Chapter 21
Ternary Metal Oxides/Graphene Hybrids for Lithium-Ion Batteries

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Introduction

Energy has become the greatest concern globally owing to the continuous exploitation of fossil fuels in order to meet the increasing demands of the energy of our ever-growing population, which on the other hand, has been imposing a great threat to the environment causing pollution, whereas there is rapidly increased harnessing of renewable energy sources from wind energy and solar energy, the intermittent nature of these energy sources urges for the development of energy storage devices as an equally important one. Lithium-ion batteries are rechargeable clean energy storage devices that can store energy from these renewable energy sources and reversibly generate energy to ground maintaining sustainability and environmental friendliness. These rechargeable batteries have become indispensable in the day-to-day mobile technology advancing in portable electronics—mobile phones, laptops, pacemakers, cameras, etc. because of its significant characteristics such as high energy density, long cycle life, no memory effect, and stable cyclicity [1]. Nevertheless, the extended demand for use in electric vehicles (EV) and hybrid electric vehicles (HEV) still necessitates improved capacity, rate capability, high energy density and power density, durability with increased safety and effective cost [2]. The rechargeable lithium-ion battery was first commercialized by Sony and Asahi Kasei team in 1991 after Akira Yoshino practically developed a prototype lithium-ion battery in 1985 based on earlier John B. Goodenough and Stanley Whittingham theories. After this, LIBs have become undisputedly popular with millions of research articles being published on the development of high-performance LIBs. LIBs have currently

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impacted the world tremendously toward a new rechargeable world, that in 2019, Akira Yoshino, John B. Goodenough. and Stanley Whittingham received the Nobel prize together for the development of LIBs. The commercial lithium-ion battery basically consists of two electrode materials—lithium cobaltite ($LiCoO_2$) as the cathode and graphitic anode dipped in an organic electrolyte containing lithium ions as a medium for the exchange of lithium ions, and a separator to insulate the electrical contact of the two electrodes. Electrode materials utilized in LIBs play a crucial role in the development of high-performance LIBs. A series of research studies have been devoted to the exploration of new cathodic and anodic materials to stimulate the efficacy of LIBs. In the quest of advance anode materials for LIBs, metal oxides are widely investigated because of their high theoretical specific capacity (>700 mAh g^{-1}) and easy maintenance with greater lithium incorporation capability as alternatives to graphite which has the comparatively less theoretical capacity (372 mAh g^{-1}) [3]. However, their advantages are still plagued by large volume change and agglomeration leading to capacity fading and also suffer from poor electrical conductivity. In this regard, metal oxides are incorporated with graphene to mitigate the problems addressed as graphene is an excellent candidate fascinated with its high electrical conductivity, large surface area, flexibility and chemical stability for energy storage applications. Graphene-based metal oxides nanocomposites received substantial attention owing to their synergistic effect enhancing the performance which is reviewed in Sun et al. and Kucinskis et al. [1, 4]. Although the problems of electrical conduction are improved, electrode pulverization still cannot be avoided. With the introduction of two kinds of metal oxides, that is, ternary metal oxides/graphene nanocomposites offer huge advancements in LIBs as anode materials lately. Recent advances in the LIBs energy storage applications encompass binary/ternary metal oxides/graphene nanocomposites as anodic material. While electrolytes, conducting agents, separators have specific roles in battery performance, the present book chapter is focused on the exploration of potential anode materials of LIBs.

