

GRAPHENE-BASED NANOCOMPOSITES FOR ENERGY STORAGE

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ABSTRACT

Since the first report of using micromechanical cleavage method to produce graphene sheets in 2004, graphene/graphene-based nanocomposites have attracted wide attention both for fundamental aspects as well as applications in advanced energy storage and conversion systems. In comparison to other materials, graphene-based nanostructured materials have unique 2D structure, high electronic mobility, exceptional electronic and thermal conductivities, excellent optical transmittance, good mechanical strength, and ultrahigh surface area. Therefore, they are considered as attractive materials for hydrogen (H₂) storage and high-performance electrochemical energy storage devices, such as supercapacitors, rechargeable lithium (Li)-ion batteries, Li-sulfur batteries, Li-air batteries, sodium (Na)-ion batteries, Na-air batteries, zinc (Zn)-air batteries, and vanadium redox flow

batteries (VRFB), etc., as they can improve the efficiency, capacity, gravimetric energy/power densities, and cycle life of these energy storage devices. In this article, recent progress reported on the synthesis and fabrication of graphene nanocomposite materials for applications in these aforementioned various energy storage systems is reviewed. Importantly, the prospects and future challenges in both scalable manufacturing and more energy storage-related applications are discussed.

1. INTRODUCTION

The ever rising world population has led to increasing energy demand with the worldwide power consumption expected to double in the next several decades. Hence, it is imperative for scientists and researchers to develop sustainable, clean, and renewable energy technologies that are economical and environmentally benign to address the growing energy demands and challenges in our society. The most common renewable

energy sources such as the sun and wind are highly intermittent and thus, require to be coupled with viable high-performance energy storage devices Supercapacitors, high-performance rechargeable lithium (Li) batteries (including Li-ion, Li-S, and Li-air chemistries), sodium (Na) batteries (Na-ion, Na-S, and Na-air batteries), zinc (Zn)-air batteries, and vanadium redox flow batteries (VRFBs), are the most promising energy storage systems on account of their high specific energy, energy and/or power density, long cycle life, excellent rate performance, and design flexibilities Hydrogen (H₂) storage is another promising energy system that is considered as a critical area for its potential applications in sustainable energy without producing harmful byproducts Increased attention to the design and synthesis of nanostructured electrode materials in recent years has proven to be critical for the tremendous advancements in energy storage technologies Particularly, graphene and graphene-based nanocomposites have received great attention and have been extensively investigated as electrode materials for these various energy storage systems.[22–40]

2. SUPERCAPACITORS

Supercapacitors also known as ultracapacitors or electrochemical capacitors offer a promising approach to meet the ever increasing power demand Supercapacitors can be classified into three main groups: electrical double-layer capacitors (EDLC), pseudo-capacitors, and hybrid/asymmetric capacitors. In EDLC the capacitance arises due to pure electrostatic charge accumulation at the electrode/electrolyte interface (non-Faradaic process where charges are distributed by physical absorption) resulting in a double layer (Figure 4). the case of pseudo-capacitors, fast and reversible faradaic processes such as redox reactions take place due to the electro-active species that result in storing the charges as shown in Figure 4 In hybrid capacitors, combination of both non-Faradaic and Faradaic processes is present.

2.1. Graphene-Based Nanostructures

Graphene modified with functional groups containing oxygen (O),[236–240] nitrogen (N),[222,241–247] sulfur (S),[248–250] boron (B),[251–254] silicon (Si)[255] have shown improved performance when used as supercapacitor electrodes. For example, reduced graphene oxides (rGOs) showed a specific capacitance of 264 F g⁻¹ . [256] Graphene-based electrode made from

electrochemically reduced GO displayed a capacitance of $\approx 165 \text{ F g}^{-1}$ and excellent durability of over 1000 cycles in an aqueous electrolyte. Partially reduced GO has capacitances of 348 and 158 F g^{-1} in aqueous and IL electrolytes, respectively. The performance improvement in modified graphene is due to synergistic effects of the electrical double-layer capacitance and pseudocapacitance. Kaner et al. used a standard lightscribe DVD optical drive to synthesize rGO with high electrical conductivity (1738 S m^{-1}) and high surface area ($1520 \text{ m}^2 \text{ g}^{-1}$). This particular study presents a simple approach for graphene synthesis that is shown chronologically in Figure 6a–g.[258] These materials could be directly used as electrodes without the need of additional binders, carbon black, and current collectors, which could help improve the energy density of the devices. Figure 6h clearly indicates similar stack resistances using both aqueous and polymer electrolytes. Figure 6i shows that the resulting device exhibited $\approx 97\%$ capacitance retention for over 10 000 cycles. The high mechanical flexibility is indicated by 95% capacitance retention for over 1000 cycles even upon bending (Figure 6j). The excellent mechanical flexibility is ascribed

to the interconnected network architecture of the material along with the gel electrolyte.

