *Chin Sci Bull*, 2014, 59: 1950–1963
- 16 Andersson A S, Kalska B, Haggström L, et al. Lithium extraction/insertion in LiFePO₄: An X-ray diffraction and Mössbauer spectroscopy study. *Solid State Ionics*, 2000, 130: 41–52
- 17 Shi S, Liu L, Ouyang C, et al. Enhancement of electronic conductivity of LiFePO₄ by Cr doping and its identification by first-principles calculations. *Phys Rev B*, 2003, 68: 195108
- 18 Barker J, Pynenburg R, Koksang R, et al. An electrochemical investigation into the lithium insertion properties of Li_xCoO₂. *Electrochim Acta*, 1996, 41: 2481–2488
- 19 Cao F, Prakash J. A comparative electrochemical study of LiMn₂O₄ spinel thin-film and porous laminate. *Electrochim Acta*, 2002, 47: 1607–1613

- 20 Ding B, Ji G, Sha Z, et al. Dual-carbon network for the effective transport of charged species in a LiFePO_4 cathode for lithium-ion batteries. *Energy Technol*, 2015, 3: 63–69
- 21 Lin M, Chen Y, Chen B, et al. Morphology-controlled synthesis of self-assembled $\text{LiFePO}_4/\text{C/RGO}$ for high-performance Li-Ion batteries. *ACS Appl Mater Inter*, 2014, 6: 17556–17563
- 22 Li X, Li T, Zhang Y, et al. Graphene nanoribbon-wrapping LiFePO_4 by electrostatic absorbing with improved electrochemical performance for rechargeable lithium batteries. *Electrochim Acta*, 2014, 139: 69–75
- 23 Fan Q, Lei L, Xu X, et al. Direct growth of $\text{FePO}_4/\text{graphene}$ and $\text{LiFePO}_4/\text{graphene}$ hybrids for high rate Li-ion batteries. *J Power Sources*, 2014, 257: 65–69
- 24 Ding Y, Jiang Y, Xu F, et al. Preparation of nano-structured $\text{LiFePO}_4/\text{graphene}$ composites by co-precipitation method. *Electrochim Commun*, 2010, 12: 10–13
- 25 Ha S H, Lee Y J. Core-shell $\text{LiFePO}_4/\text{carbon-coated reduced graphene oxide}$ hybrids for high-power lithium-ion battery cathodes. *Chem Eur J*, 2015, 21: 2132–2138
- 26 Wang B, Al Abdulla W, Wang D, et al. A three-dimensional porous LiFePO_4 cathode material modified with a nitrogen-doped graphene aerogel for high-power lithium ion batteries. *Energy Environ Sci*, 2015, 8: 869–875
- 27 Kucinskis G, Bajars G, Kleperis J. Graphene in lithium ion battery cathode materials: A review. *J Power Sources*, 2013, 240: 66–79
- 28 Wang H, Yang Y, Liang Y, et al. $\text{LiMn}_{1-x}\text{Fe}_x\text{PO}_4$ nanorods grown on graphene sheets for ultrahigh-rate-performance lithium ion batteries. *Angew Chem Int Edit*, 2011, 50: 7364–7368
- 29 Liu H, Gao P, Fang J, et al. $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{graphene}$ nanocomposites as cathode material for lithium ion batteries. *Chem Commun*, 2011, 47: 9110–9112
- 30 Tarascon J M, Guyomard D. The $\text{Li}_{1+x}\text{Mn}_2\text{O}_4/\text{C}$ rocking-chair system: a review. *Electrochim Acta*, 1993, 38: 1221–1231
- 31 Ellis B L, Lee K T, Nazar L F. Positive electrode materials for Li-ion and Li-batteries. *Chem Mater*, 2010, 22: 691–714
- 32 Prabakar S J R, Hwang Y H, Lee B, et al. Graphene-sandwiched $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode composites for enhanced high voltage performance in Li ion batteries. *J Electrochem Soc*, 2013, 160: A832–A837