Lithium-Ion Batteries

Lithium-ion batteries are rechargeable batteries based on the conduction of electricity through the transport of lithium ions back and forth between the positive electrode and negative electrode. These batteries not only serve as the basis for the future fossil-fuel-free society but also provide large energy storage tools for renewable energy sources, maintaining eco-friendliness. So, for the generation of electricity, anode materials having a high capacity to release electrons is a requisite. Lithium, being the most electropositive metal, has the greatest tendency to lose electrons and since it is the lightest metal, it offers the advantage for realizing light, wearable rechargeable batteries. It consists of three main components—electrodes, electrolyte, and separator. The basic working of LIBs is illustrated based on the first commercialized battery by Sony as depicted in Fig. 21.1.
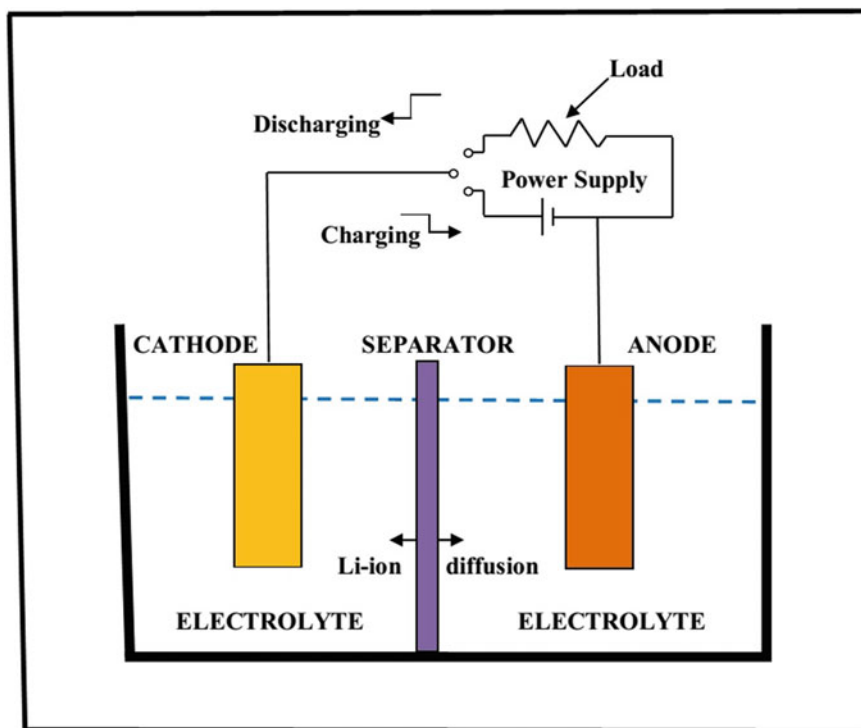
**Fig. 21.1** Electrochemical cell of a Li-ion battery

Lithium cobaltite ($LiCoO_2$) and graphite serve as the cathode and anode, respectively, dipped in an organic electrolyte composing Li-ions which are separated by a permeable membrane called separator which allows only the flow of Li-ions and not electrons and can insulate the electrical contact of the two electrodes.

In charging mode, when a power supply is connected externally to the electrode, the positive side of the external source will attract the electrons detached from the lithium metal in the compound and pass to the anode while lithium ions on the other hand also flow simultaneously through the electrolyte and gather the graphite sheet. Here, electrolyte acts as a medium for the flow of lithium ions and block the flow of electrons. Both the lithium ions and electrons combine together at the cathode and are intercalated between the graphite layers. Again, during discharging, the power supply is removed and connected through the load. Lithium being unstable on its own traced back to its form of a compound internally while the electrons flow back in the opposite direction (from anode to cathode) externally. In this manner, electrical energy is stored electrochemically in the electrodes in the form of chemical energy. The electrochemical reactions occurring at the electrodes are summarized as follows:

The half-reaction at the anode is

$$LiC_6 \leftrightarrow C_6 + Li^+ + e^-$$
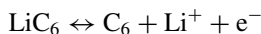
And, half-reaction at the cathode is as follows:

$$CoO_2 + Li^+ + e^- \leftrightarrow LiCoO_2$$
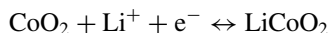
When the charging occurs, the reverse reaction occurs where the electrons flow from cathode to anode.