The doping of heteroatoms in graphene can change the electronic structure and density of state significantly, thus modifying the quantum capacitance, leading to higher interfacial capacitance values.[262] Although the presence of functional groups on the surface improved the capacities, the fabrication of these materials does require precise control and advanced synthesis techniques, which can lead to high fabrication costs. This can also lead to low loading because of the surface groups, hence limiting their practical applications. Moreover, controlling the density, order and the type of functional groups on the graphene surface still remains a challenge.

2.2. GRAPHENE-CONDUCTING

Polymer Nanocomposites Hybrid structures of graphene and electrically conducting polymers such as polyaniline (PANI), polypyrrole (PPy), poly(thiophene) (PTh), poly(hexylthiophene) (PHTh), and poly(3,4-ethylenedioxythiophene) (PEDOT) are often employed to further improve the performance of graphene-based electrodes for supercapacitors. Conductive polymers are promising owing to their high energy storage capacity, good electrical

conductivity, low cost, and environmental stability. However, conductive polymers inherently have low mechanical stability and break upon mechanical stress during cycling. Hence, efficient Faradaic charge-transfer mechanism across the electrode–electrolyte interface can significantly boost the charge storage capacity of pseudo capacitors when graphene is combined with these conductive polymers.

2.3. GRAPHENE/CARBON

Nanocomposites Different types of graphene/carbon nanocomposites can be prepared by mixing nanostructured carbons with graphene via chemical and physical methods, hence combining the material properties can lead to improved electrolyte–electrode accessibility and enhanced electrical conductivity of electrode.[295–298] Monolayer graphene sheets tend to form agglomerates and may even undergo stacking to form graphite,[299,300] which can be prevented by incorporating other carbon materials (carbon nanotubes, porous carbon spheres, activated carbon spheres, carbon black, etc.) to fabricate different graphene/carbon nanocomposites. For instance, self-assembly of multiwalled carbon nanotubes (MWCNTs) and polyethylenimine (PEI)-modified graphene

sheets leads to the formation of hybrid interconnected nanocomposite carbon films with well-defined nanopores. This nanocomposite electrode exhibited rectangular cyclic voltammograms (CV) with specific capacitance of 120 F g^{-1} at scan rate 1 V s^{-1} . Graphene/MWCNT composites synthesized via layer-by-layer-assembly can have large volumetric capacitance of $\approx 160 \text{ F cm}^{-3}$ in $0.5 \text{ M H}_2\text{SO}_4$ electrolyte. CNTs inserted between rGO sheets show enhanced cycleability and rate performance,[302,303] because 1D CNTs could physically separate 2D graphene sheets, preserving their high surface area and creating new pores.

2.4. GRAPHENE/TRANSITION

Metal Oxides (or Hydroxide) Nanocomposites Transition metal oxides including MnO_2 , Mn_3O_4 , RuO_2 , Co_3O_4 , Fe_3O_4 , SnO_2 , NiO , Nb_2O_5 , and ZnO have been widely used as electrode materials for supercapacitors. For example, MnO_2 is a promising material for supercapacitor owing to its superior electrochemical performance, environmental friendliness, and low production cost.[130,131] RuO_2 (including hydrous and amorphous RuO_2) has exceptionally high charge storage capacity due to its high conductivity and serious agglomeration,

leading to incomplete reactions during the electrochemical redox processes. In order to limit these obstacles and achieve improved electrochemical properties, many transition metal oxide/carbon composite electrodes have been investigated.