- 33 Sreelakshmi K V, Sasi S, Balakrishnan A, et al. Hybrid composites of LiMn_2O_4 -Graphene as rechargeable electrodes in energy storage devices. *Energy Technol*, 2014, 2: 257–262
- 34 Rui X, Zhu J, Sim D, et al. Reduced graphene oxide supported highly porous V_2O_5 spheres as a high-power cathode material for lithium ion batteries. *Nanoscale*, 2011, 3: 4752–4758
- 35 Rao V C, Leela Mohana Reddy A, Ishikawa Y, et al. $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ -graphene composite as a promising cathode for lithium-ion batteries. *ACS Appl Mater Inter*, 2011, 3: 2966–2972
- 36 Han S, Wu D, Li S, et al. Graphene: A two-dimensional platform for lithium storage. *Small*, 2013, 9: 1173–1187
- 37 Dahn J R, Zheng T, Liu Y, et al. Mechanisms for lithium insertion in carbonaceous materials. *Science*, 1995, 270: 590–593
- 38 Kaskhedikar N A, Maier J. Lithium storage in carbon nanostructures. *Adv Mater*, 2009, 21: 2664–2680
- 39 Pan D, Wang S, Zhao B, et al. Li storage properties of disordered graphene nanosheets. *Chem Mater*, 2009, 21: 3136–3142
- 40 Wu Z S, Ren W, Xu L, et al. Doped graphene sheets as anode materials with superhigh rate and large capacity for lithium ion batteries. *ACS Nano*, 2011, 5: 5463–5471
- 41 Ma C, Shao X, Cao D. Nitrogen-doped graphene nanosheets as anode materials for lithium ion batteries: A first-principles study. *J Mater Chem*, 2012, 22: 8911
- 42 Reddy A L, Srivastava A, Gowda S R, et al. Synthesis of nitrogen-doped graphene films for lithium battery application. *ACS Nano*, 2010, 4: 6337–6342
- 43 Wang R, Wang Y, Xu C, et al. Facile one-step hydrazine-assisted solvothermal synthesis of nitrogen-doped reduced graphene oxide: reduction effect and mechanisms. *RSC Adv*, 2013, 3: 1194–1200
- 44 Wang R, Xu C, Sun J, et al. Solvothermal-induced 3D macroscopic $\text{SnO}_2/\text{nitrogen-doped graphene}$ aerogels for high capacity and long-life lithium storage. *ACS Appl Mater Inter*, 2014, 6: 3427–3436
- 45 Wang R, Xu C, Du M, et al. Solvothermal-induced self-assembly of $\text{Fe}_2\text{O}_3/\text{GS}$ aerogels for high Li-storage and excellent stability. *Small*, 2014, 10: 2260–2269
- 46 Wang R, Xu C, Sun J, et al. Three-Dimensional Fe_2O_3 Nanocubes/Nitrogen-doped Graphene Aerogels: Nucleation Mechanism and Lithium Storage Properties. *Sci Rep*, 2014, 4: 7171
- 47 Du M, Sun J, Chang J, et al. Synthesis of nitrogen-doped reduced graphene oxide directly from nitrogen-doped graphene oxide as a high-performance lithium ion battery anode. *RSC Adv*, 2014, 4: 42412–42417
- 48 Zhou X, Yin Y X, Wan L J, et al. Self-assembled nanocomposite of silicon nanoparticles encapsulated in graphene through electrostatic attraction for lithium-ion batteries. *Adv Energy Mater*, 2012, 2: 1086–1090
- 49 Yi R, Zai J, Dai F, et al. Dual conductive network-enabled graphene/Si-C composite anode with high areal capacity for lithium-ion batteries. *Nano Energy*, 2014, 6: 211–218
- 50 Lee S E, Kim H J, Kim H, et al. Highly robust silicon nanowire/graphene core-shell electrodes without polymeric binders. *Nanoscale*, 2013, 5: 8986–8991