Recent Progress and Challenges of LIBs

Lithium-ion batteries are constantly developing in electronic technology as it offers numerous advantages over the other batteries. Lithium batteries although having higher energy density than lithium-ion batteries suffer safety hazards utilizing the inherent instability of lithium metal. Advantages of lithium-ion batteries include easy maintenance as it has no memory effect unlike Ni–Cd batteries, higher gravimetric and volumetric energy compared to other batteries delivering voltage almost three times in case of Ni batteries. This high single-cell voltage can reduce the number of cells required in a single module making it feasible for lightweight battery products. Also, energy storage depends on the lithiation process in contrast to other batteries which in case degrade the electrodes promotes the clean rechargeable reversible battery. Despite the advantages of LIBs, safety issues and high cost per unit energy stored are two critical factors that need to be taken into account most particularly, in electric vehicles (EV) and hybrid electric vehicles (HEV) because a large number of cells are required to be packed in a single module for these applications. The commercial LIBs employing lithium compound and graphite as cathode and anode suffer certain drawbacks. LIBs are usually packed with electronic protective circuits to avoid thermal runaway so as to maintain safe operation. However, this protective circuit limits the peak voltage of each cell during charge/discharge lowering the energy density of the battery. In addition, the cell temperature is monitored to prevent extreme temperatures as at high internal temperatures; otherwise, the liquid electrolyte may dry up and short-circuited leading to fire/explosion. For utilization in EV and HEV, battery capacity, cycle life, energy density, and power density still need improvement. As the parameters of battery performance such as cyclability, safety, charge/discharge rate, and specific energy are largely dependent on electrode materials, it is a prerequisite to explore and develop advanced cathodic and anodic materials. For anode materials, tin, silicon, germanium, sulfides, nitrides and metal oxide-based materials are developed as an alternative to commercial carbon anodes owing to their higher theoretical capacities in comparison to graphite and greater Li incorporation capability [5]. However, they face capacity fading and electrode pulverization caused by large volume alteration during Li insertion/extraction process, aggregation, and poor electrical conductivity. Binary hybrids have been investigated as an advancement to mitigate these issues and enhance battery performance as reviewed in

Deng's work [6]. Similarly, graphene is studied as an excellent additive for cathode materials due to its various desirable properties. Although $LiMPO_4$ (M=Fe, Mn, Co, Vn) are extensively investigated as alternatives to the commercial cathode, their poor electrical conductivity limits the rate capability of batteries. This encourages the introduction of carbonaceous materials, particularly graphene to obtain graphene-based composites cathodes. Other advancements in graphene-based composites cathodes include lithium metal oxide/graphene composites, sulfur/graphene composites, metal oxide/graphene composites [7]. Another notable challenge is in the replacement of organic electrolytes used in commercial LIBs. Organic electrolytes are highly flammable and volatile by which its damage can cause fire/explosion. In the last few decades, numerous studies on the structural characteristics and modifications of electrolytes along with alternatives to organic electrolyte—aqueous electrolytes, ceramic electrolytes, solid electrolytes, polymer electrolytes, and heavily fluorinated systems have been proposed for better safety and enhanced performance [8, 9].

Overview of Graphene-Based Anode Materials

Graphene is a promising material possessing excellent physical and chemical properties that are inherently multifunctional. In recent years where graphene has been widely explored for numerous applications including energy storage applications like supercapacitors, likewise, in lithium-ion batteries, graphene-based composites anodes are extensively studied as anode materials. Among the graphene-based composites, graphene/metal oxides composites have drawn remarkable consideration as the hybrid material yields enhanced battery performance than their individual counterparts. In LIBs, graphene acts as an excellent substrate to host active materials used in Li insertion/extraction processes nanomaterials for energy applications because of its large surface area, flexibility, and exceptionally high electrical conductivity.