2.5. GRAPHENE/TRANSITION

Metal Nitrides (or Sulfide) Nanocomposites

In addition to transition metal oxide (or hydroxides) nanocomposites, transition metal nitrides (e.g., TiN, VN, Mo₃N₂, etc.),[356–361] and transition metal sulfides (CoS₂, NiS, CoMoS₄, MoS₂, CuS, MnS, etc.),[362–366] are also promising materials for use in supercapacitors due to their high specific capacitance, exceptional electrochemical properties, and excellent electrical conductivity. However, pure transitional metal nitride or metal sulfide electrodes suffer from irreversible oxidation reactions, which lead to poor cycleability.[356–361] Hence, metal nitrides or metal sulfide in conjunction with conductive carbon, such as graphene, can prevent the oxidation reaction and improve the cycleability of these materials.[367–371] For example, an asymmetrical solid state supercapacitor constructed from graphene–TiN cathode, graphene–Fe₂N anode, and poly(vinyl alcohol) (PVA)/ LiCl-based solid

electrolyte delivered an irreversible capacitance of about 58 F g^{–1} at 4 A g^{–1}. [372] This capacitance was relatively stable for up to 20 000 cycles.[372] Moreover, both high volumetric energy density and power density can be achieved at a high current density of 8 A g^{–1}. [372].

2.6. GRAPHENE

Nanocomposites for Asymmetric Supercapacitors and Microsupercapacitors Asymmetric supercapacitors primarily combines Faradic electrode (as energy source) and capacitive electrode (as power source) to increase the operation voltage thus enhancing their energy density while retaining their intrinsic high specific power.[339,350,376,377] The different graphene and graphenebased nanocomposites with high surface area can store charges electrostatically via reversible ion absorption at the electrode/ electrolyte interface. The addition of transition metal oxides or redox conducting polymers, which use fast and reversible redox reactions at the surface of the electroactive materials for charge storage, can lead to high pseudocapacitance. In recent study, Cheng and co-workers designed a high-voltage asymmetric supercapacitor using pure graphene as a negative electrode and graphene/MnO₂

nanocomposites as a positive electrode.[323] Na₂SO₄ aqueous electrolyte-based hybrid supercapacitors that can be cycled reversibly in high voltage region have high energy density and high power density.

3. LI-ION BATTERIES

Li-ion batteries have received extensive attention from the scientific community as one of the most popular energy storage systems for applications in different areas due to their several important advantages, such as high energy density, no memory effect, long cycle life, and low self-discharging. A Li-ion cell consists of four functional components, e.g., the anode (negative electrode), cathode (positive electrode), electrolyte, and separator. During charging, an external electrical power source forces the current to pass in the reverse direction and enables the migration (diffusion) of Li ions from the cathode to the anode through the electrolyte. During the discharging process, Li ions move from back to the anode through the nonaqueous electrolyte, carrying the current (Figure 9). Graphene and graphene-based nanocomposites have attracted tremendous attention for use in rechargeable Li-ion batteries due to their superior properties. Theoretically, graphene has good Li-storage

ability, since Li can be bound on both sides of graphene sheets, sheet edges, and different types of defect sites.

3.1. ANODES

3.1.1. Graphene-Based Anodes In Li-ion batteries, the anode is considered to be a crucial component affecting the battery performance. Nanostructured materials have been extensively used as anodes in Li-ion batteries due to their high surface area and fast Li⁺ diffusion and therefore their high ability of storing more Li⁺ than that for bulk materials.[421,424–428] Li storage in graphene has been extensively explored to better understand its electrochemical properties.

3.1.2. Porous Graphene Compared with pure graphene sheet, porous graphene has a larger specific surface area and a larger number of additional defects, which increases the number of electrochemically active Li-storage sites.[231,438–441] In addition, porous graphene with well-defined pores can further accelerate the Li-ion diffusion kinetics and minimize the Li-ion insertion/extraction distance because of the interconnected channels that connect the interior active sites.[231,438–441] It was reported that the specific capacities of these

2D porous graphene nanosheets can reach an extraordinary high level.

3.1.3. Graphene Paste A Li-ion battery provides capacities through Li intercalation with an active electrode material, and therefore, its high-rate performance is largely governed by Li⁺ diffusivity and electron conductivity. However, using traditional procedure to prepare the electrode usually leads to low electrical conductivity caused by many factors such as the poor contact resistances by random pore structures, poor adhesion to the current collector, etc. This can result in poor rate capabilities for practical Li-ion battery applications.[448–450] Recently, N- and B-doped graphene pastes with conductive binders were reported to have ultrahigh electrical conductivity, leading to a good rate capability of $\approx 178 \text{ mAh g}^{-1}$ at 5.4C when used as Li-ion battery anodes.[442] In another study, the use of photoflash and laser-reduced freestanding graphene paper-based anodes with micrometer-scale pores, cracks, and intersheet voids facilitated efficient Li ions intercalation kinetics even at ultrafast charge/discharge rates more than This photothermally reduced graphene anode delivered steady capacity $\approx 156 \text{ mAh g}^{-1}$ over 1000 cycles at high rates of $\approx 40\text{C}$. More recently, reported monolithically

structured rGO anode, prepared from conductive rGO paste, delivered outstanding cycling stability and ultrahigh reversible capacity at ultrafast charge/discharge rates.