- 51 Ko M, Chae S, Jeong S, et al. Elastica-Silicon Nanoparticle Backboned Graphene Hybrid as a Self-Compacting Anode for High-Rate Lithium Ion Batteries. *ACS Nano*, 2014, 8: 8591–8599
- 52 Hassan F M, Elsayed A R, Chabot V, et al. Subeutectic growth of single-crystal silicon nanowires grown on and wrapped with graphene nanosheets: High-performance anode material for lithium-ion battery. *ACS Appl Mater Inter*, 2014, 6: 13757–13764
- 53 Nie A, Gan L Y, Cheng Y, et al. Atomic-scale observation of lithiation reaction front in nanoscale SnO_2 materials. *ACS Nano*, 2013, 7: 6203–6211
- 54 Xu C H, Sun J, Gao L. Direct growth of monodisperse SnO_2 nanorods on graphene as high capacity anode materials for lithium ion batteries. *J Mater Chem*, 2012, 22: 975–979
- 55 Xu C, Sun J, Gao L. Controllable synthesis of monodisperse ultrathin SnO_2 nanorods on nitrogen-doped graphene and its ultrahigh lithium storage properties. *Nanoscale*, 2012, 4: 5425
- 56 Liu Y, Liu P, Wu D, et al. Boron-doped, carbon-coated $\text{SnO}_2/\text{graphene}$ nanosheets for enhanced lithium storage. *Chem Eur J*, 2015, 21: 5617–5622
- 57 Zhou W, Wang J, Zhang F, et al. SnO_2 nanocrystals anchored on N-doped graphene for high-performance lithium storage. *Chem Commun*, 2015, 51: 3660–3662
- 58 Behera S K. Enhanced rate performance and cyclic stability of Fe_3O_4 -graphene nanocomposites for Li ion battery anodes. *Chem Commun*, 2011, 47: 10371–10373
- 59 Du M, Xu C, Sun J, et al. Synthesis of $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles from $\text{Fe}(\text{OH})_3$ sol and their composite with reduced graphene oxide for lithium ion batteries. *J Mater Chem A*, 2013, 1: 7154–7158
- 60 Yang S, Feng X, Ivanovici S, et al. Fabrication of graphene-encapsulated oxide nanoparticles: Towards high-performance anode materials for lithium storage. *Angew Chem*, 2010, 49: 8408–8411
- 61 Lai L, Zhu J, Li Z, et al. $\text{Co}_3\text{O}_4/\text{nitrogen modified graphene}$ electrode as Li-ion battery anode with high reversible capacity and improved initial cycle performance. *Nano Energy*, 2014, 3: 134–143
- 62 Peng L, Feng Y, Bai Y, et al. Designed synthesis of hollow Co_3O_4 nanoparticles encapsulated in a thin carbon nanosheet array for high and reversible lithium storage. *J Mater Chem A*, 2015, 3: 8825–8831
- 63 Guan X, Nai J, Zhang Y, et al. CoO hollow cube/reduced graphene oxide composites with enhanced lithium storage capability. *Chem Mater*, 2014, 26: 5958–5964
- 64 Rui X, Tan H, Yan Q. Nanostructured metal sulfides for energy storage. *Nanoscale*, 2014, 6: 9889–9924
- 65 Chang K, Chen W. L-cysteine-assisted synthesis of layered $\text{MoS}_2/\text{graphene}$ composites with excellent electrochemical perfor-

- mances for lithium ion batteries. ACS Nano, 2011, 5: 4720–4728
- 66 Chang K, Chen W. *In situ* synthesis of MoS₂/graphene nanosheet composites with extraordinarily high electrochemical performance for lithium ion batteries. Chem Commun, 2011, 47: 4252–4254
- 67 Chang K, Chen W. Single-layer MoS₂/graphene dispersed in amorphous carbon: Towards high electrochemical performances in rechargeable lithium ion batteries. J Mater Chem, 2011, 21: 17175