Fe-Based Oxides/Graphene Hybrids

Fe_3O_4 is an appealing candidate owing to its prominent features such as high specific capacity (580 mAh g^{-1}), low cost, natural abundance, and eco-friendliness [10]. Notwithstanding, high-capacity LIBs based on anodic Fe_3O_4 are hindered with the issues of large volume change and agglomeration causing electrode pulverization leading to the rapid fading of capacity after repeated charging/discharging. Strategies that have been proposed to mitigate the electrode pulverization and specific capacity of electrode materials include designing nanostructured materials, porosity control, designing unique configuration, and a combination of iron oxides with carbonaceous materials [11]. Addressing this strategy can be expected to increase the good cyclic performance as well as to maintain high structural stability. Zhou et. al synthesized

Fe_3O_4/graphene nanocomposite by an in situ reduction method which delivers the specific capacity to nearly 1026 mAh g^{-1} and 580 mAh g^{-1} at the current density of 35 and 700 mA g^{-1} after 30 cycles and 100 cycles, respectively, with enhanced cyclability and high rate capability compared to bare Fe_3O_4 particles when used as anode materials for LIBs [12]. Fu et al. demonstrated a solvothermal prepared Fe_3O_4/graphene composite for LIB applications which exhibited a reversible specific capacity above 963 mAh g^{-1} after 100 cycles at 100 mA g^{-1} current density and reported capacity retentivity after 50 cycles at increasing current densities [13].

The importance of graphene incorporation with metal oxides in LIBs can be stated pointwise.

(1) Graphene nanosheets (GNSs) possess porous structure which aids to act as a flexible confinement matrix providing remarkable buffering capacity. This can reduce electrode pulverization.
(2) GNSs act as a conductive media as it possesses high electrical conductivity and can facilitate ion transport.

On the other hand, Fe_3O_4 prevents the restacking of GNSs, and the porosity formed by lateral GNSs and Fe_3O_4 improves ion transportation. With this, the composite offers great advantages to enhance the lithium storage capacity, cyclic stability, and rate capability.

Mn-Based Oxides/graphene Hybrids

Among the transition metal oxides that can be pursued as an alternative to the commercial graphite as anode materials for LIBs, Mn_3O_4 is a potential material because of its natural abundance, low cost, high theoretical specific capacity (936 mAh g^{-1}) and non-toxicity. Nevertheless, it has very low electrical conductivity (~10^{-7} to 10^{-10} S/cm) and also practically, limited specific capacity can be realized much below the theoretical capacity. Wang et al. reported a two-step synthesis of Mn_3O_4/graphene hybrids affording a high specific capacity of 900 mAh g^{-1} approaching the theoretical capacity as well as cycling stability and good rate capability. The unique performance of the insulating Mn_3O_4 nanoparticles (NPs) grown on the graphene sheets can be ascribed to the well dispersion of Mn_3O_4 NPs over graphene sheets preventing agglomeration [14]. Another form of appealing manganese oxide is manganese dioxide (MnO_2) which has a high theoretical specific capacity (1230 mAh g^{-1}), low cost, natural abundance and eco-benignity. However, low electrical conductivity (10^{-5} to 10^{-6} S/cm), capacity loss due to huge volume alteration and aggregation hinders the wide utilization of MnO_2-based LIBs. Xu et al. discussed various approaches to enhance the MnO_2-based LIBs that have been made by several researchers (1) to design nanostructured materials, (2) to incorporate with carbonaceous materials and (3) to improve the interfacing interactions between the nanostructured materials and the conductive substrate [15]. A facile synthesis

of nanostructured MnO_2 grown over graphene sheets forming interfacial interactions is able to achieve enhanced electrochemical performance with the boosted capacity of 236 mAh g^{-1} which is nearly double times to that of the capacity of bare MnO2 [16]. Another unique hierarchical structure of MnO_2 wrapped between graphene and graphene nanoribbons is demonstrated in Li et al. work reporting well-improved cycling stability, rate capability and reversible capacity compared to individual MnO_2, MnO_2/graphene-based anodes [17].