Although metal oxides show huge improvements in capacities, they have high volume changes during the charge–discharge processes. This can lead to the development of high residual stresses and hence causing mechanical problems at the interface of metal oxides and graphene, which can ultimately cause their detachment from the surface leading to poor cyclability and total failure.

4. LI-S BATTERIES

The high specific energy Li–S chemistry is the direct result of combining two relatively light elements as primary active materials: Li metal anode (theoretical specific capacity: 3860 mAh g^{-1}) and an elemental S cathode (theoretical specific capacity: 1675 mAh g^{-1}).[624–635] During the discharging process of the Li–S cell, the anodic reaction (at the negative electrode) is the oxidation of Li: $\text{Li} \rightarrow \text{Li}^+ + \text{e}^-$ (i), while the cathodic reaction (at the positive electrode) is the reduction of S: $\text{S} + 2\text{e}^- \rightarrow \text{S}^{2-}$ (ii). The overall cell reaction is $2\text{Li} + \text{S} \rightarrow \text{Li}_2\text{S}$ (iii). However, elemental S exists as octasulfur (S₈) rings, which adopts a stable

orthorhombic crystal structure, so that equation.

4.1. OTHER INTERESTING

Studies About Graphene (or rGO)-Based Materials in Li-S Batteries Other novel research on the use of graphene-based materials for Li-S batteries also showed tremendous improvements in electrochemical performance. Among the methods used to prepare these graphene composites include, coating catalyst Pt on the surface of graphene to anchor soluble polysulfides using graphene to modify pure Li metal to protect Li anode and to minimize the shuttle phenomena and adding some inorganic nanoparticles, such as SiO₂, ZrO₂, into graphene phase to further trap polysulfides and minimize their dissolutions and prevent them from subsequent transportation between anodes and cathodes. Based on our discussion in the Li/S section of this review, several issues including the safety, S utilization, rate capability, and cyclability still need to be addressed to advance the knowledge. Current Li-S batteries use pure Li metal as the anode, which can cause serious safety issues because Li metal is highly reactive in most electrolyte solutions where dendritic and mossy metals are very often formed during

prolonged discharge/ charge cycles. In addition, the pulverized and detached Li metal formed during cycling can result in explosion when exposed to air. These drawbacks can lead to serious problems including performance degradation, device failure, low Columbic efficiency, and safety concern.

5. LI-AIR BATTERIES

Li-air batteries that compose of Li metal anode, Li⁺ conducting electrolyte, and porous air cathode have shown great promise as good candidates for high energy density energy storage devices.[786–796] A Li-air system is an integration chemistry in which the discharge process pertains to the electrochemical oxidation of Li metal at the anode and reduction of oxygen (O₂) from air at the cathode with the reaction between them leading to the formation of a series of products, Li peroxide (Li₂O₂), and Li oxide (Li₂O), which are generally referred to as “oxygen reduction reactions” (ORRs).[793,794,796–799] The charging process involves the electrochemical decomposition of Li₂O₂ (or Li₂O) to Li and O₂ and the related reaction is the so-called “oxygen evolution reaction” (OER) as illustrated in Figure 29.

5.1. Graphene

Superior properties graphene render pure graphene graphene/catalyst nanocomposites as potential cathode materials and electrocatalysts for rechargeable Li–air batteries.[673,801,802] It was reported that a pure graphene cathode can form an ideal 3D structure with well-defined diffusion channels for both the electrolyte and O₂, which can increase the reaction efficiency. Graphene also have adequate active edge sites, which significantly contribute to the superior electrocatalytic activity toward ORR and lead to an excellent discharge capacity of 8706 mAh g⁻¹ in nonaqueous electrolyte systems.[803] Sun et al. reported results on the use of graphene as a cathode catalyst for rechargeable Li–air batteries in an alkyl carbonate electrolyte, which showed higher catalytic activity than that of Vulcan XC-72 carbon-based cathode.[804] Similarly, Wang et al. drew a multi-layered graphene-based air electrode on the surface of a Li-ion conducting ceramic film-based electrolyte.