- 68 Jiang Z, Wang C, Du G, et al. *In situ* synthesis of SnS₂@graphene nanocomposites for rechargeable lithium batteries. J Mater Chem, 2012, 22: 9494
- 69 Jiang L, Fan Z. Design of advanced porous graphene materials: from graphene nanomesh to 3D architectures. Nanoscale, 2014, 6: 1922–1945
- 70 Xu Y, Sheng K, Li C, et al. Self-assembled graphene hydrogel via a one-step hydrothermal process. ACS Nano, 2010, 4: 4324–4330
- 71 Worsley M A, Pauzauskie P J, Olson T Y, et al. Synthesis of graphene aerogel with high electrical conductivity. J Am Chem Soc, 2010, 132: 14067–14069
- 72 Zhang X, Sui Z, Xu B, et al. Mechanically strong and highly conductive graphene aerogel and its use as electrodes for electrochemical power sources. J Mater Chem, 2011, 21: 6494
- 73 Chen W, Li S, Chen C, et al. Self-assembly and embedding of nanoparticles by *in situ* reduced graphene for preparation of a 3D graphene/nanoparticle aerogel. Adv Mater, 2011, 23: 5679–5683
- 74 Wei W, Yang S, Zhou H, et al. 3D graphene foams cross-linked with pre-encapsulated Fe₃O₄ nanospheres for enhanced lithium storage. Adv Mater, 2013, 25: 2909–2914
- 75 Gong Y, Yang S, Liu Z, et al. Graphene-network-backboned architectures for high-performance lithium storage. Adv Mater, 2013, 25: 3979–3984
- 76 Gong Y, Yang S, Zhan L, et al. A bottom-up approach to build 3D architectures from nanosheets for superior lithium storage. Adv Funct Mater, 2014, 24: 125–130
- 77 Chang Y H, Li J, Wang B, et al. Synthesis of 3D nitrogen-doped graphene/Fe₃O₄ by a metal ion induced self-assembly process for high-performance Li-ion batteries. J Mater Chem A, 2013, 1: 14658–14665
- 78 Zhang M, Wang Y, Jia M. Three-dimensional reduced graphene oxides hydrogel anchored with ultrafine CoO nanoparticles as anode for lithium ion batteries. Electrochim Acta, 2014, 129: 425–432
- 79 Jiang X, Yang X, Zhu Y, et al. 3D nitrogen-doped graphene foams embedded with ultrafine TiO₂ nanoparticles for high-performance lithium-ion batteries. J Mater Chem A, 2014, 2: 11124
- 80 Jiang X, Yang X, Zhu Y, et al. *In situ* assembly of graphene sheets-supported SnS₂ nanoplates into 3D macroporous aerogels for high-performance lithium ion batteries. J Power Sources, 2013, 237: 178–186
- 81 Chen K, Xue D. Preparation of colloidal graphene in quantity by electrochemical exfoliation. J Colloid Interf Sci, 2014, 436: 41–46
- 82 Chen K, Xue D. *In-situ* electrochemical route to aerogel electrode materials of graphene and hexagonal CeO₂. J Colloid Interf Sci, 2015, 446: 77–83
- 83 Nam S, Yang S J, Lee S, et al. Wrapping SnO₂ with porosity-tuned graphene as a strategy for high-rate performance in lithium battery anodes. Carbon, 2015, 85: 289–298
- 84 Park S H, Kim H K, Yoon S B, et al. Spray-assisted deep-frying process for the *in situ* spherical assembly of graphene for energy-storage devices. Chem Mater, 2015, 27: 457–465
- 85 Choi S H, Kang Y C. Fe₃O₄-decorated hollow graphene balls prepared by spray pyrolysis process for ultrafast and long cycle-life lithium ion batteries. Carbon, 2014, 79: 58–66
- 86 Zhu J, Yang D, Rui X, et al. Facile preparation of ordered porous graphene-metal oxide@C binder-free electrodes with high Li storage performance. Small, 2013, 9: 3390–3397