Sn-Based Oxides/Graphene Hybrids

Sn- and SnO_2-based hybrids are one of the most commonly studied areas as anode materials in LIBs and its developments as anode materials in LIBs are being reviewed in Deng et al. works [18]. In spite of the low cost, eco-friendly, exceptionally high theoretical capacity (782 mAh g^{-1}), and lowest operating voltages compared to other transition metal oxides makes it a promising material for energy storage applications. However, high-capacity SnO_2-based LIBs cannot be realized practically owing to three major problems: (1) large volume variation (~300%) during lithiation/delithiation processes causing electrode pulverization which in turn leads to capacity fading [19]; (2) aggregation of SnO_2 phases; (3) formation of a very thick solid interface layer (SEI). To address this issue, SnO_2/graphene hybrids are investigated as anode materials for LIBs to enhance electrochemical performance [20]. Improved results of reversible capacity, enhance cyclicity and rate capability are received when SnO_2 is hybridized with graphene in comparison to pure SnO_2 [20, 21].

Ti-Based Oxides/graphene Hybrids

TiO_2, being a low cost, naturally abundant, and non-toxic material is particularly interested to be used as anode materials in LIBs. Although the theoretical capacity of TiO_2 is comparatively low (336 mAh g^{-1}) to other metal oxides, the most interesting feature of TiO_2 is its ability to maintain structural stability during lithium intercalation which makes it feasible for use as anodes in LIBs [22]. However, the extremely low electrical conductivity (10^{-16} S/cm) limits its rate capability which encourages to combine TiO_2 with a highly conductive material such as graphene to improve the TiO_2-based anodes for LIBs applications [23]. The TiO_2/graphene composite developed by Xin et al. is able to obtain a capacity of 230 mAh g^{-1} at 17 mA g^{-1} current density and superior rate capability. The hybridization of TiO_2 with graphene can simultaneously avoid aggregation as well as boosted the conductivity [24]. In another work, a hydrothermally prepared robust TiO_2/graphene by Qiu et al. deliver a discharge capacity of 141.7 mAh g^{-1} at 5000 mA g^{-1} current density after 100 cycles without compromising the structural integrity during lithium intercalation. Another

strategy to improve the mobility of Li-ion is proposed by Zhou et al. by introducing surface amorphization. A resilient hierarchical surface amorphized TiO_2/graphene composites are developed which exhibited a substantial capacity of 103 mAh g^{-1} at 50 C, 9.3 times improvement to the capacity of TiO_2-based battery performance. The improved performance is attributed to the combining advantages of surface amorphization as well as graphene incorporation providing (1) large contact area, (2) rapid electronic/ionic diffusion channels and (3) formation of interfacial conductive layer between TiO_2 and graphene [25].

Ternary Graphene-Based Metal/oxides Nanocomposites

Although graphene/metal oxides hybrids have received remarkable enhancement in electrochemical performance, they are still plagued by electrode pulverization. Recently, to address the problem, ternary graphene-based metal/metal oxides nanocomposites are investigated as new advancements to anode materials for next-generation LIBs. The contributions from each individual component aids in the enhancement of the battery performance of the ternary nanocomposites.

Ternary SnO_2/TiO_2/graphene Nanocomposites

In the trend to explore ternary metal oxides nanocomposites, SnO_2/TiO_2 composite received substantial attention. This is because SnO_2/TiO_2 has the same lattice structure and the only slight difference in the lattice which can be easily made possible for the formation of lattice mismatch nanostructure. The induction of TiO_2 in the SnO_2/graphene composite can impact the electrochemical performance of LIBs. TiO_2 plays a vital role in maintaining the structural stability of the electrode during lithium ion insertion/extraction and can prevent the agglomeration of SnO_2 NPs. In addition, SnO_2/TiO_2/graphene nanocomposites can be expected to pursue a synergistic effect because of the following reasons:

(1) SnO_2, being high theoretical capacity and low discharge potential, is limited to high capacity, suffering from poor cycling performance and large irreversible capacity due to the dramatic volume change caused during the repeated lithium insertion/extraction process, which in turn leads to electrical conductivity loss and severe electrode pulverization.

(2) Graphene, excellent conductive material with a large surface area when introduced hybridization with SnO_2, can buffer large volume change and provide fast electronic transport. However, cracking and pulverization of the electrode cannot be avoided.