5.2. Porous Graphene

The structure of graphene electrode has a significant impact on the performance of Li–air batteries and a porous graphene electrode can help increase the performance because the pore size and pore volume can affect the

discharge capacity in Li–air battery cathode.[807,808] For example, larger pore volume allows Li oxides to be accommodated during discharge process. On the other hand, the entrance of the pores clogs easily if the pore size is too small.[807,808] Therefore, the pore size should be optimized to prevent clogging, enhance effective diffusion of oxygen over the entire pore network in graphene and to maximize the pore volume to accommodate large amount of discharge products.

Xiao and co-workers adopted colloidal microemulsion to fabricate hierarchically porous 3D graphene cathode with interconnected pore channels at both the micron and nanometer scales.[809] SEM images in Figure 30a,b clearly indicate the presence of porous architectures.

5.3. Heteroatom-Doped

Graphene (or rGO) Chemically doped graphene has been demonstrated as a catalyst with enhanced activity in Li-air battery electrodes.[811] Yoo et al. showed enhanced electrocatalytic activity of N-graphene cathode in acidic conditions.[812] According to DFT calculations, the presence of pyridine-type species in graphene (N-graphene) activates oxygen reduction due to oxygen bonding with the lone electron pair.

In another study, Li et al. used N-graphene as cathode for rechargeable Li-air batteries, which delivered large discharge capacity of 11 660 mAh g⁻¹, ~40% higher than pristine graphene.[813] The electrocatalytic activity of N-graphene for ORR in nonaqueous electrolyte was found to be 2.5 times higher than that of pristine graphene.

6. NA-ION BATTERIES

Na-ion batteries have recently attracted a great interest among researchers as an important source to energy storage devices due largely to fact that Na is environmentally friendly and inexpensive, and it is sixth most abundant element in earth's crust.[847–850] The working principle of Na-ion batteries is similar to that of Li-ion batteries where transport and kinetic behaviors of Na⁺ in host materials are based on the intercalation or alloying type of the reaction, which is dependent on the host material itself.[847–850] As shown in Figure 33, Na ions migrate back and forth in the Na ion-based electrolyte between the anode and cathode upon the application of a charge/discharge current.[851] The electron transmits through the outer electrical circuit, which counterbalances the ion flow within the electrode materials. Several materials have been used as electrodes for Na-ion

batteries including graphitic carbon, hard carbons, Na alloys (e.g. Sn, Sb, SnSb, P, etc.) and some conversion materials (such as transition metal oxides, transition metal sulfide, etc) as anodes and layered oxides, polyanionic phosphates, and pyrophosphates as cathodes Organic compounds have also been proven to be good alternative and environmentally sustainable electrode materials for Na-ion batteries.[852] However, the search for the appropriate host materials for Na⁺ is still ongoing. The relative larger ionic size of the Na ion compared to that of Li⁺ limits the number of the available host materials.[853]

7. NA-AIR BATTERIES Recently, Na-air batteries have attracted a great interest due to their extremely high energy density of about 1600 Wh kg⁻¹. In addition, Na-air batteries are considered good alternatives to replace Li-ion or Li-air batteries due to their low material costs and the natural abundance of Na, which is 30 times cheaper than Li.[967–973] Unlike Li, Na is capable of reversibly forming a stable superoxide (NaO₂) in pure O₂ environment with low overpotentials during discharge process (Figure 39).[974] This enables the Na-air battery to cycle with a charge efficiency of 80%–90% after the first cycle. The formation of peroxide (Na₂O₂), however, is

kinetically hindered as it requires a suitable catalyst. A major challenge that needs to be addressed in the Na–air battery technologies is the excessive discharge products that accumulate on the cathode surface.

8. CONCLUSIONS AND PERSPECTIVES

In this article, we have discussed the recent research progress in graphene and graphene-based nanocomposites for energy storage systems. Although a significant progress has been made, their tremendous potentials for practical applications in advanced energy storage systems still needs further explorations.[208,1026–1028] First, the development of graphene and graphene-based nanocomposites for different energy storagerelated applications are still in early stage where fundamental gaps exist to understand the atomic and molecular level processes that govern operation, limitations and failure of the devices.[22–38,208,1027] Therefore, multidisciplinary approaches are necessary to better understand the correlation between electrochemistry, materials science, engineering, microstructures, properties, and interactions to overcome the significant challenges facing these energy storage systems. These approaches will lead to the efficient use of

large but transient energy sources such as solar and wind necessary to solve the worldwide critical energy issues that are heading the list of global challenges.

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