- 87 Lu X, Wang R, Bai Y, et al. Facile preparation of a three-dimensional Fe₃O₄/macroporous graphene composite for high-performance Li storage. J Mater Chem A, 2015, 3: 12031–12037
- 88 Liu X, Cheng J, Li W, et al. Superior lithium storage in a 3D macroporous graphene framework/SnO₂ nanocomposite. Nanoscale, 2014, 6: 7817–7822
- 89 Ma D, Yuan S, Cao Z. Three-dimensionally macroporous graphene-supported Fe₃O₄ composite as anode material for Li-ion batteries with long cycling life and ultrahigh rate capability. Chin Sci Bull, 2014, 59: 2017–2023
- 90 He Y, Chen W, Gao C, et al. An overview of carbon materials for flexible electrochemical capacitors. Nanoscale, 2013, 5: 8799
- 91 Ha S H, Jeong Y S, Lee Y J. Free standing reduced graphene oxide film cathodes for lithium ion batteries. ACS Appl Mater Inter, 2013, 5: 12295–12303
- 92 Abouimrane A, Compton O C, Amine K, et al. Non-annealed graphene paper as a binder-free anode for lithium-ion batteries. J Phys Chem C, 2010, 114: 12800–12804
- 93 Hu Y, Li X, Wang J, et al. Free-standing graphene-carbon nanotube hybrid papers used as current collector and binder free anodes for lithium ion batteries. J Power Sources, 2013, 237: 41–46
- 94 Liu F, Song S, Xue D, et al. Folded structured graphene paper for high performance electrode materials. Adv Mater, 2012, 24: 1089–1094
- 95 Zhao X, Hayner C M, Kung M C, et al. Flexible holey graphene paper electrodes with enhanced rate capability for energy storage applications. ACS Nano, 2011, 5: 8739–8749
- 96 Zhao X, Hayner C M, Kung M C, et al. In-plane vacancy-enabled high-power Si-Graphene composite electrode for lithium-ion batteries. Adv Energy Mater, 2011, 1: 1079–1084
- 97 Wang R H, Xu C H, Sun J, et al. Flexible free-standing hollow Fe₃O₄/graphene hybrid films for lithium-ion batteries. J Mater Chem A, 2013, 1: 1794–1800
- 98 Liu S, Wang R, Liu M, et al. Fe₂O₃@SnO₂ nanoparticle decorated graphene flexible films as high-performance anode materials for lithium-ion batteries. J Mater Chem A, 2014, 2: 4598
- 99 Zhang K, Zhao W, Lee J T, et al. A magnetic field assisted self-assembly strategy towards strongly coupled Fe₃O₄ nanocrystal/rGO paper for high-performance lithium ion batteries. J Mater Chem A, 2014, 2: 9636
- 100 Liang J, Zhao Y, Guo L, et al. Flexible free-standing graphene/SnO₂ nanocomposites paper for Li-ion battery. ACS Appl Mater Inter, 2012, 4: 5742–5748
- 101 Wang R, Xu C, Sun J, et al. Free-standing and binder-free lithium-ion electrodes based on robust layered assembly of graphene and Co₃O₄ nanosheets. Nanoscale, 2013, 5: 6960
- 102 Huang X L, Wang R Z, Xu D, et al. Homogeneous CoO on graphene for binder-free and ultralong-life lithium ion batteries. Adv Funct Mater, 2013, 23: 4345–4353
- 103 Wang R, Xu C, Sun J, et al. Heat-induced formation of porous and free-standing MoS₂/GS hybrid electrodes for binder-free and ultralong-life lithium ion batteries. Nano Energy, 2014, 8: 183–195
- 104 Zeng G, Shi N, Hess M, et al. A general method of fabricating flexible spinel-type oxide/reduced graphene oxide nanocomposite aerogels as advanced anodes for lithium-ion batteries. ACS Nano, 2015, 9: 4227–4235