(3) To address the above problems, combining with other metal oxides are encouraged and evidenced better performance of Li-ion as it can prevent agglomeration

of SnO_2 phases with the existence of extra oxides. TiO_2 has very low volume expansion (~4%) which can act as stable barriers preventing agglomeration of SnO_2 NPs during the charge/discharge cycle.

Jiao et al. demonstrated a two-step preparation of SnO_2/TiO_2/graphene nanocomposites and attain a high capacity of 1276 mAh g^{-1} after 200 cycles at the current density of 200 mA g^{-1}. Also, the composite acquires a specific capacity of 611 mAh g^{-1} at an ultrahigh current density of 2000 mA g^{-1} superior to that of SnO_2 and SnO_2/graphene hybrids [26]. In another report by Jiang et al., SnO_2/TiO_2/graphene nanocomposites can obtain good cycling performance of 573 mAh g^{-1} at 50 mA g^{-1}, good reversible capacities of 250 mAh g^{-1} at 1000 mA g^{-1} current density in the voltage range 0.01–3 V and coulombic efficiency of 97% after 50 cycles [27]. The overall performance of the hybrid nanocomposite portraits good cycle stability and excellent lithium storage capacity owing to the synergistic effect, large surface area, intergrown SnO_2–TiO_2 structure, and conductive graphene matrix.

Ternary SnO₂/Fe₂O₃/ Graphene Nanocomposites

In preparation of ternary SnO_2/Fe_2O_3/graphene hybrids as anode materials, Fe_2O_3, SnO_2, and graphene have contemporary roles in the enhancement of overall electrochemical performance.

Graphene serves as a matrix for Li storage due to its high electrical conductivity, flexibility, and large surface area due to which Li storage capacity has increased, enhanced electronic transport, and an effective elastic buffer that can prevent agglomeration of metal oxide particles. However, one disadvantage of graphene is the restacking of its layers that lead to irreversible capacity loss.

SnO_2 has a high theoretical capacity, low working potential (~0.6 vs. Li/Li$^+$) which helps to improve the lithium storage capability and also prevents the restacking of graphene. One significant problem of SnO_2 is the large volume change during Li insertion/extraction leading to capacity loss. SnO_2 can also help in preventing the aggregation of Fe_2O_3 particles.

Fe_2O_3 has a high theoretical capacity of 1005 mAh g^{-1}, and its introduction in the composite can prevent aggregation of SnO_2 NPs which otherwise would cause structural degradation leading to capacity fading.

Xia et al. prepared SnO_2/Fe_2O_3/graphene nanocomposites where the novel composite attains initial charge and discharge capacities of 746 mAh g^{-1} and 1179 mAh g^{-1}, respectively, at a current density of 400 mA g^{-1} and nearly 100% charge/discharge efficiency are maintained during 100 cycles with capacities above 700 mAh g^{-1} [28].

Ag/TiO$_2$/Graphene Nanocomposites

TiO$_2$ is studied as anodic material for LIBs owing to its distinct characteristics such as low volume expansion (~4%) during Li-ion intercalation, low cost, high rate capability, and eco-friendliness. However, high performance in TiO$_2$-based LIBs is hindered by low theoretical specific capacity and poor ionic and electrical conductivity. To improve the capacity, some strategies that can be proposed to alleviate the above issues are as follows:

(1) To synthesize a nanostructured material so as to enhance the kinetics of the electrode.
(2) To combine TiO$_2$ with other metals/metal oxides to achieve high capacity.
(3) To incorporate with carbonaceous material as a conductive media to increase the conductivity.

Yu et al. demonstrated a solvothermal preparation of Ag/TiO$_2$/graphene nanocomposite which shows a good reversible capacity of 191.6 mAh g^{-1} after 100 cycles at 1C, and cyclability of 144.2 mAh g^{-1} after 3000 cycles at 5C with almost 100% coulombic efficiency [29].

The contribution from each individual in the achievements of the overall performance is

(1) rGO serves as a conductive substrate and can prevent the agglomeration of TiO$_2$ NPs.
(2) Ag NPs can increase intra- or intergrain connectivity.
(3) TiO$_2$ maintains the structural stability of the electrode during the charging/discharging process.

Different Preparation Methods of Ternary Material Hybrids

SnO$_2$/TiO$_2$/Graphene Nanocomposites

Jiao et al. proposed a hydrothermal method to synthesize ternary SnO$_2$/TiO$_2$/graphene nanocomposites. In a typical procedure, reduced graphene oxide (rGO) and ethanol are dispersed in water using an ultrasonicator. In the mixture, CTAB and HCl solution was added and stirred after which SnCl$_2$.2H$_2$O and TiOSO$_4$ were introduced to the mixture and kept stirring under vigorous conditions. The whole mixture is subsequently transferred to a stainless steel reactor, and the reactor is maintained at 180 °C for a day. The resultant product is centrifuged and washed thoroughly with ethanol and water and finally dried at 60 °C. To prepare SnO2/TiO$_2$/graphene nanocomposite Jiang et al. used SnCl$_4$.5H$_2$O as the source for Sn which is added to dispersed TiO$_2$ solution. The mixture is then transferred to an autoclave reactor and maintained the temperature at 180 °C for 12 h. The

final precipitate is collected and rinsed properly with water and ethanol followed by overnight drying at 50 °C to obtain the ternary composite [26].

Ag/TiO₂/Graphene Nanocomposite

In brief, a few mg of GO is taken and dispersed in DI water to form a uniform GO suspension. Two different solutions are made-in one beaker, CH_3COOAg is dissolved in DI water, and in another beaker, SDS is mixed with KCl in the ratio (2:1). The former solution is initially added slowly to the GO solution and kept stirring for 12 h using a magnetic stirrer. Then, the later solution is added to the above mixture under continuous stirring for 0.5 h. Again, a mixture of TTIP in ethanol is poured into the mixture and kept stirring for 0.5 h. The obtained mixture is shifted to a hydrothermal chamber and heated at 180 °C for around 10 h. A black composite is obtained then followed by the subsequent centrifugation and rinsing with DI water and dried overnight at 45 °C. Thus, the final Ag/TiO₂/graphene nanocomposite is obtained [29].

Fe₂O₃/SnO₂/Graphene Nanocomposite

To prepare Fe₂O₃/SnO₂/graphene nanocomposite, initially, 0.8 g of $FeCl_3.H_2O$ and 1.5 g of urea are poured into dispersed GO solution and sonicated for 30 min. The whole mixture is then transferred to a hydrothermal chamber and reacted at 120 °C for 4 h. Subsequently, the obtained product is taken out in a beaker and added with $SnCl_2.H_2O$ to reduce GO by stirring using a magnetic stirrer. After the mixture is kept stirring for an hour, the reaction is stopped and left to cooled and filtrated. The obtained precipitate is rinsed several times with water and subsequently by ethanol and placed in an oven at 80 °C for some hours for drying. Finally, the product is annealed at 400 °C for an hour to enhance the crystallization of Fe_2O_3 and SnO_2 in the ternary composite [28].

Conclusion

In summary, lithium-ion batteries serve as indispensable power sources in portable electronics and its applications are rapidly extending into transportation technology. In spite of the excellent characteristics of LIBs, applications in large-scale electric vehicles demand the improvement of battery in terms of high energy density, power density and capacity, coupling with safety maintenance and low cost. As electrode materials utilized in LIBs play a critical role in enhancing the performance of batteries, this chapter deals with the recent studies in the advancement of anodic

materials. A brief understanding of LIBs-working, advantages, recent progress, and its challenges—is also summarized in this chapter. Although the other components of LIBs-electrolytes, separators, cathode materials, binders, protective circuits etc—are accountable for the better performance of LIBs, the present chapter focuses on ternary graphene/metal oxides hybrids as anode materials and discussed their electrochemical performance. Graphene-based ternary hybrids emerge as a potential candidate for next-generation LIBs exhibiting excellent rate capability, reversible capacity, and stable cycling owing to their synergistic effect between the metal oxides and graphene and also between the two kinds of metal oxides.

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